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Al-Zawahreh

PhD Thesis

USE OF COMPOST FOR DYE REMOVAL FROM TEXTILE WASTEWATERS

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Doctoral Programme in Environmental and Natural Resources


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DOCTORAL THESIS

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Khaled Al-Zawahreh

INTERNATIONAL PHD SCHOOL OF THE UNIVERSITY OF SANTIAGO DE COMPOSTELA
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LIST OF PUBLICATIONS

This Thesis by compendium of publications includes the following articles:

Publication 1:

Paradelo, R., **Al-Zawahreh, K.**, Barral, M.T., 2020. Utilization of composts for adsorption of methylene blue from aqueous solutions: kinetics and equilibrium studies. Materials, 13, 2179.

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Publication 2:

Al-Zawahreh, K., Barral, M.T., Al-Degs, Y., Paradelo, R., 2021. Comparison of the sorption capacity of basic, acid, direct and reactive dyes by compost in batch conditions. Journal of Environmental Management, 294, 113005.

Impact factor: 8.910, position: 34/279 (Q1), Environmental Sciences (source: WOS, JCR edition 2021).

Publication 3:

Al-Zawahreh, K., Al-Degs, Y., Barral, M.T., Paradelo, R., 2022. Optimization of Direct Blue 71 sorption by organic rich-compost following multilevel multifactor experimental design. Arabian Journal of Chemistry, 15, 103468.

Impact factor: 6.212, position: 49/179 (Q2), Chemistry, Multidisciplinary (source: WOS, JCR edition 2021).

Publication 4:

Al-Zawahreh, K., Barral, M.T., Al-Degs, Y., Paradelo, R., 2022. Competitive removal of textile dyes from solution by pine bark-compost in batch and fixed bed column experiments. Environmental Technology & Innovation, 27, 102421.

Impact factor: 7.758, position: 18/158 (Q1), Biotechnology & Applied Microbiology (source: WOS, JCR edition 2021).


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RESUMO

O uso na actualidade de grandes cantidades dunha enorme variedade de colorantes sintéticos en diversas industrias (pinturas, plásticos, téxtil…) provocou a aparición de augas residuais contaminadas con estes compostos, que representan un serio problema ambiental en moitas rexións. Esta cuestión é especialmente delicada no caso da industria téxtil, xa que se estima que ata un cincuenta por cento dos colorantes usados para tinxir os tecidos non se adiren a estes e pasan polo tanto ás augas residuais. Estes efluentes líquidos deben ser tratados convenientemente antes de ser vertidos ás augas naturais, xa que a presenza de colorantes nas augas ten efectos negativos para os seres vivos e os ecosistemas: inflúen negativamente na actividade fotosintética dos organismos acuáticos debido á súa forte absorción da radiación visible, son tóxicos para moitos seres vivos, incluídos os seres humanos, e nalgúns casos son incluso mutaxénicos ou carcinoxénicos.

Sen embargo, a variedade de naturezas químicas destes compostos (xa que existen máis de 10 000 compostos dispoñibles comercialmente), a súa elevada solubilidade en auga, estabilidade e resistencia á degradación fai que non sexan doados de eliminar nas condicións das plantas de tratamento de augas residuais. Desenvolver métodos de tratamento eficaces para a eliminación destes compostos das augas é un campo de investigación de moito interese para o sector téxtil. Neste sentido, a busca de adsorbentes de baixo coste para a eliminación de colorantes en augas pode contribuír ao desenvolvemento de tecnoloxías limpas para o tratamento das augas residuais da industria téxtil. O uso de materiais orgánicos de orixe residual como adsorbentes permitiría reducir os costes dos tratamentos con respecto a materiais de uso habitual en adsorción como o carbón activo, sendo este un campo de investigación moi activo nos últimos anos. Neste sentido, a utilización de materiais compostados para este fin non se ten estudiado ata o de agora co suficiente detalle, a pesar da capacidade xa demostrada de diversos compost para o tratamento de augas contaminadas con outras sustancias, como por exemplo metais pesados ou pesticidas.

O compost é o resultado da descomposición biolóxica aerobia de residuos orgánicos por medio de microorganismos mesófilos e termófilos. Trátase dun produto tipicamente estable, con alta superficie específica, poroso, rico en materia orgánica e nutrientes, con aplicación principalmente como emendas orgánicas en agricultura e horticultura. A presenza de variados grupos funcionais (hidroxilos, carbonilos, carboxilo, amino, entre outros), que poden interactuar con distintos tipos de compostos químicos, tanto orgánicos como inorgánicos, fai que os compost teñan tamén aplicacións ambientais, reducindo a mobilidade de contaminantes en solos e augas. Estas aplicacións son especialmente interesantes para aqueles compost que, por diferentes motivos, teñan un baixo valor agronómico (exceso de salinidade, baixos contidos en nutrientes, fitotoxicidade ou altos niveis de contaminantes). Con respecto a outros adsorbentes, os compost presentan vantaxes como son a súa elevada afinidade fronte a diferentes tipos de contaminantes, facilidade de operación, adaptabilidade e baixo coste de produción e obtención.

Por todo isto, a principal hipótese desta Tese Doutoral é que o compost pode ser un adsorbente eficaz para a retirada de colorantes orgánicos de augas residuais da industria téxtil.

O obxectivo global da Tese Doutoral é contribuír ao desenvolvemento de tecnoloxías de baixo coste para o tratamento de augas contaminadas na industria téxtil. Os obxectivos específicos inclúen:

(1) avaliar a capacidade de varios compost para a retención de colorantes de distinta natureza química,
(2) comprender a influencia das condicións físico-químicas no proceso de adsorción,
(3) avaliar o efecto da competición entre distintos colorantes na súa eliminación das augas, e
(4) establecer as condicións de operación óptimas para a eliminación de colorantes mediante estes materiais.

Nesta Tese Doutoral empregáronse como adsorbentes tres compost elaborados a partir de diferentes tipos de residuos, que se analizaron seguindo os métodos normalizados da UNE-AENOR. O primeiro é un compost producido coa fracción orgánica de residuos sólidos urbanos, elaborado na planta de tratamento do Complexo Medioambiental do Barbanza (Lousame, A Coruña); presenta un pH alcalino e elevados contidos en sales (9.4 dS m^{-1}) e metais pesados (1867 mg Cu kg^{-1}, 976 mg Pb kg^{-1}, 2087 mg Zn kg^{-1}) que o fan pouco adecuado para uso agronómico. O segundo é un compost de codia de piñeiro producido na planta de Orgánica de Sustratos S.L. (O Pino, A Coruña); trátase dun compost ácido (pH 5.3), moi rico en materia orgánica pero pobre en nutrientes dispoñibles para as plantas, o que fai que teña un baixo valor como fertilizante. O terceiro é un compost elaborado con restos de poda e residuos vexetais, producido na planta de compostaxe de Irbid (Xordania); ao igual que o primeiro compost tamén presenta un pH alcalino e unha elevada salinidade (7.8 dS m^{-1}).

Polo que respecta aos colorantes, estudiáronse seis compostos de uso común na industria, pertencentes aos catro principais tipos de colorantes téxtiles: azul de metileno (Basic Blue 9), rodamina B (Basic Violet 10), vermello amaranto (Acid Red 27), Reactive Violet 4, Direct Blue 71 e Direct Blue 151. Os dous primeiros son compostos catiónicos, mentres que o resto presentan diversos grupos funcionais con carga, neste caso maioritariamente aniónicos. En todos os casos a carga dos colorantes varía co pH.

Para acadar os obxectivos mencionados realizáronse diversos experimentos en laboratorio de retención dos colorantes polos compost, en condicións de *batch* e de fluxo continuo en columna. Estudiouse en primeiro lugar a cinética do proceso de adsorción, poñendo en contacto os compost con disolucións de colorantes durante distintos tempos e determinando a cantidade retirada da disolución. As constantes de velocidade de adsorción e o tempo de equilibrio obtivéronse mediante o axuste dos modelos cinéticos de pseudo-primeira e pseudo-segunda orde aos datos experimentais.

Unha vez coñecidos os parámetros cinéticos, realizáronse diversos experimentos de adsorción no equilibrio en modo *batch*, para coñecer a capacidade de adsorción dos compost e a influencia nesta de factores como o tamaño de partícula do adsorbente, o pH e a salinidade da disolución, a temperatura de operación, a relación sólido/líquido ou a competición entre colorantes presentes simultaneamente na disolución. Construíronse curvas de adsorción para todos os experimentos e os resultados experimentais describíronse mediante os modelos de adsorción máis habituais: Langmuir e Freundlich (dous parámetros) e Sips (tres parámetros). Os axustes permitiron calcular as constantes do proceso de adsorción en cada caso.

Para achegarse máis ás condicións reais de operación dos sistemas de tratamento, realizáronse ademais experimentos de adsorción en fluxo continuo en columna, nos que se avaliou o efecto de condicións experimentais como o fluxo de entrada, a concentración inicial e a competición entre colorantes. Os resultados experimentais modeláronse mediante as ecuacións dos modelos de Thomas e BDST (*bed-depth service time*).

Finalmente, para avaliar a posibilidade de reutilización dos compost como adsorbentes, realizáronse experimentos de desorción dos colorantes adsorbidos previamente tanto en *batch* como en columna, nos que se probaron diferentes medios para a rexeneración dos materiais (auga, etanol ou ácido). No seu conxunto, estes estudios permitiron tamén obter información sobre os mecanismos de interacción entre os compost e os colorantes.

Estes experimentos deron lugar aos seguintes resultados: polo que respecta á cinética de adsorción, os tempos para acadar o equilibrio (o máximo de adsorción) foron moi variables entre colorantes, sendo de 1-2 horas para Basic Blue 9, Direct Blue 71 e Direct Blue 151, 5-6 horas para Reactive Violet 4 e Acid Red 27, e 24 horas para o Basic Violet 10. O modelo de pseudo-primeira orde describiu adecuadamente a cinética de adsorción en todos os casos, aínda que o de pseudo-segunda orde foi superior para o colorante Direct Blue 151. A constante de velocidade, k_1, oscilou desde 0,0071 h^{-1} para o Reactive Violet 4 ata 3,6 h^{-1} para o Basic Blue 9, na seguinte secuencia crecente: Reactive Violet 4 > Acid Red 27 > Basic Violet 10 > Direct Blue 151 > Direct Blue 71 > Basic Blue 9. Estes resultados coinciden co indicado na bibliografía no sentido de que a adsorción dos colorantes catiónicos e directos é máis rápida que a dos outros tipos.

Canto á adsorción no equilibrio, na grande maioría dos casos esta foi explicada satisfactoriamente mediante o modelo de Langmuir, que presenta a vantaxe de permitir estimar a capacidade máxima de adsorción dos colorantes para cada compost. Atopáronse importantes diferenzas de retención entre os distintos tipos de colorantes, sendo, con poucas excepcións, o compost de codia de piñeiro o que presentou as maiores capacidades de adsorción, o que se atribúe ao seu elevado contido en materia orgánica (95%), notablemente maior que o dos outros dous compost. Nas mellores condicións de operación, as capacidades máximas de adsorción deste compost foron de 876 mg g^{-1} para o Basic Blue 9, 204 mg g^{-1} para o Basic Violet 10, 95 mg g^{-1} para o Direct Blue 71, 54 mg g^{-1} para o Direct Blue 151, 23 mg g^{-1} para o Reactive Violet 4 e 4,1 mg g^{-1} para o Acid Red 27. No caso do compost de residuos sólidos urbanos, as capacidades de adsorción máximas foron en xeral menores: 621 mg g^{-1} para o Basic Blue 9, 36 mg g^{-1} para o Basic Violet 10, 74 mg g^{-1} para o Direct Blue 151, 38 mg g^{-1} para o Reactive Violet 4, e 1.6 mg g^{-1} para o Acid Red 27. Destas secuencias para as capacidades máximas de adsorción dedúcese a seguinte tendencia xeral, en función do tipo de colorante: básico > directo > reactivo > ácido. Esta secuencia concorda en xeral co observado na bibliografía, constatando que a afinidade dos adsorbentes orgánicos polos colorantes de tipo básico é moito maior que polo resto de tipos. Esta observación pode explicarse en boa medida polo feito de que os colorantes de tipo básico presentan carga positiva á maioría de valores de pH, o que daría lugar a unha maior interacción coas cargas predominantemente negativas dos compost, mentres que os outros tipos de colorantes son compostos aniónicos en case todas as condicións, o que reduciría a interacción co compost.

Polo que respecta á influencia dos diversos factores estudiados na adsorción por parte dos compost, non se observou efecto da temperatura de operación ou do tamaño de partícula dos compost sobre a súa eficacia, mentres que unha redución da relación sólido/líquido de 1/20 a 1/100 produciu un incremento aproximadamente proporcional da adsorción do colorante. Con respecto ás condicións de operación, a adsorción dos colorantes en fluxo continuo en columna foi significativamente menos eficiente que nos experimentos en *batch*. O menor tempo de contacto nas columnas, que non operan en condicións de equilibrio e non permiten a migración completa do colorante desde a disolución aos sitios activos do adsorbente, é o factor clave que explica este resultado.

O pH da disolución tivo unha influencia decisiva sobre a capacidade de adsorción en todos os casos, de modo que se obtiveron eficacias máximas de todos os compost a valores ácidos. Tendo en conta o efecto do pH na ionización dos grupos funcionais, tanto dos compost como dos colorantes, este factor controlará as cargas e polo tanto a interacción electrostática. En xeral, a valores de pH suficientemente ácidos, en torno a 3, increméntase a carga positiva dos compost, o que aumentaría a interacción coa maioría dos colorantes, cargados negativamente, explicándose así estas observacións.

Pola súa banda, o incremento da salinidade da disolución influíu positivamente na adsorción dos colorantes en practicamente todos os casos, especialmente nos de tipo básico. Este feito atribúese principalmente a fenómenos de agregación-dimerización das moléculas de colorante en condicións de elevada forza iónica, o que reduciría a súa solubilidade incrementando así a súa afinidade pola fase sólida.

A co-existencia de varios colorantes na disolución reduciu a adsorción de cada un deles con respecto á presenza de cada colorante individualmente, indicando a existencia dun fenómeno de competición polos sitios de adsorción dos compost. A redución da súa capacidade de adsorción foi máis notoria nos experimentos en fluxo continuo que en *batch*, e para os colorantes directos, con baixa afinidade polo compost, véndose moito menos afectados os colorantes de tipo básico.

Os experimentos de desorción dos colorantes adsorbidos previamente en diferentes condicións demostraron que os compost se poderían reutilizar adecuadamente utilizando etanol para a rexeneración, observándose que o colorante adsorbido nos compost non se podería recuperar eficazmente usando fases acuosas.

O estudio da influencia dos distintos factores na adsorción, xunto coa comparación dos espectros de infravermello (FTIR) dos compost antes e despois do contacto cos colorantes, permitiu obter información sobre os mecanismos de interacción que participan na adsorción en cada caso. O proceso de adsorción ten que ser por forza complexo, tendo en conta as tamén complexas estruturas, tanto dos colorantes como especialmente dos compost, polo que parece lóxico que os resultados non se poidan atribuír a un único mecanismo actuando en solitario. En calquera caso, a atracción electrostática é sen dúbida un dos mecanismos que máis contribúen á adsorción, xa que os colorantes son moléculas ionizables cargadas, a practicamente calquera valor de pH. Neste sentido, os espectros FTIR amosan modificacións nas bandas correspondentes a grupos hidroxilo e carboxilo dos compost tras a adsorción dos colorantes de todos os tipos, o que demostra a existencia da interacción electrostática con estes grupos funcionais. Ademais, a maior afinidade dos compost polos colorantes de tipo básico, que son moléculas catiónicas, con respecto aos outros tipos de colorantes, maioritariamente aniónicos, indica sen dúbida a importancia deste mecanismo.

Sen embargo, a atracción electrostática non é o único mecanismo de adsorción e, nalgúns casos, probablemente tampouco o principal, como demostran as observacións sobre a influencia do pH e a salinidade das disolucións na adsorción de cada tipo de colorante. O feito de que as variacións do pH da disolución modifiquen sempre a capacidade de adsorción no mesmo sentido, con independencia das variacións do signo e cantidade das cargas eléctricas de cada composto que controlan a interacción, indica sen dúbida que a atracción electrostática non pode ser o único mecanismo implicado na adsorción.

O mesmo se pode dicir do efecto da salinidade na capacidade de adsorción, que variou sempre do mesmo modo, independentemente dos cambios producidos polas distintas forzas iónicas no pH da disolución e simultáneamente nas cargas dos colorantes e os adsorbentes. Como xa se comentou, este efecto é atribuíble á dimerización das moléculas de colorante a forzas iónicas elevadas, que producen unha redución da súa solubilidade en auga incrementando a afinidade polo adsorbente, como se observou en estudos similares. Esta dimerización débese a un incremento das distintas forzas intermoleculares: dipolo-dipolo, ión–dipolo ou forzas de Van der Waals, que actúan polo tanto no proceso de adsorción.

Ademais disto, a existencia de interaccións hidrófobas entre os colorantes e a materia orgánica dos compost é outro dos mecanismos que poden explicar a adsorción en condicións desfavorables para a interacción electrostática. Por exemplo, a maior capacidade de adsorción no compost de codia de piñeiro, o máis rico en materia orgánica dos avaliados, a calquera valor de pH, apunta tamén nesta dirección. A análise dos espectros FTIR tamén aporta probas da importancia das forzas de interacción hidrofóbica, especialmente para os colorantes non catiónicos, observándose como tras a adsorción se modificou a intensidade dos distintos picos e bandas correspondentes aos enlaces C-C, C=C e C-H.

Globalmente, os compost estudiados aquí amosaron un comportamento prometedor para a eliminación de colorantes en comparación con outros adsorbentes avaliados en condicións semellantes na bibliografía. Os compost presentaron capacidades de adsorción polo menos similares ás doutros materiais máis caros ou máis custosos de producir (como carbón activo, grafeno ou polímeros), sobre todo o compost de codia de piñeiro, e especialmente no caso dos colorantes de tipo básico. Hai que indicar sen embargo que a eficacia dos compost no caso do colorante ácido Acid Red 27 foi baixa en comparación coa obtida por outros adsorbentes, tanto sintéticos como naturais.

Por máis que os resultados obtidos aquí sexan prometedores, os estudios levados a cabo tamén desvelaron a necesidade de afondar no futuro en diferentes aspectos, xa que o estado actual da investigación non é suficiente para o desenvolvemento práctico de aplicacións baseadas en compost. En primeiro lugar, non hai aínda suficiente información sobre a eficacia dos compost con respecto a todos os tipos de colorantes téxtiles existentes; especialmente no caso dos de tipo directo e reactivo existen moi poucos resultados na bibliografía e polo tanto, precisaríase realizar máis estudios de adsorción con este tipo de colorantes. Por outra banda, para confirmar que a baixa capacidade de retención observada para os colorantes ácidos é unha característica típica destes materiais, o que tería importantes repercusións prácticas, serían necesarios máis estudios utilizando outros tipos de compost.

Outra liña de traballo posible no futuro sería a modificación das propiedades dos compost para incrementar a súa eficacia como adsorbentes, o que sería de especial interese no caso dos colorantes cos que se obtiveron peores resultados. Entre as modificacións que se poderían avaliar están diversos modos de activación: tratamento con ácidos ou bases, lavado con auga para eliminar os compostos solubles, tratamentos térmicos, moído para a preparación de nanocompostos, ou a mestura con arxilas ou outros materiais con elevada afinidade por aqueles colorantes menos adsorbidos polo compost.

Por último, outro aspecto esencial da investigación futura estaría dirixida á obtención de información para levar a cabo esta aplicación en condicións reais. Ademais de realizar experimentos incrementando a escala de operación, tamén se debería avaliar a interacción con outros contaminantes habitualmente presentes en augas residuais da industria téxtil, como metais pesados ou materia orgánica disolta. Ademais, poderíase afondar nos estudios de rexeneración do adsorbente, avaliando o emprego de máis tipos de eluentes así como o efecto de distintas condicións fisicoquímicas sobre a desorción.

En conclusión, os resultados que se obtiveron nesta Tese Doutoral demostran a viabilidade científica da utilización de compost como adsorbente de baixo coste para o tratamento de augas contaminadas con distintos tipos de colorantes téxtiles. Esta aplicación sería especialmente eficaz para a eliminación de colorantes de tipo básico, e debería limitarse a aqueles compost de menor valor agronómico. Aínda que a aplicación práctica desta tecnoloxía para o tratamento de augas da industria téxtil a escala real precisará de investigación adicional no futuro, os resultados aquí presentados constitúen unha base de coñecemento sólida para o seu desenvolvemento.

SUMMARY

Finding low-cost adsorbents for organic dye removal from water is important for the development of clean technologies for the treatment of textile wastewater. In this sense, utilization of composted materials has not yet been studied in detail, although their use for the removal of other types of pollutants has been proved.

In this thesis, we studied the performance and characteristics of the adsorption of three composts (municipal solid waste compost, pine bark compost and a green waste compost) towards different classes of dyes: Basic Blue 9 (methylene blue), Basic Violet 10 (rhodamine B), Acid Red 27, Reactive Violet 4, Direct Blue 71 and Direct Blue 151. Sorption kinetics and equilibrium were studied in batch and in fixed-bed column conditions; the influence of factors including solution pH, salinity and competition with other dyes were assessed. Moreover, the potential recycling of adsorbents was evaluated by studying desorption. The mechanism of the interaction between dye and compost was also investigated.

Adsorption rates were relatively slow for Basic Violet 10, reaching equilibrium in 24 hours, and faster for the rest: around 5-6 hours for Reactive Violet 4 and Acid Red 27 and 2 hours for Direct Blue 151 and methylene blue. In general, dye sorption at the equilibrium was adequately described by the Langmuir model, what allows to estimate the maximum retention capacities for each dye by the composts. The dye adsorption capacity followed the sequence: Basic Blue 9 > Basic Violet 10 > Direct Blue 71 > Direct Blue 151 > Reactive Violet 4 > Acid Red 27, and the highest capacity among the adsorbents was obtained with pine bark compost. Sorption increased at acid pH in all cases, likely because the modification of charges of the dyes and higher electrostatic attraction. Increasing salinity also had a positive effect on sorption, which was attributed to a solute-aggregation mechanism in solution. Co-existence of several dyes in solution reduced their affinities in batch and column tests. The adsorbents could be effectively regenerated using ethanol, thus enabling reuse in the practical application of compost for textile dye removal.

The study of the influence of these factors and the FTIR spectra of the adsorbents, before and after adsorption, showed that electrostatic forces cannot be the only or even the main mechanism for the interaction between dyes and compost. Considering the complex structure of the dye molecules, the contribution of other mechanisms such as hydrophobic-hydrophobic and dipole-dipole forces should be envisaged to explain dye sorption. Hydrophobic interaction between the organic dyes and organic matter-rich composts could explain the higher affinity of dyes toward pine bark compost.

In conclusion, composts can be successfully applied for the removal of colorants from wastewater, although they would be more effective with basic cationic dyes than other types, due to more favorable electrostatic interaction with mostly negatively-charged composts.


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1 INTRODUCTION

Water contamination is still a main global concern, and all governments are paying attention to this issue (Das et al., 2014; Kyzas and Kostoglou, 2014; Hossain et al., 2015). The pollution of wastewater by hazardous materials like heavy metals, organic compounds, phenols, colorants, pesticides, and other long-living pollutants is a result of intense industrial and agricultural operations (Abdolali et al., 2014). These contaminants come to food chain and produce harmful effects, which influence the aquatic biota and human health. As a result, wastewater must be treated before being released to natural water bodies.

Among these contaminants, dyes released to the environment from the textile industry are removed from wastewater using a variety of technologies including adsorption, advanced oxidation, coagulation, and in some cases membrane separation (Ferreira et al., 2014; Kyzas and Kostoglou, 2014). Particularly, adsorption is one of the most effective processes of advanced wastewater treatment. Many review articles have been published to highlight the importance of low-cost bio-sorbents such as barks, plant peels, coconut-derived sorbents, date pits, wheat-derived adsorbents and other forest and agricultural wastes in water pollution remediation (Anastopoulos and Kyzas, 2014, 2015; Baskan and Pala, 2014; Cai et al., 2014). Many of these materials' surfaces are adsorbate-specific, such as those for phenols, organic dyes, and heavy metals. For example, coir pith showed a higher sorption affinity for organics than for heavy metals (Namasivayam et al., 2001).

Composted materials are potential adsorbents for pollutant removal from wastewaters. Composting is the biochemical transformation of organic compounds into a humus-like, stable product called compost, obtained under controlled, aerobic conditions. Composts are used as soil additives to enhance agricultural yields and fertility (López-González et al. 2015). Organic matter, as well as micro and macro nutrients, are provided by compost when applied to soils as organic amendments. Moreover, it improves soil physical properties, decreasing erosion and bulk density and increasing aggregate stability and aeration (López-González et al., 2015; Naeth and Wilkinson, 2013). In addition to agronomic uses, environmental applications of composts have been evaluated, as in soil restoration, landfill cover and sorbent for pollutants, among other uses. Regarding this last application, an overview of contemporary literature (within the last five years) will be presented in this introduction, which demonstrates the utility of composts in water treatment. A summary of pertinent published data (in terms of adsorption capacity, fitted isotherm, kinetic models, and thermodynamic features) is presented and analyzed, as well as some of the most recent key findings.

1.1 ENVIRONMENTAL PROBLEMS OF TEXTILE DYES AND NEED FOR TREATMENT OF DYE-POLLUTED WASTEWATERS

Among textile dyes, basic, direct, reactive dyes and acid classes received a high attention due to their string fixing on different fabrics and because they are available in many shades (Kausar et al., 2018). Common examples, industrial application, and hazardous effect of the earlier classes are outlined in Table 1.1.

Table 1.1. Classes of investigated textile dyes, examples, industrial applications, and hazardous effect (Kausar et al., 2018).

Class	Examples	Industrial application	Loss in effluent after dyeing (%)	Hazardous effect
Basic dyes	Rhodamine B, Methylene Blue, Basic Red 46, Malachite Green, Basic Yellow 28	Acrylic, polyester, modified polyesters, nylons	5	Cancer, Allergic skin, Skin Irritation,
Direct dyes	Direct blue 151, Direct orange 34	Cotton, leather, and silk	30	Carcinogenic
Reactive dyes	Reactive Violet 4, Reactive Yellow 2, Reactive Black 5	Cotton, Nylon, wool	50	Allergic respiratory disorder
Acid dyes	Acid Red 27, Acid Blue 25, Acid Red 57	Modified acrylics, nylon	20	Skin irritation

In what concerns the environmental effects, basic dyes (like Rhodamine B and Methylene Blue) have high visibility even at very low concentration, which can negatively affected the aquatic live in water and many other unwanted consequences (Hameed and El-Khaiary, 2008; Tripathi, 2013; Yagub et al., 2014; Kausar et al., 2018; Benkhaya et al., 2020). Most dyes can affect the photosynthetic activity in aquatic systems due to absorption of sun light; moreover they are toxic to aquatic life due to the presence of aromatic compounds (Hameed and El-Khaiary, 2008; Yagub et al., 2014). In fact, organic dyes are carcinogenic, affect our respiratory system, are skin irritant, mutagenic for humans, and can cause serious damage to human kidney, liver, and central nervous system (Hameed and El-Khaiary, 2008; Kadirvelu et al., 2000).

Reactive, acid, and direct classes can be more easily leached to water (after final fabric washing) in comparison to basic class, which is due to their higher water solubility and reduced fixation to fabric (See Table 1.1). As a result, these classes produce brightly colored effluents that have detrimental effects on aquatic habitats (Amin, 2009; Tripathi et al., 2013; Kausar et al., 2018; Benkhaya et al., 2020). Additionally, these classes easily pass through water treatment facilities because to their low biodegradability and chemical stability, making their treatment of paramount importance.

1.1.1 Characteristics of textile wastewater

Textile industries are classified according to the types of fabrics they produce, which include cellulosic fabrics made from plants (such as cotton, rayon, and linen), protein fibers made from animals (such as wool, silk, and mohair), and synthetic fabrics made artificially (e.g. nylon, polyester and acrylic).The dyes applied depend on the type of fiber (Sivakumar, 2014); for instance, cellulose fiber needs the application of reactive, direct, azo, vat or sulfide dyes; acid dyes are used to dye silk and wool, while azo and disperse dyes are applied to the polyester fiber. A large volume of textile dyes is released into water due to their variable degree of fixation to fibers, as summarized in Table 1.1. The properties and the volume of textile wastewater mainly depend to the applied process, where dyeing is the most important step, which needs large water volumes during the process, but also during the rinsing step. Finishing is also significant process to generate textile wastewater.

The composition of textile wastewater is complex and may contain acids, salts, toxic heavy metals and pigments, in addition to dyes (Babu et al., 2007; Yaseen and Scholz, 2019). Moreover, the composition of textile industry wastewater varies from mill to mill and from country to country, depending on the process, the equipment used in the factory, type of fabric produced, chemicals applied, the weight of the fabric, season (Brik et al., 2006) and the trends in fashion (Kehinde and Aziz, 2014).

Typical chemical parameters of real textile wastewater are provided in Table 1.2 (Ghaly et al., 2014; Yaseen and Scholz, 2019). They are characterized by alkaline pH (up to 12.0), temperature (10-45 °C), high BOD (8-6000 mg L^{-1}) and COD (100-30,000 mg L-1), chlorinated compounds, detergents, stabilizers and formaldehyde, which are added to improve the dye sorption by the fiber (Brik et al., 2006) and can affect the nature of textile wastewater (Babu et al., 2007). The presence of certain heavy metals like Cu, Zn, Al and Cr in the dyeing water is caused by the presence of these metals in the chemical structure of some dyes employed.

Table 1.2. Typical chemical characteristics of textile effluents.

Parameter[a]	Range[b]
Temp °C	10-45
pH	5-12
Color (Pt-Co)	50-2500
COD (mg L^{-1})	100-30,000
BOD (mg L^{-1})	80-6000
EC (µS cm^{-1})	0-1000
TS (mg L^{-1})	6000-7000
TSS (mg L^{-1})	15-8000
TDS (mg L^{-1})	1800-6000
Chlorine (mg L^{-1})	1000-6000
Chlorides (mg L^{-1})	1000-6000
TA (mg L^{-1}) as $CaCO_3$	15-800
TKN (mg L^{-1})	70-80
NO_3-N (mg L^{-1})	0-5
Free ammonia (mg L^{-1})	10-20
Na_2CO_3 (mg L^{-1})	0-20
NaOH (mg L^{-1})	0-10
NaCl (mg L^{-1})	0-300
Phosphate (mg L^{-1})	0-10
Sulphates (mg L^{-1})	500-1000
Sulphides (mg L^{-1})	5-10
Oil and grease (mg L^{-1})	5-30
Dye (g L^{-1})	0-70
Zink, Nickel, Iron, Copper, Chromium, Mercury (mg L^{-1})	0-10
Na (mg L^{-1})	400-7000

[a] COD chemical oxygen demand, BOD 5-day biochemical oxygen demand, TOC total organic carbon, EC electrical conductivity, TS total solids, TSS total suspended solids, TDS total dissolved solids, TVS total volatile solids, TA total alkalinity, TH total hardness, TKN total Kjeldahl Nitrogen, NO_3-N nitrate-nitrogen.

[b] The provided ranges of all parameters of textile wastewater were provided from eight countries (Yaseen and Scholz, 2019).

1.1.2 Technologies for dye removal from textile wastewater

As was previously described, textile wastewater has many unwanted chemicals including dyes. Hence, they should be fully treated to remove dyes, toxic metals and other materials to be safe enough to be discharged into water streams. In the literature, many various physicochemical methods for cleaning wastewater, including textile waters, were proposed. Table 1.3 lists the main remedy options for textile wastewaters, along with their benefits and drawbacks (Salleh et al., 2011; Dawood and Sen, 2013).

Table 1.3. Treatment methodologies for textile dyes along with advantages and disadvantages to the environment.

Treatment method	Advantages	Disadvantages	References
	Biological methods		
Aerobic degradation	Operational cost is low. Effective in removal of azo dyes	Provides suitable environment for growth of microorganisms. Very slow process	Dawood and Sen, 2013; Salleh et al., 2011
Anaerobic degradation	By-products can be used as energy resources	Formation of methane and hydrogen sulphide	Salleh et al., 2011; Tripathi et al., 2013; Benkhaya et al., 2020.
	Chemical methods		
Fenton reagent	Low-priced reagent. efficient procedure	Disposal issues and sludge production	Salleh et al., 2011; Dawood and Sen 2013
Photo-catalyst	Operational cost is low and economically feasible	Some photo catalyst degrades into toxic by-products.	Salleh et al., 2011
Ozonation	No sludge generation	Operational cost is very high, half-life is short (20 min)	Toor et al., 2015.
	Physicochemical methods		
Coagulation/ Flocculation	Simple, economically feasible	High sludge production, handling and disposal problems	Hu et al., 2007.
Membrane filtration	Effective for all dyes with high quality effluents	Effective for all dyes with high quality effluents	Anirudhan and Ramachandran, 2015
Ion exchange	No loss of sorbents	Not effective for disperse dyes	Makhoukhi et al., 2010
Adsorption	High adsorption capacity for all dyes	Low surface area for some adsorbents, high cost of adsorbents	Mushtaq et al., 2016

The biological methods are based on degradation under aerobic or anaerobic conditions (Salleh et al., 2011; Dawood and Sen, 2013). Aerobic degradation methods are more applicable for textile water due to its lower operational cost and more efficient for azo dyes (Salleh et al., 2011). Anaerobic methods can remove textile dyes, but the disadvantage is the formation of methane gas. Chemical treatments (like photolysis and photo-catalytic, Fenton reagent, and ozonation) are very popular, as they oxidize organic dyes to carbon dioxide, but also present some disadvantages (Tripathi et al., 2013). For the use of Fenton reagent, the main disadvantage is the large volume of sludge produced after the treatment. Photocatalyst methods are very efficient to treat textile dyes, but they produce toxic by-products (Salleh et al., 2011). Ozonation is a safe cleaning procedure for dyes oxidation, but it has very high operational cost.

The preferred methods are those based on adsorption or ion-exchange (i.e., physicochemical methods), due to their low operational cost and because they do not generate toxic by-products. Among these methods, adsorption or sorption methods have found many applications in wastewater and textile wastewater due to their effectiveness for the removal of many pollutants. The main disadvantage of the adsorption methods is the high cost of some adsorbents such as activated carbon (Mushtaq et al., 2016).

The efficiency of some listed methods toward dyes cleaning is summarized in Table 1.4.

Table 1.4. Efficiency of different methods for removing common classes of dyes from water (Fu and Viraraghavan, 2001).

Class	Adsorption/ activated carbon	Biological treatment	Ozonation	Sludge	Coagulation
Reactive	Suitable	Unsuitable	Highly suitable	Unsuitable	Unsuitable
Acid	Suitable	Unsuitable	Suitable	Unsuitable	Unsuitable
Basic	Highly Suitable	Unsuitable	Suitable	Suitable	Unsuitable
Direct	Suitable	Unsuitable	Unsuitable	Suitable	Unsuitable

In general, the biological treatment is not effective for all classes of dyes due to their high stability towards this type of treatment. However, anaerobic sludge treatment was effective for basic and direct dyes. Among the tested methods, ozonation was shown to be the most efficient for reactive dyes. Fu and Viraraghavan (2001) found that all classes of dyes were favorably removed by activated carbon adsorption, with preferable uptake for basic dyes. The only problem associated with this technology is the high production cost of activated carbon (Fu and Viraraghavan, 2001).

In general, treatment of dyes by adsorption was the most efficient and therefore it seems to be the upcoming methodology for textile water cleaning. For this reason, many research papers tested the applicability of natural and prepared materials for textile dyes adsorption, including natural clay, fly ash, red mud, zeolite, fruit peels, coffee, coconuts, human hair, sawdust, pine leaves, sugarcane bagasse and Activated-rice husk (Tripathi et al., 2103; Benkhaya et al., 2020). In addition to the aforementioned adsorbents, there is great interest among researchers to apply composts of different origins to remediate dyes and heavy metals from solution, as will surmised soon.

1.2 ADSORPTION: THEORETICAL BACKGROUND

Adsorption is a fundamental process that is employed in academic research and industry for a variety of applications. Adsorption in the liquid phase is particularly useful for removing a wide range of substances from effluents (dyes, heavy metals, phenols and pharmaceuticals), recovering valuable metals from leachates (gold, silver and cobalt), and purifying products during industrial processing (fuels, juices, liquors and wines) (Ruthven, 1984; Do, 1998; Worch, 2008; Bonilla-Petriciolet, 2017).

The determination, modelling and interpretation of equilibrium isotherms is a vital and essential research for all of these applications. Equilibrium isotherms, for example, provide parameters for the researcher's decision-making regarding the adsorption capacity of a specific adsorbent, as well as a sense of how the adsorbent–adsorbate interaction occurs. The adsorption capacity of an adsorbent is a fundamental parameter from a technological standpoint (Ruthven, 1984; Do, 1998).

Based on the foregoing, this section of the thesis discusses the scientific aspects of adsorption equilibrium isotherms in the liquid phase. The following topics are covered in this section: adsorption, types of isotherms, rate of adsorption, and breakthrough curves, estimation of a model parameter and error analysis.

1.2.1 Mechanisms of the adsorption processes

Adsorption can occur from gaseous or liquid phase (Worch, 2008; Bonilla-Petriciolet, 2017). In this last instance, a solute (adsorbate, such as a dye) is transported from solution to the adsorbent surface by the physical or chemical process of adsorption. Adsorption is complete when the adsorbate molecules have completely occupied the active sites (adsorption sites). The kind of solute, adsorbents and presence of solvent all affect how a solute interacts with an adsorbent. Activated carbon, clay, silica gel, colloids, metal oxides and compost are examples of adsorbents (Ruthven, 1984). Desorption, on the other hand, is the process of removing adsorbate from a surface. The adsorption and desorption of an adsorbate onto a solid surface are depicted in Figure 1.1.

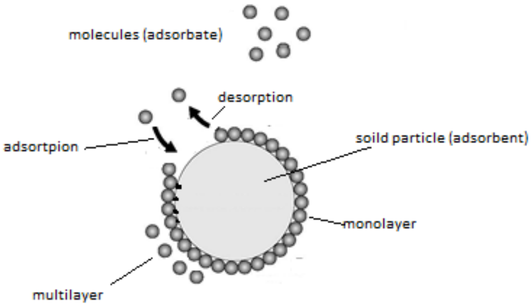

Figure 1.1. Adsorption of a solute (dye) onto a solid surface (compost).

1.2.2 Types of adsorption

Based on the forces that interact between the adsorbent and the adsorbate, adsorption, whether from a gaseous or liquid phase, is separated into two groups (Ruthven, 1984; Bonilla-Petriciolet, 2017):

Physical adsorption: Physisorption is another name for this kind of adsorption. Weak Van der Waals forces between adsorbent and adsorbate are dominated.

Characteristics of physical adsorption (Bonilla-Petriciolet, 2017):

(a) Physical forces are what lead to this kind of adsorption.
(b) Physisorption is a weak phenomenon.
(c) This adsorption involves multiple layers.
(d) Physical adsorption occurs anywhere on the adsorbent and is not selective.
(e) Physical adsorption is influenced by surface area, temperature, pressure and adsorbate type.
(f) Low activation energy (20–40 kg mol^{-1}).

Chemical adsorption: Another name for this kind of adsorption is chemisorption. It is caused by powerful chemical forces of the bonding kind between the adsorbent and the adsorbate. Adsorbent and adsorbate may occasionally undergo a chemical reaction.

Chemical adsorption characteristics (Bonilla-Petriciolet, 2017):

(a) Chemical forces are what lead to this kind of adsorption.
(b) This kind of adsorption nearly always occurs in a single layer.
(c) Chemisorption is very selective.
(d) Chemisorption is influenced by surface area, temperature and type of adsorbate.
(e) The activation energy ranges from 40 to 400 kJ mol^{-1}.

A schematic presentation of physisorption and chemisorption is provided in Figure 1.2.

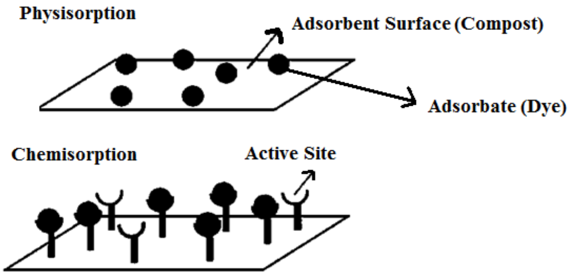

Figure 1.2. A schematic presentation of physisorption and chemisorption

1.2.3 Adsorption isotherms

When the two phases are in dynamic equilibrium at a given temperature, adsorption isotherms are a relationship between the amount of adsorbate adsorbed on the adsorbent (q_e) and the amount of adsorbate remaining in the liquid phase (C_e). The isotherm curves are significant in liquid phase adsorption systems for the following reasons (Bonilla-Petriciolet, 2017; Al-Ghouti and Daana, 2020):

A - The maximum adsorption capacity of a specified adsorbent under various experimental factors –including mass of adsorbent, adsorbate concentration, solution pH, agitation time, and particle diameter– can be calculated using the isotherm parameters. The adsorbent's maximum adsorption capacity is a good indicator of its quality.

B - It is also feasible to gain information on the energetic, steric, and affinity properties from the isotherm parameters.

C - The shape of the isotherm can give information about the mechanism of interaction between the adsorbent and the adsorbate.

The classification of isotherms from solution is outlined in the following section.

1.4.3.1 Classification of equilibrium isotherms

The shape of the equilibrium curve can help explain some of the processes that occur when the adsorbate (dye) interacts with the adsorbent (compost). As a result, the isotherm shape not only represents the conceivable manner of interaction between adsorbate and adsorbent, but also the affinity between the adsorbate and the surface (Wong et al., 2004; Al-Ghouti and Daana, 2020). The classification of liquid–solid adsorption isotherms can be used to determine the adsorption mechanism and to obtain information about the physical nature of the adsorbate and the adsorbent surface (Giles and Smith, 1974; Al-Ghouti and Daana, 2020). The equilibrium curves are classified into four primary classes, depending on the initial slope, with subgroups given for each class based on the forms of the upper sections and slope changes. The classification proposed by Giles (Giles and Smith, 1974) is depicted in Figure 1.3.

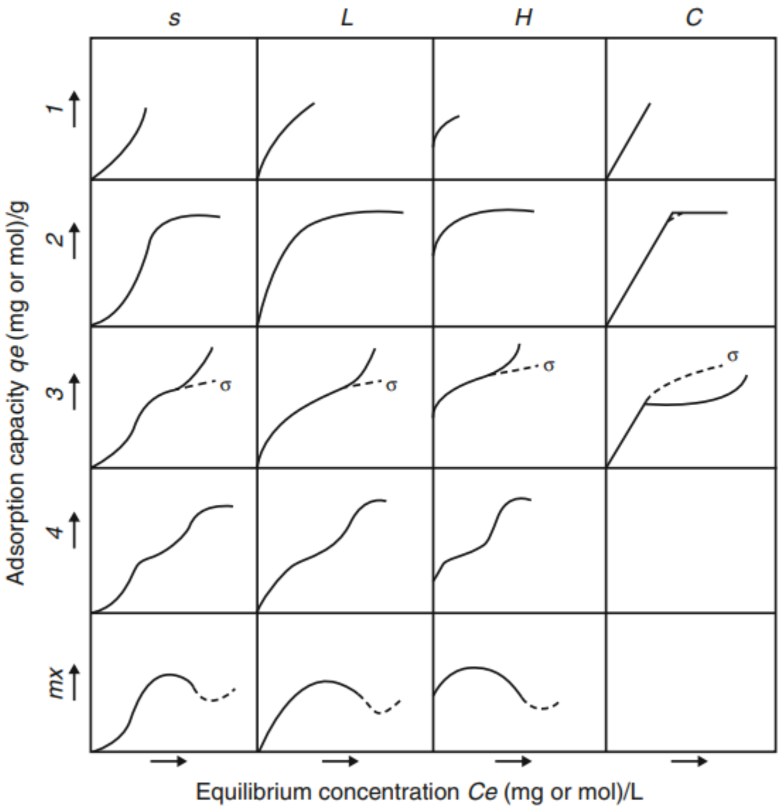

Figure 1.3. Classification of adsorption isotherms in solution (Giles and Smith, 1974; Bonilla-Petriciolet, 2017).

The main classes are (i) S curves or vertical orientation isotherms, (ii) L curves or normal or "Langmuir" isotherms, (iii) H curves or high affinity isotherms, and (iv) C curves or constant partition isotherm. Only types L and H will be discussed, as they are often reported for dyes uptake from solution (Giles and Smith, 1974; Bonilla-Petriciolet, 2017).

L Curves: The normal or Langmuir isotherms are the most typically encountered for solute adsorption from aqueous solutions (Bonilla-Petriciolet, 2017). The adsorption happens due to relatively weak forces, such as van der Waals forces. The initial shape of the equilibrium curve follows the basic premise that the higher the solute concentration, the greater the adsorption capacity, until the number of possible adsorption sites is restricted, at which point competition between solute molecules for available sites occurs. It usually indicates that the molecules are adsorbed flat on the surface or, in rare cases, that the adsorbed ions are vertically orientated and have a particularly high intermolecular attraction (Bonilla-Petriciolet, 2017; Al-Ghouti and Daana, 2020).

H Curves: The starting point of the equilibrium curve is where the normal or L type isotherms deviate from the high affinity isotherm. While the L type isotherm starts at the origin, the H type isotherm has an initial part with a vertical orientation, and adsorption capacity (q_e) values are greater than zero, even when the solute concentration approaches zero. This isotherm type denotes electrostatic chemisorption. This type of isotherm (H-type) is also measured in irreversible adsorption systems, which arise when adsorption occurs at a high concentration and do not affect the adsorption capacity when the concentration is low. Large molecules, such as ionic micelles or polymeric molecules, are frequently adsorbed in this way. They can, however, be simple ions that exchange with others with a considerably lower affinity with the adsorbent surface (Al-Ghouti and Daana, 2020).

1.2.4 Factors affecting adsorption from solution

In the previous sections, the definition, mechanisms, and types of isotherms were outlined. In this section experimental factors affect adsorption from solution will discussed, including mass of adsorbent, solution pH, temperature, particle size, ionic strength and equilibrium time (Iftekhar et al., 2018). Herein, the potential influence of the earlier factors on the extent of adsorption will be summarized.

Effect of adsorbent mass. In general, the extent of a solute's uptake rises as the concentration of an adsorbent increases, because more active sites are available for the adsorbate. Generally, the amount of removed adsorbate (per unit of the adsorbent mass) from solution increases with the mass of adsorbent; however, solute uptake per unit weight of an adsorbent might decrease as adsorbent mass rises (Xie et al., 2015). The optimum adsorbent mass is mainly related to availability of surface-active sites, which is related to the presence of surface functional groups. Addressing the effect of the mass of adsorbent, along with its optimization, is a required condition in adsorption studies (Iftekhar et al., 2018).

Effect of contact time on adsorption. The contact time intensely affects the adsorption from solution. It influences the rate of adsorption and therefore the economic effectiveness of the process. Hence, contact time is another performance governing factor in adsorption process (Srivastava et al., 2015).

Effect of solute concentration: The effect of solute concentration is very significant. Surface saturation is highly dependent on the initial concentration of adsorbate. Surface saturation is often achieved at high adsorbate concentration.

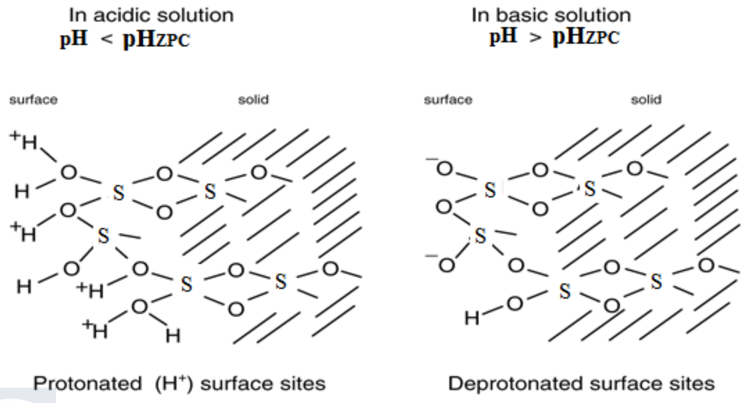

Figure 1.4. Variations in a surface charge of an adsorbent (pH_{ZPC} 7.0) Al_2O_3 in suspensions of different acidity.

Effect of solution pH. Among the examined factors, solution pH is one of the most significant operational factors that can directly affect uptake of adsorbate, as it can affect the extent of solute ionization as well as the surface characteristics of an adsorbent. To understand the influence of pH on solute uptake, the definition of pH_{zpc} (pH at zero point of charge) is often considered (Marwani et al., 2013; Al-Degs et al., 2008; Zhao et al., 2017; Al-Zawahreh et al., 2021). Solid adsorbents can acquire surface charge in solution. The nature of this surface charge depends on the pH of the solution in which they are present (i.e., the pH of surrounding solution). The pH_{zpc} (pH at which the net surface charge of adsorbent is zero) is constant and can be determined experimentally for any material (Marwani et al., 2013; Zhao et al., 2017). The net surface charge (positive, negative or neutral) is determined by comparing the solution pH and the pH_{zpc} of the surface. If solution $pH > pH_{zpc}$ then surface charge is negative and if $pH < pH_{zpc}$ then the net surface charge is positive and if $pH = pH_{zpc}$ then the net surface charge is zero (neutral surface). Ionization of a surface (pH_{zpc} 7.0) with solution pH is depicted in Fig 1.4.

1.3 ADSORPTION OF TEXTILE DYES BY ORGANIC ADSORBENTS

To have a better insight on the removal capacity of natural and synthetic adsorbents for different types of dyes, the literature was reviewed on this point. In the following sections, more than 100 adsorbents were gathered from published articles (1995-2022) that considered adsorption of different classes of dyes including reactive, acid, basic and direct by adsorbents of different natures. In general, the summary already provided information about the nature of adsorbent, class of dye, sorption conditions, applied models, and the maximum retention capacity. In the first part, sorption of dyes by adsorbents other than compost was examined, and the removal of dyes by compost is outlined in a separate section. In Table 1.5, a comprehensive summary of materials used for dyes uptake is provided.

Table 1.5. Sorption parameters of different classes of textile dyes by organic adsorbents.

Adsorbent	Dye	Maximum sorption capacity (mg/g)	Reference
Activated carbon	Direct Blue 106	58	Amin, 2009
Rice husk	Acid Yellow 36	87	Malik, 2003
Pine tree leaves	Basic Red 46	71	Deniz and Karaman, 2011
Peat	Acid Blue 25	14	Ho and McKay, 2003
Carbon nanotubes	Acid Scarlet 3 R	-	Shabaana et al., 2020
Treated banana peel	Rhodamine B	10	Oyekanmi et al., 2019
Activated carbon-bamboo waste	Reactive Black 5	212	Ahmad et al., 2013
Peanut hull	Reactive Black 5	55	Tanyildizi, 2011
Jute fiber carbon	Acid Red 87	31	Porkodi and Kumar 2007
Jute fiber carbon	Malachite green	136	Porkodi and Kumar 2007
Jute fiber carbon	Crystal violet	28	Porkodi and Kumar 2007
Beech wood sawdust	Direct Brown 2	416	Dulman and Cucu-Man, 2009
Beech wood sawdust	Basic Blue 86	136	Dulman and Cucu-Man, 2009
Eucalyptus angophoroides bark	Solar Direct Red BA	54	Tahira et al., 2016
Eucalyptus angophoroides bark	Solar Direct Brittle Blue	55	Tahira et al., 2016
Coconut Shells	Reactive Black 5	1.0	Jóźwiak et al., 2018
Coconut Shells	Reactive Yellow 84	1.0	Jóźwiak et al., 2018
Coconut Shells	Acid Yellow 23	0.5	Jóźwiak et al., 2018
Coconut Shells	Acid Red 18	0.7	Jóźwiak et al., 2018

Adsorbent	Dye	Maximum sorption capacity (mg/g)	Reference
Coconut Shells	Basic Red 46	50	Jóźwiak et al., 2018
Coconut Shells	Basic Violet 10	26	Jóźwiak et al., 2018
Orange peel	Acid Violet 17	20	Sivaraj et al., 2001.
Orange peel	Congo red	22	Namasivayam et al., 1996
Orange peel	Procion orange	1.3	Namasivayam et al., 1996
Orange peel	Rhodamine B	3.2	Namasivayam et al., 1996
Saw dust – activated carbon	Acid Yellow 36	184	Malik, 2003
Rice husk – activated carbon	Acid Yellow 36	87	Malik, 2003
Coir pith	Acid Violet 43	2.0	Namasivayam et al., 2001
Coir pith	Acid Brilliant Blue	17	Namasivayam et al., 2001
Coir pith	Rhodamine B	203	Namasivayam et al., 2001
Coir pith	Methylene blue	-	Namasivayam et al., 2001
Poppy bagasse	Reactive Red 2	7	Uçar et al., 2011
Sugar beet bagasse	Reactive Red 2	11	Uçar et al., 2011
Orange peel	Reactive Red 2	4	Uçar et al., 2011
Poppy bagasse	Reactive Blue 4	9.5	Uçar et al., 2011
Sugar beet bagasse	Reactive Blue 4	12	Uçar et al., 2011
Orange peel	Reactive Blue 4	2.5	Uçar et al., 2011
Durian seed activated carbon	Malachite green	476.2	Raval et al., 2017
Rice husk activated carbon	Malachite green	63.85	Raval et al., 2017
Activated carbon	Malachite green	26.19	Raval et al., 2017
Potato peel waste	Acid Blue 113	11.7	Hoseinzadeh et al., 2104
Potato peel waste	Acid Black 1	1.8	Hoseinzadeh et al., 2104
Chemically activated carbon	Acid Yellow 17	161.3	Gerçel and Gerçel, 2009
Chemically activated carbon	Acid Orange 7	455.0	Gerçel and Gerçel, 2009
Commercial activated carbon	Direct Yellow 50	256.0	Yavuz and Aydin, 2006
Commercial activated carbon	Direct Blue 71	100.0	Yavuz and Aydin, 2006
Commercial activated carbon	Direct Red 80	141	Yavuz and Aydin, 2006

As shown in Table 1.5, most of the tested adsorbents have an organic nature, including banana and orange peels, coir pith, coconut shells and other organic wastes. These materials are applied either without treatment or with a simple chemical activation. Activated carbon (a high-priced commercial product compared to other organic materials) was also tested for the removal of textile dyes, with promising performance. As indicated in Table 1.5, the tested adsorbents can remove all classes of dyes, including acid, reactive and direct, but with higher affinity for basic ones. In general, the performance of all these non-composted adsorbents for textile dyes was variable and range from 0.5 to 10 mg g^{-1} for Acid Yellow 23, Acid Violet 43 and Basic Violet 10, using banana peels-coconut shells, to 455-476 mg g^{-1} for malachite green and Acid Orange 7, using activated carbon.

Sorption affinity of organic adsorbents for the four types of dyes is presented in Figure 1.5, as the average value for each class of dye. As indicated in the figure, the average sorption affinity of all classes was in the range 48-102 mg g^{-1}. The following sorption trend has been observed: basic > direct >> acid > reactive. The sorption capacity for basic and direct dyes is higher than that of the reactive and acid dyes, with sorption values of 85-102 mg g^{-1}. The high sorption affinity of the cationic/basic dyes (as is the case for methylene blue and malachite green) by many adsorbents has been repeatedly reported in the literature. In turn, sorption of reactive and acid dyes was reported to be lower than that of cationic dyes in many published reviews (Gupta et al., 2009; Gupta and Suhas, 2009; Tripathi, 2013; Jóźwiak et al., 2018). For instance, sorption of Acid brilliant blue (anionic dye) and Rhodamine B (cationic dye) by coir pith under the same conditions showed a higher affinity of Rhodamine B compared to Acid brilliant blue, with saturation values of 203 and 17 mg g^{-1}, respectively (Namasivayam et al., 2001). The same adsorbent (coir pith) showed very modest sorption affinity for Acid Violet 43, with a value of 2.0 mg g^{-1}.

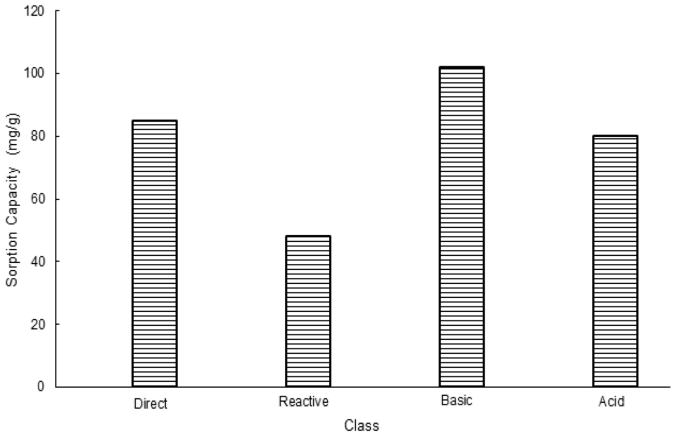

Figure 1.5. Sorption affinity of organic adsorbents for different classes of dyes. Adsorption capacities displayed in the Figure represents the average of the adsorptive capacities that were recorded at the best sorption conditions for a number of dyes from the same class. For example, the adsorption capacity of direct dyes (102 mg g^{-1}) represents the average of adsorption of seven direct dyes by different adsorbents.

1.4 ADSORPTION OF TEXTILE DYES BY COMPOST

1.4.1 Compost and composting process

Composts are produced as a result of the transformation of different types of organic waste. Composting is the biological decomposition of the organic matter contained in wastes by mesophilic and thermophilic microorganisms, leading to stabilized organic amendments with fertilization potential (de Bertoldi et al. 1983). Composting can be a multi-step, closely monitored process that requires measured inputs of water, air, and an adequate mixture of carbon- and nitrogen-rich raw materials. To achieve the required initial conditions composting often necessitates the mixing of brown and green biological waste components. Leaves, grass, and food wastes are examples of greens, which are nitrogen-rich materials. Browns contain more woody, carbon-rich elements like stalks, paper, and wood chips (Manu et al., 2021; Shanm et al., 2021; Liu et al., 2021; Lü et al., 2021; Yin et al., 2021). Composting is a slow process that usually takes months to complete. Most standards require at least a 60–90 days for the composting process to reach maturity (Shanm et al., 2021; Liu et al., 2021).

There are several systems for composting, of different complexity and technical requirements. In all of them, the decomposition process is aided by shredding the raw materials, adding water, and ensuring optimum aeration by regularly turning or active aeration of the mixture. Fungi, earthworms and other detritivores break down the organic matter. The aerobic bacteria and fungi transform the organic materials into a stabilized organic matter, releasing heat, water vapor, carbon dioxide and ammonium (Trimmer et al., 2019; Bahramisharif and Rose, 2019; Shanm et al., 2021; Liu et al., 2021).

Urban waste was initially the most common type of feedstock used for composting, including municipal solid waste and sewage sludge, in response to the needs of waste management in growing cities. Extension of composting to the treatment of materials of agricultural and industrial origin has resulted in the worldwide use of these processes. Composting and vermicomposting are now routinely used in the treatment of municipal solid waste (Farrell and Jones, 2009) and sewage sludge (U.S. EPA, 2002), animal residues such as solid and liquid manures (Larney et al., 2006), agricultural waste (Mortier et al., 2016), food-processing waste, such as winery or olive oil mill waste (Cegarra and Paredes, 2008), and industrial waste, including textile, papermill and tannery waste (Bhat et al., 2018).

In addition to its use as a waste management treatment, composting also yields valuable products. Composts are typically stable, safe products, with neutral or slightly alkaline pH. They are rich in organic matter (often more than 50% of weight) and, consequently, they are highly porous and have a low bulk density and a high water-holding capacity. They are also characterized by high concentrations of plant nutrients (N, P, K), in different forms, and by large amounts and varieties of microbial communities. Thus, the composts produced by these processes have properties that make them valuable resources in several fields.

1.4.2. Main uses of compost

Composts have diverse applications, including agronomic uses as organic amendments in agricultural soils (Hargreaves et al., 2008; Diacono and Montemurro, 2010), as components in soil-less horticultural substrates (Carmona and Abad, 2008; Paradelo et al., 2012, 2019a), and for the remediation of degraded or polluted soils (Semple et al., 2001; Paradelo et al., 2007, 2009a,bc, 2011; Park et al., 2011; Huang et al., 2016). Therefore, gardening, landscaping, horticulture, urban agriculture, organic farming and environmental applications are potential fields for compost use.

Compost can be used as a soil improver, giving humus and nutrients to soil or other matrices used for plant growth (Liu et al., 2021; Lü et al., 2021; Manu et al., 2021; Shanm et al., 2021; Yin et al., 2021). For this end, compost provides several benefits, including fertilization, functioning as a soil conditioner, increasing the humus content of the soil, and bringing helpful microbial colonies to the soil (Bhatia et al., 2013; Ayilara et al., 2020; Rynk et al., 2021; Shanm et al., 2021; Yin et al., 2021). One of the most relevant benefits comes from the natural interplay of soil, plant roots and nutrients/microorganisms in compost, which improves soil structure and thus the ability of the soil to hold water and control erosion. Land reclamation, landfill cover, stream rehabilitation and environmentally friendly wetland formation are all common uses for compost. Also, compost can help plants become more resistant to diseases and pests (Manu et al., 2021; Chen et al., 2020). Compost can be tilled directly into the soil or growth medium to increase organic matter levels and overall soil fertility (Lalander et al., 2018; Bahramisharif and Rose, 2019; Chen et al., 2020). Mixed with soil or other components it can be used as growing media (Cendón et al., 2008; Paradelo et al., 2019a,b; Trimmer et al., 2019; Bahramisharif and Rose, 2019; Chen et al., 2020). Direct planting into a compost is generally not suggested due to the speed with which it might dry, the possibility of phytotoxins in immature compost inhibiting germination, and the possibility of nitrogen tying up by incompletely digested lignin.

In addition to this common agronomical usage of composts, they also found many applications for removing pollutants from soils and waters (Pennanen et al., 2020; Anastopoulos and Kyzas, 2015; Paradelo et al., 2011; Kocasoy and Güvener, 2009). Composts are rich in organic matter with functional groups (polar ionisable and non-ionisable groups, non-polar aromatic and aliphatic groups) that can interact with neutral, cationic and anionic compounds, showing a high adsorption capacity for a wide range of organic and inorganic substances. They are also rich in microorganisms that can promote the biodegradation of organic compounds. These characteristics give composts a potential value for the treatment of waters polluted with a range of substances, including metallic elements, pesticides and other organic compounds such as dyes. This represents an excellent alternative use for composts that are not suitable for agronomic purposes because of unfavorable properties such as phytotoxicity or low nutrient contents. In addition, composts can be produced inexpensively from by-products and waste materials, and their elaboration usually requires little processing. Compared with the cost of activated carbon (> 300 \$ m^{-3}), composts can typically be produced from urban waste at much lower cost, typically around 20-30 \$ m^{-3} (Eggerth et al., 2007; Askarany and Franklin-Smith, 2014).

As a result of these characteristics, composted materials have frequently been assessed as potential biosorbents for the removal of pesticides and inorganic pollutants from water (Boni and Sbaffoni, 2009; Kocasoy and Guvener, 2009; Paradelo and Barral, 2012; Carrillo-Zenteno et al., 2013; Barral et al., 2014; Singh and Kaur, 2015; He et al., 2017). We propose that readers consult the work of Anastopoulos and Kyzas (2015), which summarizes the studies on the use of composts as biosorbents for the removal of heavy metals and dyes from wastewater, spanning over a period ranging from 2003 until 2014.

Thus, it can be concluded that the use of composts as adsorbents for treating polluted waters is a promising field of study. Nevertheless, despite the existence of an extensive number of articles related to heavy metal removal, a surprisingly low number of papers exist regarding dye removal by compost materials (Paradelo et al., 2019b). Therefore, research in this specific field is still at a preliminary stage.

1.4.3. Potential application of composts for dye removal

Prior to the beginning of this PhD Thesis, very few studies existed on the application of composts for dye removal, and these have been specifically reviewed in Paradelo et al. (2019b). Despite the small amount of available research, the current section summarizes the progress made in the field of dye adsorption or dye decolorization utilizing composts.

Some studies have investigated natural-colored effluents from the wine industry (Paradelo et al., 2009a; Pérez-Ameneiro et al., 2014, 2015), which are distinctly red colored and similar to the color of commercial amaranth dye (Pérez-Ameneiro et al., 2014). However, most existing studies refer to pure dye solutions and, among these, methylene blue and malachite green (also known as Basic Green 4) are the most commonly studied dyes. Regarding the chemical nature of the molecules analyzed in the research involving pure dye solutions, most studies have investigated basic dyes, which are cationic molecules at most pH values. Only three studies included more than one type of dye (Tsui et al., 2003; Jozwiak et al., 2013; Toptas et al., 2014), of which only one compared four types of dyes (Tsui et al., 2003). Anionic dyes, including acid dyes, direct dyes (molecules with high affinity for fiber) and reactive dyes (molecules that react with fiber) have been much less well studied than basic dyes.

Approaches to the treatment of dye-contaminated waters also vary widely. Some studies included detailed adsorption studies (Kyziol-Komosińska et al., 2010; McKay et al., 2011; Jozwiak et al., 2013; Toptas et al., 2014; Bhagavathi et al., 2015; Anastopoulos et al., 2018), whereas others have only investigated dye removal without considering the adsorption process (Tsui et al. 2003; Bhagavathi et al. 2016a,b; Anastopoulos et al., 2018). In addition to studies focused on eliminating dyes from water by contact with an adsorbent, one study addressed bioremediation of dyes during composting (Dey et al., 2017).

In their review, Paradelo et al. (2019b) declare that many uncertainties remain regarding the potential application of composts for dye removal. Therefore, further research is necessary in order to overcome these limitations. The small number of studies, in addition to the variable experimental conditions (common in adsorption studies), make it difficult to reach sound conclusions about this issue. Varying conditions of ionic strength, pH or solid/liquid ratios during adsorption experiments make it problematical the valid comparison of different studies. Moreover, the results are not always reported in the same way: although in most cases complete adsorption parameters are provided, some researchers only report removal percentages. Another drawback is the scarcity of results regarding the removal of each dye, apart from methylene blue. Although some researchers report the removal of more than one dye by the same adsorbent, under comparable conditions, additional studies are necessary before strong conclusions can be reached, in particular for direct dyes. Besides, studies comparing the performance of several composts with different properties on the removal of one or more dyes remain scarce.

Moreover, very few molecules have been studied to date, and additional research on dyes of all classes is required to determine which compounds or groups of compounds are most suitable for this treatment. Further studies evaluating the removal of one or more dyes by several composts under comparable experimental conditions are also required to obtain further information about the effect of composts properties on dye removal. In conclusion, these introductory studies highlight both the unexplored potential of the process of dye removal by adsorption onto composts and the need for further investigation of the processes leading to color removal.

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2 HYPOTHESES AND OBJECTIVES

Reuse of composted residuals as adsorbents in environmental remediation is a relevant field of study due to the possibility of using low-cost materials without an unfavorable environmental impact in these applications. These materials are rich in organic matter, with functional groups that can interact with cationic and anionic compounds, and with microorganisms that can promote biodegradation of organic compounds. Utilization in remediation or pollutant removal is an excellent option for some types of composts that can be inadequate for agronomic purposes. Few works have been published dealing with compost use for the removal of dyes and other colored compounds, although preliminary results show that these materials are good sorbents.

Therefore, the main hypothesis here is that compost will be an adequate low-cost biosorbent for removal of dyes from textile wastewaters.

The global objective of this PhD Thesis is to contribute to the development of low cost technologies for the treatment of polluted waters from the textile industry.

The specific objectives are the following:

1. To evaluate the capacity of composts for adsorption of dyes of different chemical nature. Hence, the removal of basic, acid, direct and reactive dyes will be studied. This objective is addressed in publications 1 and 2.
2. To understand the influence of physicochemical conditions on the process of dye adsorption. The influence of compost particle size, solution pH and ionic strength on dye removal will be studied. This objective is addressed in publications 1 and 2.
3. To establish the optimal operational conditions for dye removal by compost. To this end, multilevel multifactor optimization will be used to select the best values for solution pH, ionic strength, temperature or contact time on dye removal by compost. This objective is addressed in publication 3.
4. To evaluate the influence of competition between dyes, which could be simultaneously present in wastewaters, on their removal by compost, in conditions close to real application. For this, simultaneous removal of dyes from solution by compost will be assessed in continuous flow conditions. This objective is addressed in publication 4.

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3 METHODOLOGY

3.1 MATERIALS

3.1.1 Composts

Three composts were tested for dyes uptake from solution. Two Spanish composts produced from pine bark and municipal solid waste, and a Jordanian compost prepared from local organic municipal solid wastes.

Spanish composts: Two composts were used in this work, produced in industrial composting facilities in the region of Galicia (Spain). Municipal solid waste compost (MSWC) was obtained by aerobic large-scale composting of source-separated organic fraction of municipal solid waste at the Complexo Medioambiental do Barbanza (Lousame, A Coruña, Spain). Composted pine bark (CPB) was obtained after aerobic composting of pine bark in windrows and supplied by the company Orgánica de Sustratos S.L. (O Pino, A Coruña, Spain).

Jordanian compost: The compost employed in the study was kindly donated by Irbid Composting Plant (Irbid, Jordan). Briefly, the compost was produced under aerobic conditions from 700 kg of N-rich vegetables including tomato, cabbage, and radish, blended with 300 kg of C-rich branches of olive and cypress trees, previously chopped and air-dried. The pile was turned over on a daily basis to avoid rising temperature above 60 ºC and prevent ash formation in the final product. The process of pile mixing continued until the temperature stabilized around 25 ºC for few days, which required approximately 70 days from the start of composting. The final compost was mechanically sieved, air-dried, and packed in plastic bags.

Methods for compost analysis. The pH of the composts was measured in a 1:5 (v/v) compost/water suspension. The pH at which the net surface charge on the compost surface is zero (pH of point of zero charge, pH_{pzc}) was measured by the pH drift method (Sunjuk et al. 2019). The initial pH (pH_i) of different solutions (25.0 mL of 0.01 M KCl in different conical flasks) was adjusted over the range 2.0 to 10.0 (accuracy ± 0.1 unit) by adding acid or base. To the flasks, 0.25 g compost was added and the final pH (pH_f) was recorded after 24 h shaking at 25 ºC. The difference (pH_i - pH_f) was then plotted against pH_i and the pH_{pzc} was estimated as the point at which the difference is zero. Contents of C, H, and N were quantified using CHN elemental analyzer (ELTRA CW multiphase determinator, Italy). Cation exchange capacity (CEC) and specific surface area (SSA) were measured following standard methylene blue adsorption test (Yener et al., 2012). To test metals leaching, 0.50 g compost were shaken with 50 ml of distilled water for 24 hours, the solution was filtered and analyzed by ICP-OES to detect the eluted Cu, Pb, and Zn (Al-Saqarat et al. 2017). Additional properties of the composts can be found at Paradelo et al. (2020).

Surface characteristics of composts were obtained using standard N_2–adsorption techniques (Quantachrome, Nova, Surface Area and Pore Size Analyzer, USA); specific surface area and pore size distribution were determined following the Barrett-Joyner-Halenda (BJH) method. For the study of dye adsorption mechanisms on compost, dye-loaded composts were separated from solution, washed with distilled water, and dried at

105 ◦C. Then, 100 mg of each compost were thoroughly mixed with 300 mg dried KBr and pressed at 10 bar to produce the disc for the preparation of the spectra. FTIR spectra were obtained within the range 400–4000 cm^{-1} using a PerkinElmer Dynascan Interferometer AVI (Waltham, MA, USA).

The main physicochemical parameters of the composts are provided in Table 3.1.

Table 3.1. Physicochemical parameters of the composts. pH$_{ZPC}$: pH at point of zero charge; OM: organic matter; EC: electric conductivity; AEC: anion exchange capacity; CEC: cation exchange capacity; SSA: specific surface area.

	CPB	MSWC	JCOM
pH	5.3	8.5	8.6
pH$_{ZPC}$	4.4	8.2	8.2
OM, %	95.3	43.8	76.6
EC, dS m^{-1}	0.98	9.4	7.8
Total K, mg kg^{-1}	79.8	466	2.9
Total Cu, mg kg^{-1}	15.2	1867	ND
Total Pb, mg kg^{-1}	7.4	976	9.8
Total Zn, mg kg^{-1}	33.8	2087	ND
C, %	53.6	22.9	46.8
H, %	5.16	2.95	4.2
N, %	0.93	2.83	1.87
C/N ratio	58	8	25
AEC, cmol$_{(-)}$ kg^{-1}	4.6	3.6	-
CEC, cmol$_{(+)}$ kg^{-1}	25.4	18.8	-
SSA, m^2 g^{-1}	152	104	263

3.1.2 Adsorbates

Six textile dyes were used belonging to the main dye classes: basic, acid, direct and reactive dyes. The dyes were Basic Blue 9 (MB, methylene blue), Basic Violet 10 (also known as rhodamine B), Acid Red 27 (also known as amaranth dye), which were purchased from Panreac (Barcelona, Spain). Direct Blue 151, Direct Blue 71 and Reactive Violet 4 were purchased from Sigma–Aldrich® chemicals.

Methylene blue is d[7-(dimethylamino) phenothiazin-3-ylidene] dimethylazanium chloride. Methylene blue is a cationic dye and has three cyclic rings and one S atom.

Basic Violet 10 is 9-(2-carboxyphenyl)-3,6-bis(diethylamino)xanthylium chloride. Moreover, this dye has many polar functional groups. For Basic Violet 10, the molecule is variable as Zwitterion at pH >3.7 and has no azo bond in its structure.

Acid Red 27 is trisodium (4E)-3-oxo-4-[(4-sulfonato-1-naphthyl)hydrazono] naphthalene-2,7-disulfonate. Acid Red 27 has one azo bond with three ionizable sulfonate groups.

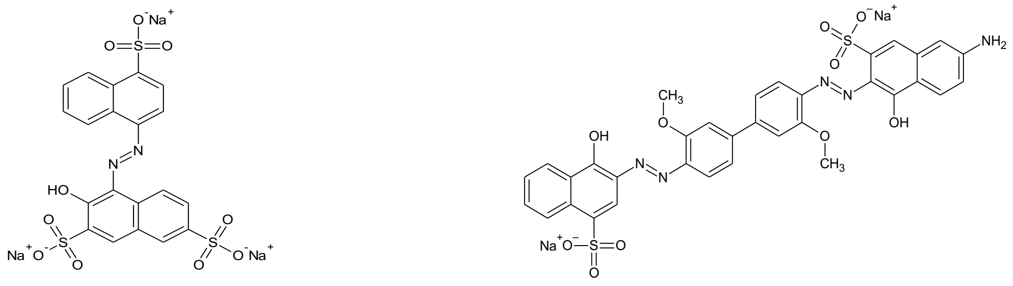
Direct Blue 151 is disodium 7-amino-4-hydroxy-3-[[4-[4-[(1-hydroxy-4-sulfonatonaphthalen-2-yl)diazenyl]-3-methoxyphenyl]-2-methoxyphenyl] diazenyl] naphthalene-2-sulfonate. This molecule has two azo bond N=N, two ionizable sulfonate groups conferring them an anionic character, polar groups (N-H, O-H, C-O), and a large hydrophobic skeleton.

Direct Blue 71 is tetrasodium 3-[[4-[[4-[(6-amino-1-hydroxy-3-sulfonatonaphthalen-2-yl)diazenyl]-6-sulfonatonaphthalen-1-yl]diazenyl]naphthalen-1-yl]diazenyl]naphthalene-1,5-disulfonate. This dye has three azo bonds N=N, four ionizable sulfonate groups, polar functional groups (N-H and O-H), and a high hydrophobic skeleton made up of four naphthalene molecules.

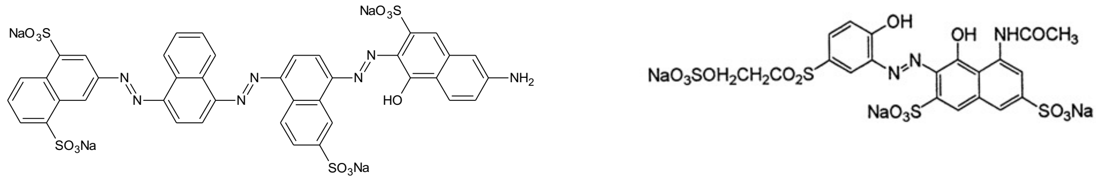
Reactive Violet 4 is copper trisodium 5-acetamido-4-oxido-3-[[2-oxido-5-(2-sulfonatooxyethylsulfonyl) phenyl] diazenyl] naphthalene-2,7-disulfonate. Reactive Violet 4 is also an azo dye, with one azo bond, three sulfonate groups, and O-H as polar functional group.

For basic dyes like Methylene Blue and Basic Violet 10, the most common application is for acrylic, polyester, modified polyesters, and nylons dyeing. For Acid Red 27, the application is for modified acrylics and nylon dyeing. For direct dyes like Direct Blue 151 and Direct Blue 71 the application is for cotton, leather and silk dyeing. Reactive Violet 4 is used for cotton, nylon, and wool dyeing.

Methylene Blue *Basic Violet 10*



Acid Red 27 *Direct Blue 151*



Direct Blue 71 Reactive Violet 4

Figure 3.1. Molecular structures of tested textile dyes.

The p*K*$_a$ of the dyes was determined from the half-point of pH-V_{NAOH} titration plot of 0.010 M dye solutions. As model dye, MB was tested for comparison purposes, the dye has protonated N atom (i.e., cationic one). The measured p*Ka* values and chemical structures of the dyes are provided in Table 3.2 and Figure 3.1.

Table 3.2. Chemical properties of tested textile dyes.

Dye	Molecular formula	Molecular weight (g mol^{-1})	pKa	Water solubility
Methylene Blue (MB)	$C_{16}H_{18}ClN_3S$	319.8	3.8	High
Basic Violet 10 (BV10)	$C_{28}H_{31}ClN_2O_3$	478.5	3.7	8 to 15 g L^{-1}
Acid Red 27 (AR27)	$C_{20}H_{11}N_2Na_3O_{10}S_3$	604.5	2.61, 7.41	50 g L^{-1}
Direct Blue 151 (DB151)	$C_{34}H_{25}N_5O_{10}S_2Na_2$	773.7	2.68	High
Direct Blue 71 (DB71)	$C_{40}H_{23}N_7Na_4O_{13}S_4$	1029.9	2.71	High
Reactive Violet 4 (RV4)	$C_{20}H_{16}N_3Na_3O_{15}S_4$	799.1	4.55	High

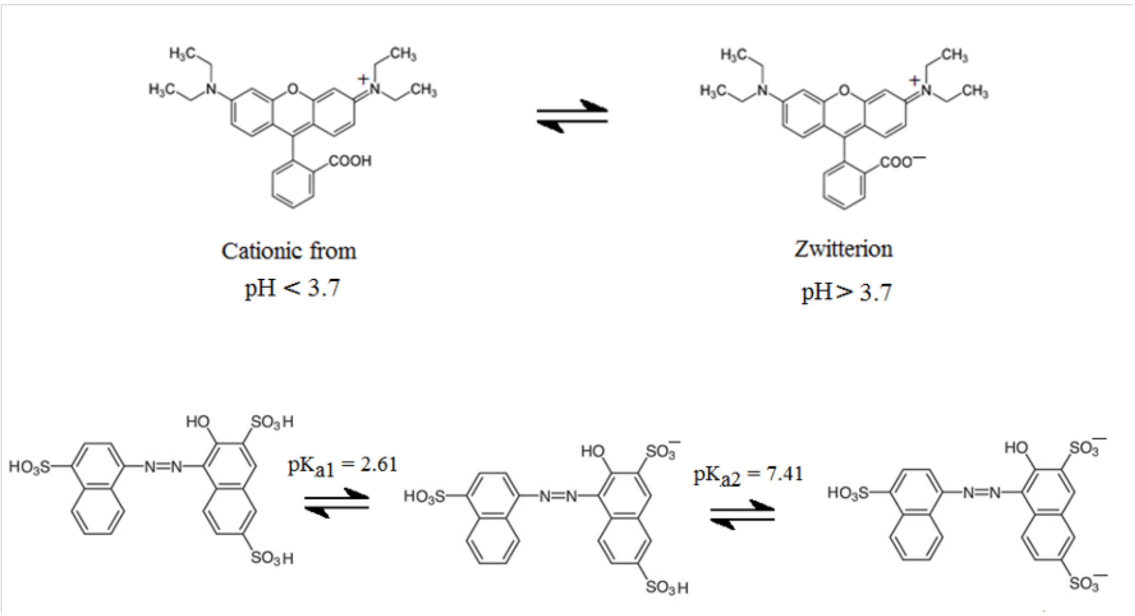


Figure 3.2. The various chemical forms of Basic Violet 10 (top) and Acid Red 27 (bottom) depending on solution pH.

3.2 METHODS FOR THE STUDY OF DYE REMOVAL

3.2.1 Preliminary experiment: Kinetics and equilibrium adsorption of methylene blue

In a preliminary experiment to test the potential capacity of composts for dye removal, the batch adsorption capacity was studied using a widely used dye, methylene blue. Kinetics and equilibrium batch experiments were performed using this dye and the two Spanish composts.

3.2.1.1 Kinetics

For the study of adsorption kinetics, 500 mg of each compost (<5 mm) were weighed in polypropylene centrifuge tubes with 10 mL or 50 mL of a 200 mg/L methylene blue solution. Suspensions were shaken at 60 rpm on a rotary shaker at room temperature (25 ±1°C) for different times (1, 2, 4, 8, 16, 24 and 48 h), and centrifuged at 4000 *g* for 5 min. Aliquots from the supernatant were analyzed immediately for methylene blue by measuring absorbance at 665 nm in a UV/VIS spectrophotometer (Varian Cary 100, Agilent Technologies, Inc., Santa Clara, CA, USA). The amount of methylene blue adsorbed (mg/g) was calculated as the difference between the amount of dye added initially and the amount of dye that remains in the solution at the end. Blanks without compost were run in parallel to test dye adsorption on the tubes. All the experiments were performed in triplicate.

3.2.1.2 Equilibrium adsorption and effect of pH, salinity and particle size

For the study of adsorption, a contact time of two hours was selected, following the results of the kinetics studies. For the experiments, 500 mg of each compost were weighed in polypropylene centrifuge tubes with 50 mL of solutions with different concentrations of methylene blue (100–5000 mg L^{-1}). Suspensions were shaken on a rotary shaker at 60 rpm at room temperature (25 ± 1ºC) for 2 h and centrifuged at 4000 g for 5 min. The supernatant was removed and analyzed immediately for methylene blue. The amount of dye adsorbed was calculated as the difference between the dye added initially and the amount that remains in the solution at the end. All the experiments were performed in triplicate. Blanks without compost were run in parallel to test dye adsorption on the tubes.

To test the effect of ionic strength, adsorption curves were prepared following the general procedure, but methylene blue solutions were prepared in 1.0 M KCl as background electrolyte.

The effect of pH was assessed preparing adsorption curves as explained in the general procedure, but the pH of the suspensions was modified by adding the necessary volume of 1M NaOH or 1M HCl to reach final pH 3.0, 5.0, and 7.0 with accuracy ± 0.4.

In order to test the effect of compost particle size on adsorption, composts were ground to pass through a 1-mm mesh sieve and then adsorption curves were performed following the general procedure.

3.2.2 Comparison of batch adsorption of different types of dyes and influence of experimental factors

Adsorption of four textile dyes of different natures, namely Basic Violet 10 (BV10), Acid Red 27 (AR27), Direct Blue 151 (DB151) and Reactive Violet 4 (RV4), onto pine bark compost (CPB) and municipal solid waste compost (MSWC) was studied here. Adsorption kinetics and equilibrium adsorption at different solution pH values (3.0–7.0) and salinity (0–1.0 M KCl) conditions have been assessed in batch experiments.

3.2.2.1 Kinetic studies

The effect of contact time on dye removal by compost was studied by shaking 50.0 mL of 20-500 mg L^{-1} dye solutions with 0.5 g of compost. The suspensions were shaken for different times (5–1440 min) at 25 °C. At specific times, 2.0 mL of the solution were withdrawn and filtered. The dye concentrations in the extracts were quantified by measuring absorbance in an UV/VIS spectrophotometer (Thermo evolution 100 electro corporation, USA) at 556 nm for Basic Violet 10, 522 nm for Acid Red 27, 554 nm for Direct Blue 151, and 558 nm for Reactive Violet 4.

3.2.2.2 Equilibrium adsorption

Equilibrium sorption was first investigated at room temperature (22-24 ºC). Batch adsorption tests were carried out by agitating 50.0 mL of the dyes solutions, at various initial concentrations (C_0, mg L^{-1}), with 0.50 g adsorbent, in a thermostated shaker (GFL, Germany) at 25 °C for 24 h. Then, the particles of compost were removed by centrifugation at 5000 rpm for 5.0 min and the clean supernatant was filtered in preparation for spectral analysis. The effect of the solution pH on dyes uptake was studied over the range 3.0-7.0 (±0.3) by adjusting the pH of the initial dye solution with 0.5 N NaOH or 0.5 N HCl; the pH was regularly adjusted during sorption tests. The effect of solution salinity on dye removal was studied at 0.1 and 1.0 M KCl background solution. All tests were carried out in triplicate. The spectra of dyes were insensitive to variations in pH and salinity, so their quantification in the extracts was carried out as explained above.

3.2.2.3 Desorption

For the study of desorption, 500 mg of each compost were suspended in 50 mL of dye solutions in triplicate, with initial concentrations of 2000 mg L^{-1} for BV10, 700 mg L^{-1} for DB151, 200 mg L^{-1} for RV14 and 50 mg L^{-1} for AR27. Suspensions were shaken on a rotary shaker at 60 rpm at room temperature (25 ± 1 °C) for 24 h and centrifuged at 4000 g for 5 min. The supernatant was removed and the centrifuged residues were weighed to calculate the amount of dye solution occluded in the solid. Then the composts were resuspended in 50 mL of water, shaken again for 24 h and centrifuged. Supernatants were analyzed immediately for dye concentrations as explained above and desorption was expressed as percentage of the previously absorbed dye.

3.2.2.4 IR measurement of composts and dye-loaded composts

FTIR spectra of initial and dye-loaded composts were measured within the range 400–4,000 cm^{-1} using a PerkinElmer instrument (PerkinElmer Dynascan Interferometer AVI, Waltham, MA, USA). Dye-loaded composts were separated from the solution after adsorption, washed with distilled water, and dried at 105 °C before scanning. Typically, 100 mg compost was thoroughly mixed with 300 mg dried KBr and pressed at 10 bar to produce the needed disc for measurement.

3.2.3 Optimization of the process in batch conditions: A case study with DB71

In this experiment, the adsorption capacity of local Jordanian compost was tested for DB71 (as a model textile pollutant). The experiment was designed to find the best combination of adsorption factors (mass, concentration, pH, salinity, temperature, and contact time) for dye removal. Adsorption isotherms, uptake in fixed-bed adsorber and desorption tests were carried out.

Table 3.3. Four-level six-factor factorial experimental design matrix.

Code	Factor (unit)	Levels			
		-2	-1	+1	+2
X_1	Mass (g)	0.20	0.40	0.60	0.80
X_2	Concentration (mg L^{-1})	200	300	400	500
X_3	pH	3.0	5.0	7.0	9.0
X_4	Contact time (h)	60	120	180	240
X_5	Temperature (^{0}C)	20.0	30.0	40.0	50.0
X_6	Salinity (M)	0	0.3	0.6	0.9

3.2.3.1 Design of experiment, factor coding and optimization

Following a multilevel multifactor design, the optimum combination of factors leading to the best dye uptake with minimum experimental efforts can be determined.

The combined influence of six factors (sorbent mass, pH, concentration, contact time, temperature, and salinity) on DB71 retention by compost was studied using a balanced multilevel multifactor design (Brereton, 2007). Multilevel multifactor design is necessary to save time while studying the influence of all factors on dye retention by running limited number of tests. Moreover, the factorial design can detect the possible interaction between factors.

The proper selection of the levels of the factors and coding of these levels is necessary to end up with meaningful outputs. Four levels for each factor were selected and coded as -2, -1, +1, and +2 (the selected levels along with codes for the factors are provided in Table 3.3). Coding of levels is necessary because of the high numerical differences between levels from factor to factor, so coding allows to balance these variations and improve modelling quality. To generate an orthogonal design, the proper number of experiments N must be a multiple of a power of the number of levels l so that $N = k\,l^r$, where r is at least 2 (Brereton, 2007). Setting k equal to 1 and r to the minimum value, this implies that $N = l^2$. Hence for a four-level design, 16 experiments should be performed.

Table 3.4. Experimental design based on the selected variables of the factors.

Sorption test[a]	X_1	X_2	X_3	X_4	X_5	X_6
1	-2	-2	-2	-2	-2	-2
2	-2	-1	-1	2	-1	-2
3	-1	-1	2	-1	-2	1
4	-1	2	-1	-2	1	1
5	2	-1	-2	1	1	-1
6	-1	-2	1	1	-1	1
7	-2	1	1	-1	1	-2
8	1	1	-1	1	-2	2
9	1	-1	1	-2	2	2
10	-1	1	-2	2	2	1
11	1	-2	2	2	1	2
12	-2	2	2	1	2	-2
13	2	2	1	2	-2	-1
14	2	1	2	-2	-1	-1
15	1	2	-2	-1	-1	2
16	2	-2	-1	-1	2	-1

[a] For a multilevel multifactor design, number of experiments = l^2 where l is number of selected levels of the factors. Each test was repeated three identical times (n=3)

Sixteen tests were carried out to determine the best combination of the six factors giving the maximum retention of DB71 by compost. It is common in factorial analysis to model experimental data by building a relationship between the factors or x-independent variables (mass, pH, temperature, salinity, contact time, etc.) and y dependent variables or dye sorption value. A typical model between factors (independent variables) and dye sorption (dependent variable) is numerically provided as:

$$\begin{gathered}\text{Dye sorption} = b_1 \cdot \text{Mass} + b_2 \cdot \text{Conc} + b_3 \cdot \text{pH} + b_4 \cdot \text{Time} + b_5 \cdot \text{Temp} + b_6 \cdot \text{Sal} + \\ b_1 \cdot b_2 \cdot \text{Mass} \cdot \text{Conc} + b_1 \cdot b_3 \cdot \text{Mass} \cdot \text{pH} + b_1 \cdot b_4 \cdot \text{Mass} \cdot \text{Time} + b_1 \cdot b_5 \cdot \text{Mass} \cdot \text{Temp} + \\ b_1 \cdot b_6 \cdot \text{Mass} \cdot \text{Sal} + b_2 \cdot b_3 \cdot \text{Conc} \cdot \text{pH} + b_2 \cdot b_4 \cdot \text{Conc} \cdot \text{Time} + b_2 \cdot b_5 \cdot \text{Conc} \cdot \text{Temp} + b_2 \cdot b_6 \cdot \text{Conc} \cdot \text{Sal} \\ + b_3 \cdot b_4 \cdot \text{pH} \cdot \text{Time} + b_3 \cdot b_5 \cdot \text{pH} \cdot \text{Temp} + b_3 \cdot b_6 \cdot \text{pH} \cdot \text{Sal} + b_4 \cdot b_5 \cdot \text{Time} \cdot \text{Temp} + b_4 \cdot b_6 \cdot \text{Time} \cdot \text{Sal} + \\ b_5 \cdot b_6 \cdot \text{Temp} \cdot \text{Sal}\end{gathered}$$

Linear terms (b_1-b_6) allow for a direct relationship between dye sorption and a given factor. The factor with higher coefficient has higher linear effect on dye uptake. For example, if $b_1>b_2$ ($b_1\&b_2>0$) then dye sorption is strongly correlated with mass compared to concentration. In the same line, positive coefficient reflects a direct correlation of the factor with sorption and vice versa. Interaction terms b_1b_2-b_5b_6 (often significant for modelling sorption systems) are necessary to understand the nature of interaction between factors. For example, solute retention at low pH and high compost mass may be higher than at the same mass and higher pH, and this can figured out by interaction terms of both factors. In fact, influence of two factors (pH and temperature for example) on solute retention is rarely independent. For example, if $b_{12}>>b_{13}$ ($b_{12}\&b_{13}> 0$) then interaction between mass and concentration is more significant than mass and pH. Moreover, negative interaction coefficients indicate better sorption if both factors are maintained at their opposite limits. Initial analysis indicates that non-linear terms (mass×mass, pH×pH, Time×Time, etc.) were not significant for dye uptake, hence they are excluded (Brereton, 2007).

Student's *t*-test was applied to assess the significance of all terms (b_1-b_{56}) provided that number of tests (16) were more than number of factors (6). The significance *t*-test was carried out as follows (Brereton, 2007): (a) the square covariance matrix was calculated and the variances (v) (the diagonal values of covariance matrix) were obtained, (b) the error sum of squares S_E were calculated from the experimental sorption values and the ones predicted from the equation above, (c) estimation of mean error sum of squares (s) by dividing S_E by the number of degrees of freedom which equals to N-P, where N is number of experiments (16) and P is the number of factors (6), and (d) estimation of *t*-value, $t = b/(sv)^{1/2}$ and the higher this ratio, the more significant is the factor at the desired confidence level. For all terms, the calculated t value was less than 0.003 confirming the statistical significance of all coefficients.

3.2.3.2 Batch adsorption tests

Based on the outputs of multifactor design, the optimum levels of tested factors will be ascertained and used to conduct kinetic, sorption, and column tests. All tests employed air-dry sieved compost (≤ 106 μm). Batch tests were performed by agitating 0.400 g dry compost with 150.0 mL solution of DB71 covering the concentration range (5-400 mg L^{-1}), in a thermostated shaker (GFL, Germany) at 50 °C and pH 3.0 for 240 min. Compost particles were removed by centrifugation at 5000 rpm for 5.0 min and the supernatant was filtered for analysis. Dye concentration in the extract (Ce, mg L^{-1}) was determined in a UV/VIS spectrophotometer at 584 nm. Sorption kinetics were studied by suspending 0.400 g of adsorbent in 150.0 mL of 100 mg L^{-1} dye solution. The suspensions were then agitated for different times (5–240 min) at 50°C, pH 3.0 and 0.6 M NaCl. At each time, 2.0 mL of the solution were withdrawn and filtered to measure its absorbance and afterwards returned to the original solution. For comparison purposes, the adsorption capacity of the tested compost towards DB71 was compared with a commercial Spanish compost CPB.

3.2.3.3 Desorption test

In order to assess the potential recycling of the biosorbent, 400 mg of compost were agitated with 15 mL of 400 mg L^{-1} solution of DB71 (pH 3.0, 0.6 M NaCl, and 50 °C) in 250 mL-conical flasks for 4.0 hours. The supernatant was then removed and the dye-loaded compost re-suspended in 15 mL of different solvents (0.1 M HNO_3, *n*-hexane, water, 0.1 M NaOH, and ethanol) for 4.0 hr and treated as described earlier. Desorption of dye-loaded compost with water was performed with a 0.6 M NaCl solution at pH 3.0 and 50 °C, whereas desorption by other solvents was done at 25 °C without adjusting pH or adding salt. This procedure was repeated for two more cycles using fresh solvents and DB71 was measured in the extracts after each desorption cycle. The percentage of dye desorption was estimated from the retained amount and the amounts removed in the consecutive desorption cycles.

3.2.3.4 Fixed-bed column test

In practice, the column type continuous flow operation is more useful in large-scale wastewater treatment, easy to run, it attains a high yield and can be easily scaled up from a laboratory-scale procedure (Al-Degs et al., 2009). The stages in the separation process in column adsorber can also be automated and high degrees of cleaning can often be achieved in a single step process. Column tests were carried out on a glass column with internal diameter of 1.0 cm and 20 cm height, filled with a known amount of compost (3.0-7.0 g or bed-depth 5.1-12.8 cm). To provide a uniform inlet flow, a layer of glass beads was placed at the top of the packed compost. The tests were carried out by pumping the DB71 dye solution through the column in downward flow mode, using a peristaltic pump (Smith and Nephew Watson-Marlow, England). All experiments were conducted at 20-22 °C, pH 3.0, and 0.6 NaCl. The effect of various operational factors including flow rates (1.0, 1.5 and 2.0 mL min^{-1}), bed-depth height (5.1, 8.8 and 12.8 cm) and influent DB71 levels (10, 15 and 20 mg L^{-1}) have been investigated. The concentration of dye was measured in the effluent solution, which was periodically collected in 5-mL glass vials. The column is considered essentially exhausted when the effluent concentration reaches 90% (i.e., $C_{effluent}/C_{influent} = 0.9$ or 0.95) of initial concentration and the breakthrough point when $C_{eff}/C_{inf} = 0.01$.

3.2.4 Competitive and column adsorption

In this experiment, the practical assessment of pine park compost (CPB) adsorption toward BV10 and DB151 was assessed by running fixed-bed adsorber tests, carried out under different conditions including bed-depth, inlet concentration and flow rate. Moreover, single and competitive removal of BV10 and DB151 was studied under batch and column conditions.

3.2.4.1 Adsorption isotherms of single and bi-solute systems

Adsorption isotherms (at 25±1 °C) for both dyes were determined individually in batch experiments using the concentration–variation method. Samples of 0.50 g (±0.01 g) of CPB (particle range 250-500 μm) were added to 50.0 mL solutions containing different concentrations of dyes. The tests were operated at pH 3.0 (±0.3) as this maximize the sorption affinity of both dyes toward compost (Al-Zawahreh et al., 2021). For single and bi-solute (i.e., competitive) systems, the concentration ranges were 5.0-2000 and 5.0-700 mg L^{-1} for BV10 and DB151, respectively. To have equal chance for dyes sorption from solution, competitive tests were carried using equal molar concentration of both dyes (Issa et al., 2017). The suspensions were sealed and placed in a thermostated shaker (GFL, Germany) for 24 h, the equilibrium time as determined from earlier kinetic studies. After equilibrium, the supernatants were separated and the dyes were measured using predetermined calibration graphs for each dye. The absorbance values of the solutions were measured using double-beam spectrophotometer (Thermo evolution 100 electro corporation, USA) at 547 nm and 554 nm for Basic Violet 10 and DB151, respectively. For single-solute solution, dye concentration was estimated from Beer`s law, while for bi-solute solution modified Beer`s law was solved at the maximum wavelengths of both dyes. Surface concentrations of dyes were estimated from the mass balance equation. Blank solutions, containing no compost, were also included in the study. Adsorption isotherms were repeated in triplicate and the average values were reported.

3.2.4.2 Fixed bed column adsorber tests for single and bi-solute systems

Column or fixed bed adsorber experiments are recommended for testing practical application. For this, a glass column with internal diameter of 1.0 cm was filled with a known amount of pine bark compost. To provide a uniform inlet flow, a layer of 3.0 mm-glass beads was placed at the top of the packed compost. The column tests were carried out by pumping the dye solution through the column in downward flow mode, using a peristaltic pump (Smith and Nephew Watson-Marlow, England). All experiments were conducted at 25.0 °C and pH 3.0 (±0.3). The effect of various operational factors including flow rates (10-30 mL min^{-1}), bed-depth height (5.1-17.8 cm) and influent dye levels (50-150 mg L^{-1}) were investigated. The column was considered to be essentially exhausted when the effluent concentration reached 90% (i.e., $C_{eff}/C_{inf} = 0.9$) of initial concentration and the breakthrough point was fixed at $C_{eff}/C_{inf} = 0.01$. The effluent solutions were collected from the column at certain intervals, and the dye concentrations in the effluent were analyzed as outlined above. In addition to single dye uptake, bi-solute competitive adsorption was examined at different bed-depths of adsorber. For the binary mixtures, dyes were quantified as outlined earlier.

3.2.4.3 Regeneration of compost fixed-bed adsorber

Desorption tests can clarify the nature of adsorption and the potential recycling of the exhausted compost. If the adsorbed dyes can be eluted by distilled water, then the dye is attached to the adsorbent by weak bonds. Although this would facilitate its recycling, it would not be desirable from the point of view of wastewater treatment. Hence, desorption tests were performed for batch and column system using different solvents including water. In the batch study, 0.1 M of H_2SO_4, CH_3COOH, or CH_3CH_2OH were added to the dye-loaded compost and shaken for 5.0 h. The suspensions were centrifuged at 5000 rpm for 5.0 minutes and the supernatants were analyzed for dye content. The chemical reagent with the higher dye recovery was then selected for desorption in the column test. In this case, the columns saturated with dyes were regenerated by passing the solvent through the adsorber at a low flow rate of 5.0 mL min^{-1} and effluents were recovered and analyzed as explained above, until the eluted dye content was under 1.0 mg L^{-1}.

3.3. MATHEMATICAL MODELLING

3.3.1 Kinetics

The amount of dye adsorbed by the compost (q_t, mg g^{-1}) at a time t was calculated as follows:

$$q_t = (C_0 – C_t) \cdot V/m$$

where C_0, V and m are initial dye concentration, the volume of solution (L) and mass of compost (g), respectively.

Adsorption kinetics data were described using the Lagergren's pseudo-first order and pseudo-second order models, defined respectively by the following equations:

$$q_t = q_e(1 - e^{-k_1 t})$$

$$q_t = \frac{k_2\, q_e^2\, t}{1 + k_2\, q_e\, t}$$

where q_t (mg g^{-1}) is the amount of dye adsorbed by the compost at a time t, q_e (mg g^{-1}) is the amount of dye adsorbed by the compost at equilibrium (this parameter is fitted by the model), k_1 (h^{-1}) is the pseudo-first-order rate constant, and k_2 (g mg^{-1} h^{-1}) is the pseudo-second-order rate constant.

The possibility of internal-diffusion was explored by using the common internal diffusion model (McKay et al., 2011):

$$q_t = k_d t^{1/2}$$

where k_d (mg g^{-1}min$^{-1/2}$) is the internal diffusion coefficient.

3.3.2 Equilibrium adsorption curves

3.3.2.1 Non-competitive adsorption

Isotherm data were adjusted to different models, including two and three parameter models (Ayawei et al., 2017). These models were tested to predict the maximum uptake capacity, formation of multilayer sorption, variability of active sites, porosity and heterogeneity of composts. Among known models, only three were found applicable: the Langmuir, Freundlich and Sips models. The Langmuir equation has the following form:

$$q_e = \frac{Q_L K_L C_e}{1 + K_L C_e}$$

where q_e (mg g^{-1}) is the amount of dye retained by the compost at equilibrium, C_e (mg L^{-1}) is dye concentration in solution at equilibrium, Q_L (mg g^{-1}) and K_L (L mg^{-1}) are the maximum sorption capacity and the affinity constant of the dye toward the compost, respectively. The model assumes equal-energy active sites, no interaction with adsorbed solutes, and one mono-layer coverage (Ayawei et al., 2017). This model had been applied for many systems including dye-compost systems.

The Freundlich isotherm model expression defines the heterogeneity of the surface as well as the exponential distribution of the active sites and the active sites energies:

$$q_e = K_F {C_{eq}}^{1/n}$$

where K_F is the Freundlich constant ($L^n\ mg^{1-n}\ g^{-1}$) and can indicate uptake capacity while $1/n$ (dimensionless) measures favorability of the process and both are system specific constants (Ayawei et al., 2017). This model is commonly used to present adsorption data for heterogeneous surfaces (including composts) over wide concentration ranges (Sunjuk et al., 2019).

Sips model is a three-parameter model often applied to present sorption isotherm data over a wide concentration range. A combination of both Langmuir and Freundlich isotherm models resulted in the formation of the Sips isotherm model, which is deduced to predict the heterogeneity of the adsorption systems as well as to circumvent the limitations associated with the increased concentrations of the adsorbate of Freundlich model. This, in turn, leads to the production of an expression that have a finite limit at high concentration. Sips model has the validity in localizing the adsorption without the adsorbate-adsorbate interaction (Sips, 1948):

$$q_e = \frac{Q_S K_S C_e^{n_S}}{1 + K_S C_e^{n_S}}$$

where Q_s ($mg\ g^{-1}$), K_s ($L\ mg^{-1}$)^{ns}, and n_s are Sips maximum adsorption capacity ($mg\ g^{-1}$), Sips equilibrium constant, and the model exponent (Sips, 1948; Ayawei et al., 2017).

The selection of the appropriate model plays a vital role in the objective of the research work. The relative error of prediction (*REP%*) was used as a criterion to select the optimum model as equilibrium data was fitted by more than one model. *REP%* is estimated as follows:

$$REP\% = 100 \cdot \sqrt{\frac{\sum_{i=1}^{n}(q_{i,pred} - q_{i,act})^2}{\sum_{i=1}^{n}(q_{i,act})^2}}$$

where $q_{i,pred}$, $q_{i,act}$, and n are predicted sorption value, actual sorption value, and number of experimental points, respectively. Lower *REP%* indicates better model fitting to data.

3.3.2.2 Competitive adsorption

For competitive dyes systems, the isotherms were modelled using the earlier equations. The competition between dyes was assessed by estimating the competition factor as follows (Issa et al., 2017):

$$CF = Q_{max}\ (bi\text{-}solute\text{-}system) / Q_{max}\ (single\text{-}solute\text{-}system)$$

where Q_{max}(bi-solute-system) and Q_{max}(single-solute-system) are the maximum retention capacities estimated from single and bi-solute systems, respectively. In case of positive competition, the competition factor (CF) is higher than unity and adsorption is enhanced by the other solutes. For CF=1, adsorption takes place without competition. The general case is CF<1, meaning that solute affinity is reduced due to negative competition with other solutes (Issa et al., 2017).

3.3.3 Column adsorption

3.3.3.1 Mass transfer zone and breakthrough curve

The relation between the nature of breakthrough curve and fixed-bed adsorption was adequately explained by mass transfer zone MTZ (Walker and Weatherley, 2000). As the compost becomes exhausted over time, the MTZ moves downward across the adsorbent bed, leaving behind the portion of the adsorbent bed that is saturated with dyes. Thus, when MTZ reaches the end of the column, breakthrough occurs. Typically, the column is saturated with dye when $C_{inf} = C_{eff}$. As a result, MTZ forms at the front of the column, where adsorption occurs. Many factors influence the depth of MTZ, including the type of the adsorbate, adsorbent properties, adsorber mass (or bed-depth), adsorbent particle size, adsorbate inlet concentration, solution pH, and solution flow rate (Faust and Aly, 1987; Walker and Weatherley, 2000). Among these variables, flow rate, solute concentration, presence of competing solutes and bed-depth notably affect the lifetime of fixed-bed adsorber (Patel et al., 2019). MTZ forms in the adsorbent bed and goes down until it reaches the adsorber end, when the effluent solute concentration begins to rise in the aqueous phase (Faust and Aly, 1987; Walker and Weatherley, 2000). The height of mass transfer zone (MTZ) often depends on sorption rate and flow rate of solution. The height of mass transfer zone HMTZ is estimated as follows (Alardhi et al., 2020):

$$HMTZ = H \cdot (t_{ex} - t_b)/t_{ex}$$

where H, t_{ex}, and t_b are bed-depth (cm), time needed for adsorber exhaustion (min), and time for breakthrough point (min). The more rapid sorption kinetics, the shallower is the HMTZ. The time needed for mass transfer zone (TMTZ) to develop and move down to the end of column adsorber is estimated as (Al-Degs et al., 2009):

$$TMTZ = V_{ex} / u$$

where V_{ex} and u are total volume of feed solution needed for saturation and volumetric flow rate, respectively. Furthermore, axial dispersion, external film resistance, and intraparticle diffusion resistance are all factors that affect solute removal in the adsorber (Patel et al., 2019). As a result, axial dispersion, external mass transfer, intraparticle diffusion, and nonlinear isotherms are assumed in the mathematical correlations for adsorption in fixed-bed columns (Patel et al., 2019).

The breakthrough curve plots the ratio of effluent dye concentration to influent dye concentration (C_{eff}/C_{inf}) as a function of process time (t) or treated volume (V). Two common models were used to model the curves: the Thomas and Bed Depth Service Time (BDST) models. The Thomas model was used to estimate dye saturation values and influence of competition, while BDST model was used to estimate service time of the adsorber at different bed-depths.

Fixed-bed capacity at saturation. At a certain saturation point (i.e., $C_{eff}/C_{inf} = 0.9$) the total capacity of the column is calculated as follows (Calero et al., 2009):

$$q_{bed} = \frac{u \cdot C_0}{m \cdot 1000} \int_{t=0}^{t=t_{saturation}} \left(1 - \frac{C_{eff}}{C_{inf}}\right) dt$$

where u is the feed flow rate (mL min^{-1}), C_{eff} is the effluent concentration at time t (mg L^{-1}), C_o is the inlet concentration (mg L^{-1}) and $t_{\text{saturation}}$ is the time required for the bed to become saturated (min) at $C_{eff}/C_{inf} = 0.9$.

3.3.3.2 Thomas model

The Thomas model is the most commonly utilized for column investigations. The rate constant and maximum solid-phase concentration of adsorbate on adsorbent are calculated using data from continuous column investigations, using the Thomas adsorption model. The Thomas model is based on the premise that rate driving forces follow second-order reversible reaction kinetics and that there is no axial dispersion in Langmuir adsorption–desorption kinetics (Thomas, 1944; Patel, 2019). The Thomas model is also used to establish breakthrough curves over long service time, and it is often applied to model dye removal in column experiments (Negrea et al., 2020). Hence, it has been frequently adopted to study adsorbents of high capacity at dynamic conditions.

The Thomas equation is linearly presented as follows (Thomas, 1944; Negrea et al., 2020):

$$ln(\frac{C_{inf}}{C_{eff}} - 1) = \frac{K_{Th} q_{Th} m}{u} - K_{Th} C_0 t$$

where C_{inf} is the concentration of influent solution (mg L^{-1}); C_{eff} is the solution concentration at time t in the effluent solution (mg L^{-1}); K_{Th} is the Thomas rate constant, (L mg^{-1} min^{-1}); q_{Th} is the equilibrium solute uptake per gram of compost (mg g^{-1}); m is the mass of adsorbent (g); u is the volumetric flow rate (mL min^{-1}).

3.3.3.3 Bed-depth service time BDST model

The basic relations correlating C_{inf}/C_{eff} and column service time (t) for purification in a flowing system have been proposed by Bohart and Adams (1920). This model offers a simple approach and rapid prediction of adsorber design and performance (McKay et al., 1990; Al-Degs et al., 2009). The rationale for BDST model is that equilibrium does not occur immediately in bed, hence the rate of sorption is proportional to the fraction of sorption capacity left on the media. In terms of process concentrations and adsorption factors, this model is based on the relationship between bed depth and service time (Patel, 2019). This model assumes that the adsorption rate is proportional to both the residual capacity of activated carbon and the concentration of the adsorbing solute. The Adams–Bohart model is presented as follows:

$$\ln\left(\frac{C_{inf}}{C_{eff}} - 1\right) = \ln\left(e^{\frac{k_a N_{oH}}{u}} - 1\right) - k_a C_0 t$$

where C_{inf} (mg L^{-1}) is the inlet dye concentration and C_{eff} (mg L^{-1}) is the maximum acceptable limit concentration which could be at 50 % exhaustion, t is the fix-bed service time (s) and H is the bed-depth (m). N_o is the column adsorption capacity (mg L^{-1}), u is the volumetric flow rate (m^3 s^{-1}) of solution, K_a is the BDST rate constant (L mg^{-1} s^{-1}).

As the exponential term is usually much larger than the unity, then the relation is reduced to:

$$t = \frac{N_0}{C_{inf}u}H - \frac{1}{k_a C_{inf}}\ln\left(\frac{C_{inf}}{C_{eff}} - 1\right)$$

A plot of service time t against H should generate a straight line with slope equal to ($N_0/C_{\text{inf}}\,u$) and intercept equal to:

$$-\frac{1}{k_a C_{inf}}\ln\left(\frac{C_{inf}}{C_{eff}} - 1\right)$$

From the slope and intercept, both N_0 and K_a can be calculated. At 50% breakthrough ($C_{\text{inf}}/C_{eff} = 0.5$), the second term on the right-hand side of the previous equation is reduced to zero, generating the following simplified equation (Zulfadhly et al., 2001; Al-Degs et al., 2009):

$$t_{0.5} = N_o/C_o\,u \cdot H$$

A plot of $t_{0.5}$ (service time at 50% breakthrough or $C_{eff}/C_{inf} = 0.5$) versus H should yield a straight line with a slope of (N_0/C_0u) and this slope represents the time required to exhaust a unit length of the adsorber under the applied experimental variables. In fact, the equation can be used to estimate column service time at C_{eff}/C_{inf} range 0.1-0.5 or saturation% from 10-50 (Nidheesh et al., 2021).

3.3.3.4 Utilization factor

The adsorbent utilization factor (η) relates the total capacity achieved in adsorber (q_{bed}) with the total capacity obtained in equilibrium batch isotherm (Q_{max}) and therefore represents the amount of active sites that are not utilized in the adsorber (Canteli et al., 2014):

$$\eta = q_{bed} / Q_{max}$$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4 GENERAL DISCUSSION

4.1 COMPOST PROPERTIES AND USE

Because of population growth, industrialization, and anthropogenic activities involving industrial processes, commercial activities and agricultural practices, environmental pollution resulting from the uncontrolled mobility and build-up of heavy metal ions, organic pollutants and dyes has been gradually occurring. As a result, research and development activities have been stepped up in the hope of developing a variety of approaches and protocols for the removal of harmful substances. While it would be impractical to go over all the various clean-up methods in detail here, due to the abundance of original research findings and critical reviews on these topics of environmental remediation in the literature, the focus of the downstream discussions herein will be on the adsorptive sequestration pathway of a variety of environmental pollutants using composts as new sorbents. In comparison to other materials such as soils, minerals, activated carbon and nanoparticles, composts (which are typically formed from organic wastes and other organic process leftovers) have been researched less as adsorbents.

Compost is the result of the aerobic biological decomposition of organic matter present in wastes by the activity of mesophilic and thermophilic microorganisms. Many types of composts can be produced from a wide range of waste materials and by-products, such as urban wastes or agro-industrial wastes, and their elaboration usually can be achieved with low costs. Typically, composts are safe and stable products, often with neutral or slightly alkaline pH, highly porous and rich in organic matter. Their main applications are in the field of agronomy and take advantage of their high organic matter and nutrient content, so that they are mostly used as organic amendments in agricultural and horticultural soils, and as components in soilless horticultural substrates. In addition, composts contain microorganisms that can achieve biodegradation of many organic substances, and present a diversity of functional groups that can interact with organic and inorganic compounds. This often results in a reduction of mobility and bioavailability of pollutants in soils amended with compost, particularly in the case of heavy metals.

The sorption capacities of various composts for a variety of pollutants have been gradually garnering attention in recent years. The presence of functional groups (e.g. carbonyl, carboxylic, and amino groups) on the surface of composts, which play a critical role in successful binding or complexation, is one of the primary reasons for the preferential sorption of environmental pollutant species onto composts. For these reasons, they are advantageously used for soil and water remediation processes, where composts can be employed as amendments for pollutant immobilization.

In the upcoming section, more details will be given regarding the characterization of the three composts employed in this thesis: pine bark compost (CPB), Spanish municipal solid waste compost (MSWC), and Jordan urban waste compost (JOCOM). In addition, the main physicochemical parameters that are usually reported for composts to assess their final application, either for agricultural purposes or for environmental applications, will also be discussed.

4.1.1 Physicochemical characterization of compost

Various physicochemical tests can be carried out to decide the most adequate application for composts, their capacity as organic amendments or their potential for pollutant removal. Table 4.1. summarizes the most common parameters in compost characterization, along with its proper applications.

Table 4.1 Typical physicochemical properties of composts with suggested practical applications or drawbacks.

Parameter	Suggested or not recommended applications
Solution pH	pH >7.0, compost is used to reduce soil acidity
Electrical conductivity, dS m^{-1}	Composts with high EC are not suitable for agronomical purposes
N content, %	Compost with high N-P-K content is good as a fertilizer, if EC is low
Soluble P, %	
K content, %	
C/N ratio	Low C/N ratio indicates maturity of compost, relevant for agronomic use
Ash content, %	High ash content indicates better usability as filler or adsorbent
Specific surface area, m^2 g^{-1}, porosity	High surface area and porosity predict a better usability as adsorbent for organic compounds.
Heavy metals content, mg kg^{-1}	High metal content indicates a poor usability as amendment and fertilizer
Cation exchange capacity, $cmol_{(+)}$ kg^{-1}	High CEC indicates high usability as cation exchanger material

Neutral to acidic pH values are typically observed for most composts (Anastopoulos et al., 2018; Anastopoulos and Kyzas, 2015), although it depends on the raw materials composted. In the composts employed in this Thesis, solution pH ranged from 4-9 and this variation would be attributed to the chemical nature of compost`s feedstocks (Publications 1-3). Thus, compost prepared from pine bark is acidic, whereas those prepared from municipal solid wastes are alkaline, so that these could be used for the neutralization of soil acidity (Publication 2).

The value of pH_{PZC} determines the net charge of compost at different pH values and therefore affects its adsorbent behaviour for ions and charged molecules. It has been found in this study that the position of pH_{PZC} (acidic or basic) can be related to the affinity for the dye. For instance, the uptake of DB151 by CPB compost was improved at pH 3.0 compared to 7.0, and this was related to the surface charge developed on the adsorbent (Publication 2). However, in other studies it was found that the removal of MB by olive-tree compost was almost unchanged over the pH range 2-8 (Anastopoulos et al., 2018; Anastopoulos and Kyzas, 2015).

It has been pointed that the electrical conductivity, EC (often expressed as dS m^{-1}), is the main parameter that determines the proper application of compost. In an excellent review on the subject, the agronomical application of different composts was evaluated based on their electrical conductivity (Gondek et al., 2020). In general, EC was found to be in the range 2-15 dS m^{-1}. Typically, composts derived from woody materials (like pine bark) have low EC (3-5 dS m^{-1}) and composts derived from municipal solid waste have high EC 10-19 (Gondek et al., 2020). The authors outlined that those composts of EC higher than 5.0 dS m^{-1} are not suitable for agronomical purposes, as they increase salinity of the soil and reduce water absorption by plant. In this sense, the composts MSWC and JOCOM, tested in publications 1 and 3, are more applicable as dye adsorbents than for agronomic use due to their high EC (7-7.8 dS m^{-1}). Obviously, this not exclude the use as adsorbent of low EC composts, as is the case for the pine bark compost CPB, which has a low EC (0.37 dS m^{-1}), but shows a high ability for dyes uptake, as outlined in publications 1-3.

Composts can be applied as soil fertilizers when their N-P-K contents are high. The chemical analysis of some of the composts (Publications 1-3) revealed that N-P values were low compared to that of K. McKay et al. (2011) have also reported a high K level compared to N and P for compost derived from organic municipal solid wastes. The low concentration of N-P of the tested composts is a good reason to give these materials an environmental application. In particular, composted pine bark presented extremely low nutrient contents, so it could not be adequately used as soil fertilizers, and application in environmental remediation would be a better option.

Although there are many detailed studies linking the performance of compost as fertilizer with its properties, research linking them with dye adsorption capacity are less common. Qayyum et al. (2016) suggested ash content, surface area and C, N, and P contents as physicochemical parameters indicating the general applicability of composts as adsorbents: composts of high surface area, >50 m^2 g^{-1}, and low salinity, <3 dS m^{-1}, would have high adsorption performance in solution. In this sense, the composts tested in this Thesis would be adequate for their use as adsorbents due to their surface area (5-22 m^2 g^{-1}), and their low N-P content that discourages their use as fertilizers. It is the case for the extremely low content of N-P (<1%) for CPB, which is a good reason for this material to be used as adsorbent instead of as fertilizer. In turn, MSWC and JOCOM have high N-P content (2%), but they are not recommended as soil amendments due to their high salinity (publication 2).

The C/N ratio is an important parameter as it reflects the stability of the final compost material (Manu et al., 2021; Lu et al., 2021; Domingo and Nadal, 2012). For its application to agricultural soils, a C/N ratio < 20 is recommended. However, this need does not appear to be as restrictive for its use as an adsorbent, as compost with C/N ratios greater than 25 performed well in this regard (Publication 3). Also, a C/N ratio of 21 was reported for water hyacinth compost, which manifested high affinity for basic dyes (Pushpa et al., 2016b).

To be used in a real filtration system, the adsorbent should be mechanically stable to withstand the applied pressure. Hence, ash content can reflect the inorganic part of an adsorbent and hence its mechanical stability (Dawood and Sen, 2013). Variable levels of ashes were reported for composts (Anastopoulos and Kyzas, 2015). Here, the urban waste compost presented a high ash content (58%), whereas for the Jordanian compost prepared from vegetable wastes and the pine bark compost lower ash values were found (21% and 9%, respectively) (Publications 1, 3). In any case, it must be taken into account that higher ash contents imply lower organic matter contents and thus lower reactivity of the adsorbents, so perfect properties in this sense could not be reached.

It is suggested that the large fraction of organic matter in composts (50-90%) (Manu et al., 2021; Lu et al., 2021) has a significant role for attraction of pollutants from water (Publication 2; Paradelo et al., 2018). Composts containing 40-90% OM were found efficient for removing a wide selection of pollutants, including organics and heavy metals (Anastopoulos and Kyzas, 2015). Although not listed in Table 4.1, IR analysis was used to detect surface functionality and presence of high organic matter in composts.

Publications 1-3 discussed the importance of organic matter and functional groups in removing organic dyes from solution.

From a physical point of view, high surface area (SSA) and porosity should positively contribute to the sorption capacity of an adsorbent (Issa et al., 2017). This is true for compost, as a high SSA and porosity are necessary for the diffusion of dyes inside the material (McKay et al., 2011). As outlined in Publication 2, composts of high surface area and porosity (like CPB) manifested better uptake for dyes.

Finally, another important issue that determines the suitability of compost for agronomic uses, but also for environmental applications, is the content of heavy metals. Composts of high metal contents (which would be the case for those derived from municipal solid wastes without a separation in the origin) are not useable as amendment or fertilizer. For their use as adsorbents a low leachability of metals -if present- is also necessary. This question was discussed and connected with dye uptake from solution by McKay et al. (2011) and Pushpa et al. (2016b). In general, the levels of toxic metals in the tested composts were not high and did not leach into solution (Publication 2).

4.1.2 Application of composts as adsorbents

In addition to the common agronomical usage of composts, composts found application as adsorbents for removing heavy metals (Pennanen et al., 2020; Anastopoulos and Kyzas, 2015; Paradelo and Barral, 2012; Paradelo et al., 2011; Kocasoy and Güvener, 2009) and organic pollutants (Anastopoulos and Kyzas, 2015), in particular dyes (Paradelo et al., 2020; Anastopoulos and Kyzas, 2015).

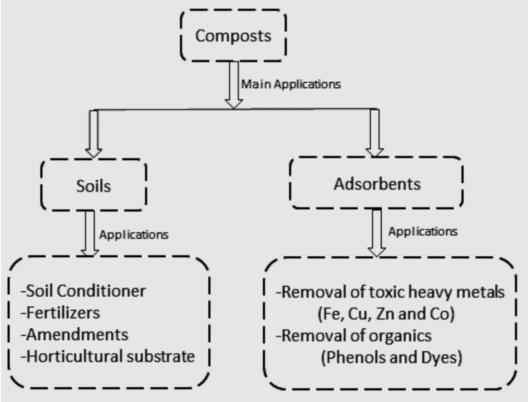

Figure 4.1. Agricultural and industrial applications of composts.

As shown in Figure 4.1, composts can be used as soil conditioners, fertilizers, amendments, and for erosion control. On the other hand, compost can be used as adsorbent for many types of water pollutants, including heavy metals and organics. The application of composts derived from different sources for dyes uptake was outlined in several publications, as mentioned above. In publication 1, derived from this thesis, two composts, MSWC and CPB, were used to remove methylene blue. In publications 2 and 3, the application of composts for removing different classes of dyes (cationic, acidic, basic and reactive) was demonstrated. In publication 4, the practical uptake of dyes in compost fixed-bed adsorber and under different operational conditions was outlined.

According to Patel (2019), solid adsorbents are classified into three categories: (a) Synthetic adsorbent: porous materials with high adsorption capabilities are produced in the laboratory. The expensive production process is the main disadvantage of these adsorbents. (b) Natural adsorbent: natural materials such as plant roots, leaves, and agricultural wastes, which are dried, crushed, and washed before being utilized as an adsorbent for target pollutants. Although natural adsorbents are inexpensive, its adsorption capacity is rather limited. (c) Semi-synthetic adsorbent: natural materials are activated biologically, chemically or physically to produce a highly porous surface. The main benefits of these adsorbents are their low cost, high efficiency, and no production of chemical or biological sludge as by-products.

Many types of adsorbents have been tested for pollutants removal from wastewater, including heavy metals and dyes. Textile dyes can be removed by inorganic and organic adsorbents, including compost. Adsorbents are classified in activated carbon, non-conventional, nanomaterials, and composites (Singh et al., 2018) (Fig. 4.2.).

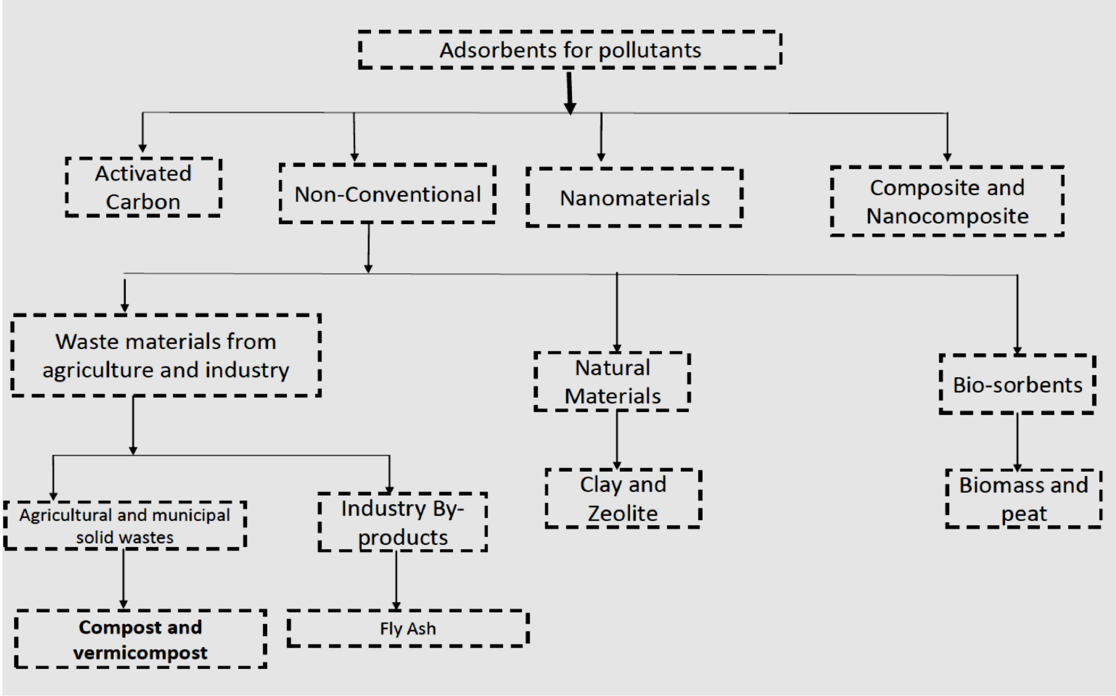

Figure 4.2 Classification of adsorbents used for pollutants removal (including dyes) from wastewater.

Compared to other adsorbents, activated carbon is the best adsorbent for dyes due to its high surface area (1000-2000 m^2 g^{-1}) and high density of surface functional groups (Singh et al., 2018). However, its high costs of preparation and regeneration were the principal reasons to shift to natural and semi-synthetic adsorbents. Recently, the application of nanomaterials and nano-composites for dyes uptake was reported (Kyzas and Kostoglou, 2014). The high affinity of nanomaterial for dyes was also connected with the high surface area and presence of surface functional groups on the surface (Kyzas and Kostoglou, 2014).

As indicated in Fig 4.2, compost would be categorized as a non-conventional adsorbent. Its properties for dye adsorption will be explained later. In this category, other adsorbents are included, in addition to compost, which showed high efficiency for dye uptake, such as biomass, clay and fly ash (Singh et al., 2018). The high efficiency of these adsorbents is attributed to their relatively high surface area and availability of surface functional groups (Singh et al., 2018).

4.2 DYE REMOVAL BY COMPOST

4.2.1 Overall performance of compost compared to other adsorbents

Despite the small number of research papers available on this subject, the current section summarizes the progress made in the field of dye adsorption or dye decolorization utilizing composts over the last decade. We propose that readers consult the work of Anastopoulos and Kyzas (2015), which summarizes the studies on the use of composts as biosorbents for the removal of heavy metals and dyes from wastewater, spanning over a period ranging from 2003 until 2014. Many articles related to heavy metal removal were included in the review, but a significantly lesser number of papers were reported related to dye removal by compost materials. The review papers published by Qian et al. (2009), Toptas et al. (2014) and Tsui et al. (2003) also highlighted the importance of compost as adsorbent for water pollutants. Regarding dye removal by composts, the review by Paradelo et al. (2019a) also summarized the information available at the time.

The present section aims at filling the gaps from these reviews to account for the recent studies performed from the year 2010 onwards. Therefore, in this section, the published papers over the last ten years (2010–2022) regarding compost applications for dye removal are analyzed. The number of published papers and reports on the use of compost for dyes treatment was rather limited in this period, when compared to other natural materials like activated carbon, silicate minerals, and natural organic materials. This fact suggests that the application of compost as dye adsorbent is not so popular and hence more research is needed in this area.

Table 4.2 summarizes the application of composts to sequestrate different classes of textile dyes. The experimental conditions are also provided in the table, since comparisons between adsorbents should consider factors such as the S/L ratio, solution pH, application in column, rate of sorption rate, recycling of exhausted adsorbent, cost of adsorbent, the reduction of waste dumping in landfills, and the possibility of removing all classes of textiles. Municipal solid wastes, cellulosic, mushroom, pine bark, kitchen waste, leaf, paper, and water hyacinth wastes were the main ingredients of the prepared composts.

Table 4.2. Sorption parameters for different classes of textile dyes by composts derived from different wastes.

Compost feedstock	Dye	Type-isotherm	Model	Experimental conditions	Sorption (mg g^{-1})	Reference
Municipal solid waste	Basic Green 4	L	Langmuir	-	69.4	Anastopoulos and Kyzas, 2016
Municipal solid waste	Direct Blue 71	L	Langmuir	-	22	Anastopoulos and Kyzas, 2016
mushroom	Acid Red 111	L	Langmuir	S/L 0.1g/100ml, time 8 hrs, pH 2-3	141	Toptas et al., 2014
mushroom	Reactive Levafix Braun E-RN	L	Langmuir	S/L 0.1g/100ml, time 8 hrs, pH 2	170	Toptas et al., 2014
mushroom	Basic Red 18	L	Langmuir	S/L 0.1g/100ml, time 10 hrs, pH 9	400	Toptas et al., 2014

Compost feedstock	Dye	Type-isotherm	Model	Experimental conditions	Sorption (mg g^{-1})	Reference
cellulosic materials	Acid Blue 9	L	Freundlich, D-R	S/L 2 g/ml, pH 6.1, 24 hr	7.0	Kyziol-Komosinska et al., 2011
cellulosic materials	Acid Green 16	L	Freundlich, D-R	S/L 2 g/ml, pH 5.7, 24 hr	24	Kyziol-Komosinska et al., 2011
cellulosic materials	Acid Black 1	L	Freundlich, D-R	S/L 2 g/ml, pH 8.0, 24 hr	21	Kyziol-Komosinska et al., 2011
cellulosic materials	Acid Red 18	L	Freundlich, D-R	S/L 2 g/ml, pH 7.7, 24 hr	10	Kyziol-Komosinska et al., 2011
Urban waste	Reactive red 134	L	Langmuir	S/L 4g/100ml, pH 7.4, 5 hr	1.5	McKay et al., 2011
Kitchen waste	Malachite green	L	Lagmuir and Sips	S/L 4g/L, pH 8, 400 min,	150.8	Pushpa et al., 2015
Kitchen, leaf, paper, water Hyacinth wastes	Basic Crystal violet	-	-	S/L 6 g/L, pH 7, 6 hr	45	Pushpa et al., 2016a
Water hyacinth	Methylene blue	L	Toth	S/L 4.5g/L, pH 7.5	367	Pushpa et al., 2016b
Water hyacinth	malachite green	L	Toth	S/L 4.5g/L, pH 7.5	155	Pushpa et al., 2016b
Water hyacinth	Basic Blue 41	L	Toth	S/L 4.5g/L, pH 7.5	186	Pushpa et al., 2016b
Pruning waste	Methylene blue	L	Langmuir	S/L 0.1g/30 ml pH 6-8, 10 min	277	Anastopoulos et al., 2018
Municipal solid waste	Methylene blue	L	Langmuir	S/L 1/20 – 1/100 g/ml, pH 7	110	Publication 1
Pine bark	Methylene blue	L	Langmuir	S/L 1/20 – 1/100 g/ml, pH 5-7	125	Publication 1
Pine bark	Rhodamine B	L	Langmuir	S/L 1.0 g/100ml, KCl 1.0 M, pH 3.0, 25 ºC, 5 hr	205	Publication 2
Pine bark	Reactive Violet 4	L	Langmuir	S/L 1.0 g/100ml, KCl 1.0 M, pH 3.0, 25 ºC, 5 hr	32	Publication 2
Pine bark	Acid Red 27	L	Langmuir	S/L 1.0 g/100ml, KCl 1.0 M, pH 3.0, 25 ºC, 5 hr	4.1	Publication 2

Compost feedstock	Dye	Type-isotherm	Model	Experimental conditions	Sorption (mg g^{-1})	Reference
Pine bark	Direct Blue 151	H	Sips	S/L 1.0 g/100ml, KCl 1.0 M, pH 3.0, 25 ºC, 5 hr	70	Publication 2
Municipal solid waste	Rhodamine B	L	Langmuir	S/L 1.0 g/100ml, KCl 1.0 M, pH 3.0, 25 ºC, 5 hr	36	Publication 2
Municipal solid waste	Reactive Violet 4	L	Langmuir	S/L 1.0 g/100ml, KCl 1.0 M, pH 3.0, 25 ºC, 5 hr	35	Publication 2
Municipal solid waste	Acid Red 27	L	Langmuir	S/L 1.0 g/100ml, KCl 1.0 M, pH 3.0, 25 ºC, 5 hr	3.3	Publication 2
Municipal solid waste	Direct Blue 151	H	Sips	S/L 1.0 g/100 ml, KCl 1.0 M, pH 3.0, 25 ºC, 5 hr	71	Publication 2
Plant waste (Jordanian company)	Direct Blue 71	L	Langmuir and Sips	S/L 0.4 g/100ml, KCl 0.4 M, pH 3.0, 50 ºC, 3 hrs	103.8	Publication 3

As shown in Table 4.2, composts have been used for the removal of dyes of different classes, such as direct, acid, reactive, and basic, although it is rare to find an adsorbent that shows high affinity for all classes of dyes. In the experiments of this Thesis, we observed that sorption of cationic dye by compost was much higher than that of other classes, with a value of 204 mg g^{-1}. Unfortunately, the retention of the acid dye was very modest, close to 4.0 mg g^{-1} (Publication 2). The following sorption trend was derived from Fig. 4.3A: basic >> direct ≈ reactive > acid. As indicated in the figure, the average sorption capacity of direct, reactive and acid dyes was over the range 30-59 mg g^{-1}, reaching an average value of 175 mg g^{-1} for basic dyes, which was notably higher than for other classes. As an example, sorption of methylene blue (125 mg g^{-1}) was much higher than that of Acid Red 27 (4.1 mg g^{-1}), using pine bark compost as adsorbent under comparable sorption conditions. The same behavior was also reported for municipal solid waste compost toward Basic Violet 10 and Acid Red 27 under the same operational conditions (Publication 2). The high sorption affinity of cationic or basic dyes (like methylene blue and Basic Violet 10) for many adsorbents has already been consistently reported in literature (Salleh et al., 2011). In turn, the observed lower removal capacity for anionic dyes, including reactive and acid dyes, also agrees with findings from published reviews (Gupta et al., 2009; Gupta and Suhas, 2009; Salleh et al., 2011; Tripathi 2013; Jóźwiak et al., 2018).

The sorption affinity of organic, inorganic and composts adsorbents toward different classes of dyes is presented in Figure 4.3 A ,based on the previously mentioned literature, compared with the results of this study (Figure 4.3. B). For the results reported in the literature, the following general trend is deduced for organic adsorbents: basic > direct > acid > reactive; for inorganic adsorbents, the sequence is: basic > acid > direct > reactive, while for compost, the trend would be: basic > reactive ≈ direct > acid. In general, sorption of basic dyes was higher compared to other classes of dyes, with average capacities of 175.4, 102.6 and 77.3 mg g^{-1} for compost, organic and inorganic adsorbents, respectively (Fig 4.3A, publication 1-3; Hu et al., 2007; Tripathi et al., 2007; Salleh et al., 2011; Shabaana et al., 2020).

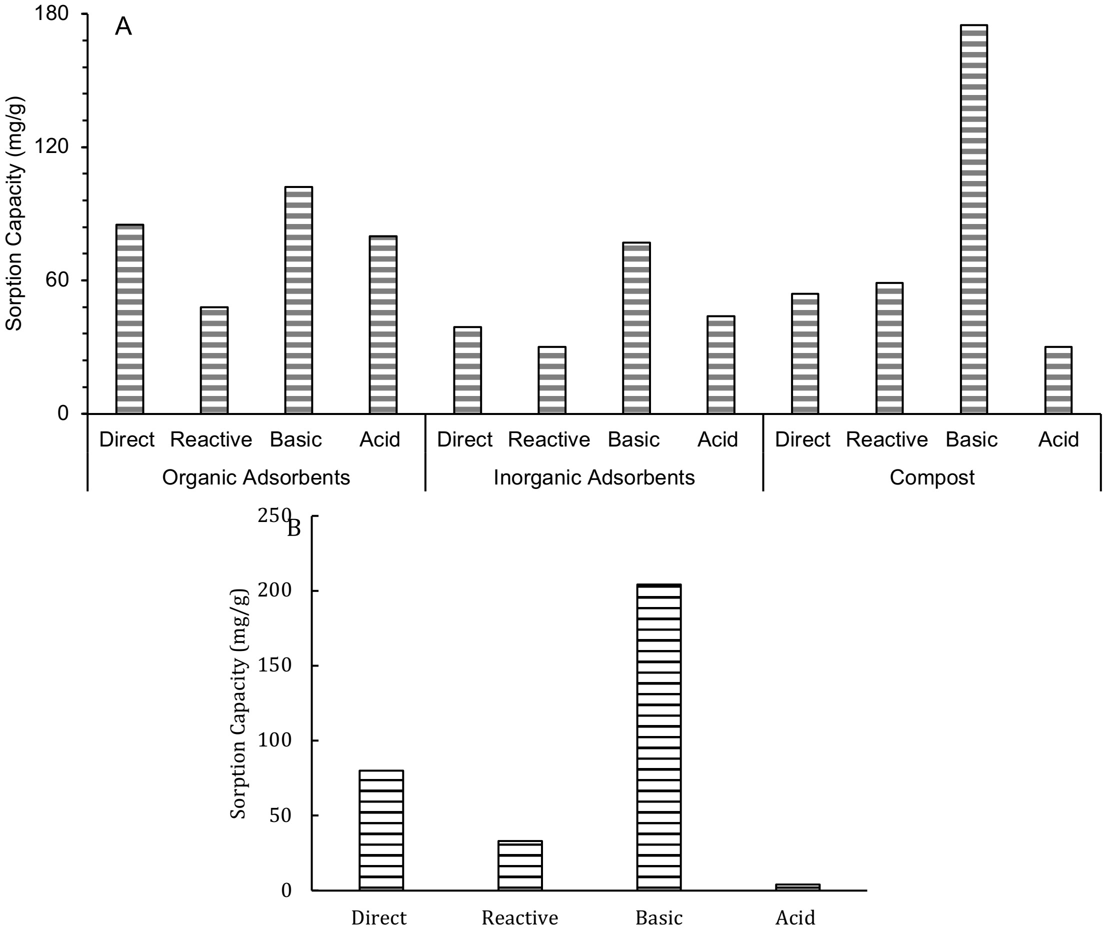

Figure 4.3 Sorption capacity of different adsorbents toward different classes of dyes in the literature (A) and in the results reported in this Thesis (B).

The interesting point regarding compost is its similar performance toward direct and reactive dyes, which is not observed for other classes of adsorbents, with lower affinity of acid dyes (Publications 1-3; Gupta et al., 2009; Gupta and Suhas, 2009; Tripathi 2013; Jóźwiak et al., 2018).

As shown in Table 4.2, the sorption capacity of compost adsorbents for textile dyes reported in the literature is variable and range from 1.5 mg g^{-1} (for Reactive Red 134) to 400 mg g^{-1} (for Basic Red 18) (Toptas et al., 2014; McKay et al., 2011).

Overall, the composts studied here presented an affinity towards the tested dyes comparable to that of other composts used as adsorbents. In this Thesis, the retention capacity of two basic dyes (BV10 and MB) by the composts was relatively high, 200-600 mg g^{-1} (Publication 1), as was the uptake of basic dyes (45-400 mg g^{-1}) reported to other composts (Toptas et al., 2014). The removal capacity of direct dyes by our composts was around 70-100 mg g^{-1} (Publication 2,3), which is high compared with other composts, which showed a modest retention of 22 mg g^{-1} (Anastopoulos and Kyzas, 2016). On the contrary, the removal of reactive dyes by composts in the literature was 2-170 mg g^{-1} (Table 4.2), which is relatively higher than the values reported by us in Publication 2 (7-40 mg g^{-1}). Finally, the removal of acid dyes by our composts was low, as shown by the comparison between the values from the literature indicated in Table 4.2 (10-24 mg g^{-1})

and in Publication 2 (3-4 mg g^{-1}); this suggests that using compost for the removal of these dyes may be not practical in this case.

Overall, we can state that composts can be employed for the removal of a wide range of dyes, with performance at least similar to those of other biosorbents, and even higher in some cases, as is the case for basic dyes. Considering the low price of compost material, its application is commercially appealing.

4.2.2 Factors influencing compost performance for dye removal

In this section, the main experimental factors that affect dye uptake by compost are discussed, including pH, salinity and operation conditions. The influence of some of these factors on dye sorption by compost is summarized in Figure 4.4, including the results of this thesis and others from the literature (Table 4.2). In Figure 4.4A, and for each class, the average of maximum capacities of composts was represented. In Figure 4.4B, the average of optimum pH values for dye retention was indicated. For Figure 4.4C, the average of optimum S/L ratios for dye retention was represented. In few cases, the authors do not provide the complete conditions of sorption tests.

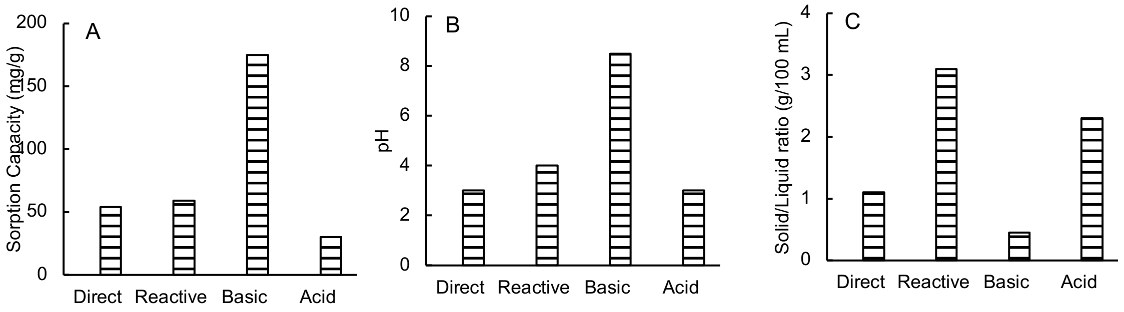

Figure 4.4 Influence of different factors on the sorption affinity of different classes of dyes for composts.

4.2.2.1 Sorption kinetics in batch and fixed-bed adsorber

The rate (or kinetics) of pollutant uptake is often evaluated in batch conditions before conducing further adsorption studies. In general, the sorption rate of organic compounds (as is the case for dyes) is slower than that of inorganic ions, given the lower diffusivity of organic molecules in solution (Gupta et al., 2009). Adsorption kinetics of dyes by materials such as activated carbon, clay and compost is often modelled using pseudo-first and pseudo-second order models (Baskan and Pala, 2014; Gupta et al., 2009). Most of the published research indicated the applicability of pseudo-first order model and pseudo-second order models, with some superiority of the latter model in representing sorption rate of dyes by composts (Anastopoulos and Kyzas, 2014). The parameters of these models (k_1, min^{-1} and k_2, g mg^{-1} min^{-1}) determine the sorption rate of the pollutant, so the higher the value the faster uptake from solution under batch conditions (Gupta et al., 2009).

Diffusion-based models are also often investigated for porous adsorbents (Gupta and Suhas, 2009). Considering the moderate porosity of the composts tested in this Thesis (Publication 2), pseudo-first and pseudo-second order models were used to present kinetics of dyes by composts, as outlined in Publications 1-3. Pseudo-first order model described better the results than pseudo-second order model, with k_1 values of 0.22, 0.11, 0.03, and 0.01 min^{-1} for DB151, BV10, AR27 and RV4, respectively. These values reflect the high sorption rate of direct and basic dyes compared to the rest of classes (Publication 2) and agree with previous observations indicating that, in general, the kinetics of the removal of cationic and direct dyes by composts is higher in comparison with that of reactive dyes (Paradelo et al., 2019a; Pushpa et al., 2016; Anastopoulos et al., 2018).

For column experiments, adsorption kinetics of pollutants is often described using the Thomas model (Publication 4), whose parameter K_{TH} (L mg^{-1} min^{-1}) is proportional to the rate of uptake from solution (Publication 4).The sorption rates of direct and basic dyes in the column experiments, as estimated by Thomas model for selected basic and direct dyes, did not agree with those obtained under batch conditions, as the sorption rates, under column conditions, were 0.00094 and 0.00081 L mg^{-1} min^{-1} for of BV10 and DB151 respectively. A comparable trend has been reported in the literature for other adsorbents (Aguayo-Villarreal et al., 2013).

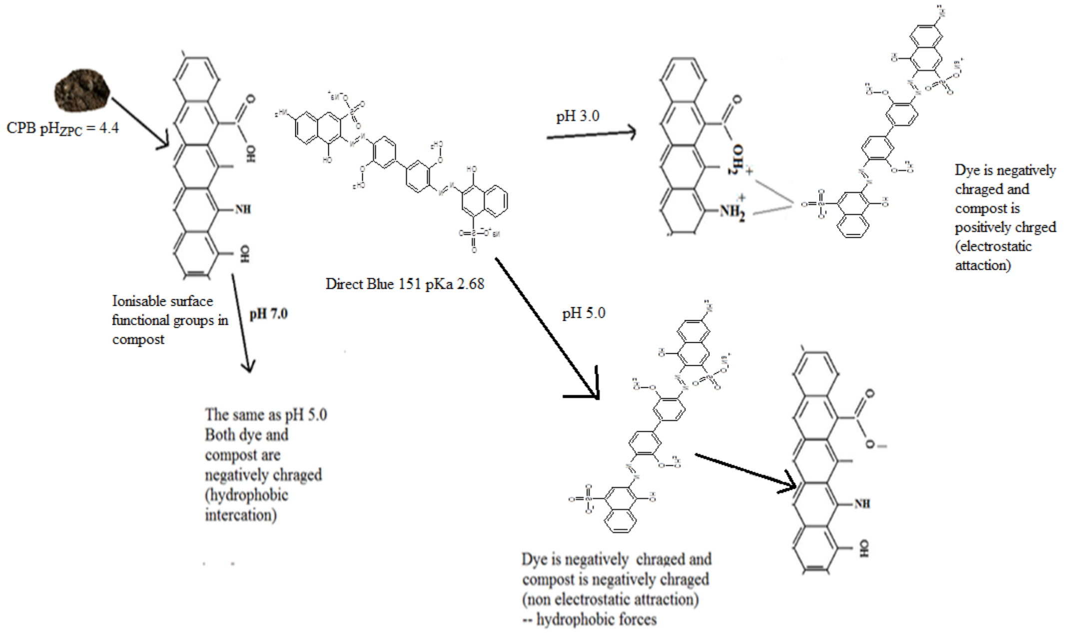

Figure 4.5 Effect of solution pH on DB151 (pKa 2.68) uptake by CPB (pHzpc 4.4) (Publication 2).

4.2.2.2 Effect of pH

The influence of pH on dye uptake by compost adsorbents is summarized in Figure 4.4B, where the pH values provided correspond to average pH values taken from Table 4.2. In the literature, sorption of direct, reactive, and acid dyes was higher in the acid pH range 3.0-4.0, while basic dyes were more favorably removed at basic pH (8.5). Nevertheless, in this Thesis, the effect of pH on the adsorption of BV10, DB151, RV4 and AR27 was studied in detail in Publication 2, and the maximum removal was found at pH 3 for all dyes.

Solution pH can affect both dye and compost ionization and may explain the effectiveness (or not) of electrostatic forces for dye uptake. As an example, the effect of solution pH on DB151 uptake by CPB is pictured in Fig 4.5. At pH 3.0, the dye is negatively charged while the compost is positively charged, and this improves dye attraction to the surface. However, at pH 5.0 and 7.0 both compost and dye were similarly charged, and this reduces dye uptake.

4.2.2.3 Effect of salinity

As indicated in Table 4.2, few studies considered the effect of salinity on dyes uptake, but in those who studied it was found that salinity had a high influence in the retention of all classes of dyes by compost. In all cases analyzed in this thesis (publications 1-3), increasing salinity had a favorable effect on dye sorption that was more pronounced for MB and DB151 than for the other dyes, with the weakest effect on AR27, as outlined in Publication 2. This positive influence of salinity on the removal of anionic dyes from water was attributed to the dimerization of dyes at high ionic strength. This dimerization can be due to an increase in intermolecular forces, such as dipole–dipole, ion–dipole or van der Waals dispersion forces at high salinity, which produce a reduction of the repulsive interaction between dyes, reducing dye solubility and increasing sorption.

4.2.2.4 Effect of solid-to-liquid ratio

The mass:volume ratio of the adsorbent suspension is an important parameter to be tested, in particular for new adsorbents like compost. In this thesis, this factor was evaluated only for methylene blue (Publication 1), for which two ratios were tested (1:20 and 1:100), observing an approximate five-fold increase in maximum sorption capacity at the lowest ratio. Regarding results from the literature, the variations in S/L ratio are displayed in Fig 4.3C, based on data from Table 4.2. Ratios of 1:1000 are typically used for activated carbon adsorbents, while higher ratios (5-6 g 100 mL^{-1}) are more common for natural materials (Singh et al., 2018). As deduced from these studies, the optimal S/L for dye removal would be highly variable (0.45-3.1 g 100 mL^{-1}) and dependent on the class of dye. The lowest S/L ratio was reported for basic dyes (Fig 4.4C), in relation with the stronger affinity of adsorbents for this kind of dyes in comparison to acid and reactive dyes (Shabaana et al., 2020; Gupta et al., 2009; Gupta and Suhas, 2009; Tripathi 2013; Jóźwiak et al., 2018). For acid and reactive classes, a higher S/L ratio are needed to achieve high retention as shown in Figure 4.4C.

4.2.2.5 Effect of operation mode

For a better assessment of adsorbent application, their performance in fixed-bed adsorber conditions was also tested, because this scenario is more similar to the actual application for wastewater dye treatment (Publication 4; Patel, 2019, 2021). Both batch and fixed-bed (column) sorption modes have their own advantages and disadvantages (Patel 2019, 2021). The main advantages of batch sorption mode are: a) it is a very easy and cheap technique, and b) it is the best way to determine the feasibility of adsorbent-adsorbate system (estimated maximum uptake capacity). The main disadvantages are: a) small volumes of wastewater are treated, which is not practical for industrial applications and b) extra cost related to adsorbent separation from treated water. On the other hand, the main advantages of column sorption mode are a) it is applicable to high volume of wastewater with high concentration of pollutants, b) it is closer to real industrial application where the adsorbate is continuously in contact with a given quantity of fresh adsorbent. The main disadvantages of this treatment mode are: a) the difficulty associated with optimization of fixed-bed operational factors, since retention capacity of column is very sensitive to changes in operational factors like flow rate or bed-depth, and b) the recycling of fixed-adsorber may not be efficient and need long time.

Table 4.3 summarizes some relevant published studies that addressed the application of column adsorber for removing textile dyes, including basic, direct, reactive and acid classes, under different operational conditions. The type of adsorbent, class of dyes, adsorber conditions, and saturation value are also indicated, although in many cases the collection of experimental details was not straightforward as some authors do not give details on these conditions. The mathematical equations applied for predicting column saturation capacities and experimental conditions are also shown. Moreover, the average column saturation values for different dye classes are plotted in Figure 4.6.

Table 4.3. Sorption capacity of different adsorbents for textile dyes uptake in fixed-bed adsorber.

Adsorbent	Dye/class	Column conditions	Model	Column saturation capacity (mg/g)	Citation
Fertilizer plant waste	methylene blue	flow rate of 1.5 mL/min bed height 3.1 cm Conc. 240 mg/L	Estimated from breakthrough curve	92	Gupta et al., 2016
Fertilizer plant waste	acid blue 113	flow rate of 1.5 mL/min bed height 3.1 cm 3.0-7.5×10^{-4}M	Estimated from breakthrough curve	219	Gupta et al., 2016
activated carbon	reactive orange 84	flow rate 10 mL/min bed height 7.0 cm Conc. 150 mg/L	Thomas model	212	Charola et al., 2018
Bottom ash	crystal violet	flow rate 10 mL/min bed height 4.5 cm Conc. 15 mg/L	BDST model	244	Nidheesh et al., 2021
Activated carbon	reactive yellow	flow rate 5 mL/min bed height 3 cm Conc. 190 mg/L	BDST model	541	Al-Degs et al., 2009
Activated carbon	remazol reactive black	flow rate 5 mL/min bed height 7.5 cm Conc. 190 mg/L	BDST model	107	Al-Degs et al., 2009
lignocellulosic waste	drimarine black CL-B	flow rate 1.8 mL/min bed height 3.5 cm Conc. 100 mg/L	Estimated from breakthrough curve	15	Noreen et al., 2013
magnetic nanoporous MCM-41/inorganic	methyl green	flow rate 0.8 mL/min bed height 6 cm Conc. 20 mg/L	Thomas model	21	Alardhi et al., 2020
Waste watermelon	methylene blue	flow rate 1.5 mL/min bed height 9 cm Conc. 50 mg/L	Thomas model	114	Lakshmipathy and Sarada (2016)
Tamarind seed Powder	acid yellow 17	flow rate 15 mL/min bed height 15 cm Conc. 50 mg/L	Thomas model	979	Patel and Vashi (2012)
modified rice husk	methylene blue	flow rate 5 mL/min bed height 3 cm	Thomas model	101	Chowdhury and Saha (2013)
Macroalga *Azolla Filiculoides*	acid blue 15	flow rate 5.0 mL/min bed height 25 cm Conc. 100 mg/L	BDST & Thomas models	36	Padmesh et al. (2006)

Adsorbent	Dye/class	Column conditions	Model	Column saturation capacity (mg/g)	Citation
modified cotton fibers	acid blue 25	flow rate 5 mL/min Conc. 50 mg/L	BDST	181	El Ghali et al. (2013)
Pecan nut shells	acid blue 74	flow rate 3.0 mL/min Conc. 100 mg/L	Thomas model	0.1	Aguayo-Villarreal et al. (2013)
Pecan nut shells	acid blue 25	flow rate 3.0 mL/min Conc. 100 mg/L	Thomas model	0.2	Aguayo-Villarreal et al. (2013)
Pecan nut shells	reactive blue 4	flow rate 3.0 mL/min Conc. 100 mg/L	Thomas model	0.01	Aguayo-Villarreal et al. (2013)
Modified sugarcane bagasse	direct yellow 50	bed height 4.0 cm Conc. 50 mg/L	BDST & Thomas models	11	Sadaf et al. (2015)
Activated Prunus Dulcis	acid green 25	flow rate 8 mL/min bed height 5.0 cm Conc. 100 mg/L	Thomas and Yoon-Nelson models	38	Jain and Gogate (2018)
Activated carbon	reactive red 198	flow rate 2.0 mL/min bed height 4.0 cm Conc. 40 mg/L	Thomas and Yoon-Nelson models	129	Alimohammadi et al. (2016)
Gulmohar leaf	congo red	flow rate 15 mL/min bed height 20 cm Conc. 60 mg/L	BDST, Yoon-Nelson and Thomas models	14	Patel (2018)
Modified-Gulmohar leaf	congo red	flow rate 15 mL/min bed height 20 cm Conc. 60 mg/L	BDST, Yoon-Nelson and Thomas models	32	Patel (2018)
Compost	direct blue 71	flow rate 10 mL/min bed height 17.8 cm Conc. 100 mg/L	Thomas model and from breakthrough curve	20	Publication 4
Compost	rhodamine B (single-solute)	flow rate 10 mL/min bed height 17.8 cm Conc. 100 mg/L	Thomas model and from breakthrough curve	102	Publication 4
Compost	rhodamine B (bi-solute)	flow rate 10 mL/min bed height 17.8 cm Conc. 100 mg/L	Thomas model and from breakthrough curve	78	Publication 4
Compost	direct blue 151 (single-solute)	flow rate 10 mL/min bed height 17.8 cm Conc. 100 mg/L	Thomas model and from breakthrough curve	36	Publication 4
Compost	direct Blue 151 (bi-solute)	flow rate 10 mL/min bed height 17.8 cm Conc. 100 mg/L	Thomas model and from breakthrough curve	19	Publication 4

Adsorbent	Dye/class	Column conditions	Model	Column saturation capacity (mg/g)	Citation
Waste material from boron industry	acid red 183 (single-solute)	flow rate 1.0 mL/min bed height 6.0 cm Conc. 100 mg/L	Thomas model	91	Atar et al., 2011
Waste material from boron industry	acid red 183 (bi-solute)	flow rate 1.0 mL/min bed height 6.0 cm Conc. 100 mg/L	Thomas model	66	Atar et al., 2011
Waste from boron industry	reactive blue 4 (single-solute)	flow rate 1.0 mL/min bed height 6.0 cm Conc. 100 mg/L	Thomas model	87	Atar et al., 2011
Waste from boron industry	reactive blue 4 (bi-solute)	flow rate 1.0 mL/min bed height 6.0 cm Conc. 100 mg/L	Thomas model	55	Atar et al., 2011
Modified waste sugarcane bagasse	rhodamine B (single-solute)	flow rate 7.8 mL/min Conc. 144 mg/L	Bohart-Adams model	254	Yu et al., 2019
Modified waste sugarcane bagasse	rhodamine B (bi-solute)	flow rate 7.8 mL/min Conc. 144 mg/L	Bohart-Adams model	91	Yu et al., 2019
Modified waste sugarcane bagasse	methylene blue (single-solute)	flow rate 7.8 mL/min Conc. 95 mg/L	Bohart-Adams model	551	Yu et al., 2019
Modified waste sugarcane bagasse	methylene blue (bi-solute)	flow rate 7.8 mL/min Conc. 95 mg/L	Bohart-Adams model	112	Yu et al., 2019

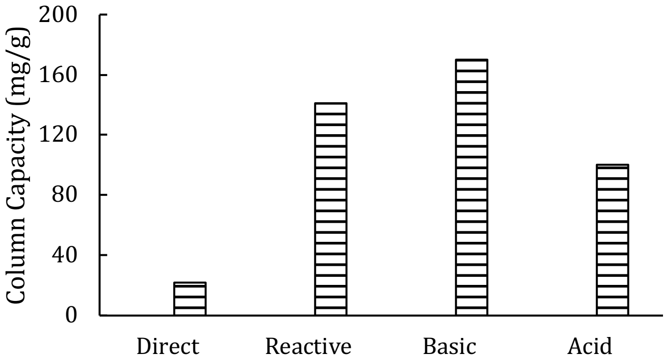

Figure 4.6. Sorption affinity of different classes of dyes using different sorbents in column adsorber (the provided capacities were obtained from Table 4.3)

It can be seen from the literature that the adsorbent performance of compost is in general poorer in column conditions than in batch experiments. Accordingly, in this Thesis, the sorption capacity estimated from batch mode was notably higher than in column mode, as shown for cationic (BV10) and direct (DB151) dyes classes (Publication 4). This lower affinity in columns is attributed to shorter contact times between adsorbent-adsorbate system, as outlined in Publication 4 and in the literature (Patel 2018), which does not permit the complete migration of solute inside the pores of adsorbents.

Considering the results of published column studies, the sorption trend is the following: basic > reactive > acid. The high affinity of basic dyes compared to acid and reactive ones was already reported in batch studies (Fig 1A, 2A, and 4A), due to the higher affinity of cationic dyes compared to negatively charged dyes, like acid and reactive ones. Very few column studies have been carried out for direct dyes (Table 4.6), so the capacity shown in Figure 4.6 (≈20 mg g^{-1}) may not accurately reflect the overall affinity of this class under column operation.

Overall, utilization of compost in column operation mode is feasible, especially for basic and direct dyes (Publication 4). The performance of compost fixed-bed adsorber capacity for cationic dyes (like BV10) is very promising when compared with inorganic adsorbents and even commercial materials like activated carbon, as shown in Table 4.3 (Atar et al., 2011; Alardhi et al. 2020; Nidheesh et al., 2021).

4.2.2.6 Effect of competition between dyes

Another interesting issue to be discussed when studying dyes uptake is the presence of another competing dye(s). However, few research studies have reported simultaneous sorption of more than one dye by compost (i.e., competitive adsorption) (Publication 4; Atar et al. 2011; Yu et al., 2019). The scarce number of studies on this topic may be attributed to the difficulties in the simultaneous analysis of mixtures of dyes.

Figure 4.7 summarizes the results of competitive adsorption of BV10 and DB151 under column and batch modes obtained in this Thesis (Publication 4). In both conditions, the simultaneous presence of dyes in binary systems reduced their uptake in comparison with single solute systems, and this is attributed to the competition for active sites. For both systems, the basic dye BV10 favorably competes with the direct DB151, which was attributed to the higher affinity of basic dyes for compost (Publication 4). Similar observations have been reported for food dyes uptake in single, bi, and ternary mixtures, in the sense that the dye with higher affinity in single-solute solution competes advantageously in the mixture, when compared with the dye with lower affinity (Issa et al., 2017).

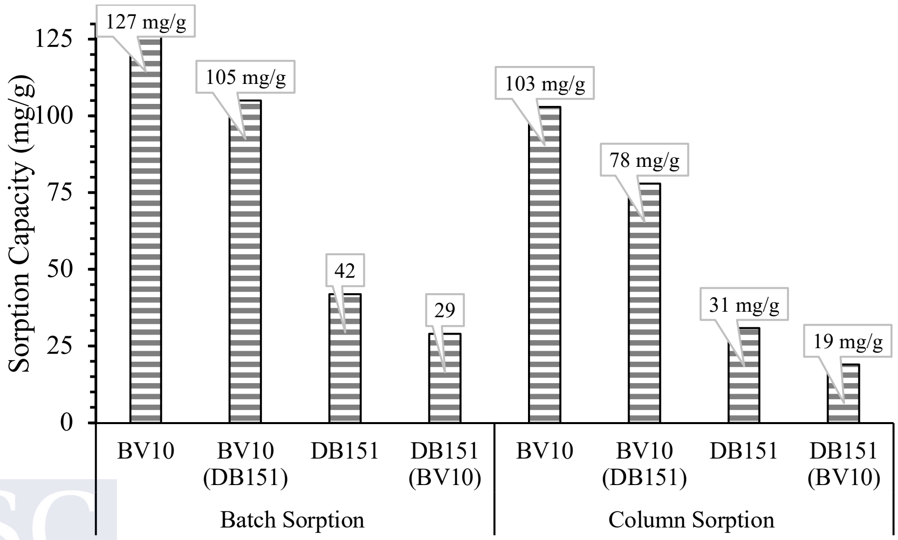

Fig 4.7. Competitive uptake of dyes BV10 and DB151 in batch and column modes.

The results obtained in this thesis are in general agreement with those reported in the literature. As indicated in Table 4.3, the co-occurrence of two dyes in the solution reduced their retention on the adsorbent compared to their retention from single-solute solution (i.e., no solute competition). For instance, sorption capacities of methylene blue were reduced from 551 to 122 mg/g and that of rhodamine B from 254 to 91 mg/g, due to the competitive behavior of both dyes (Yu et al., 2019). In fact, the competition between dyes was reported to be more intense in column operation compared to batch conditions (Publication 4). Hence, to overcome dye competition under column conditions longer bed-depths are required, as well as potentially surface modification of the adsorbent.

4.2.3 Mechanisms of interaction between dyes and compost

Dye adsorption by compost is a complex process and there is no single mechanism that can account for the nature of this interaction. The results obtained in the study of the effect of pH and salinity on dyes uptake, in addition to FTIR analysis, have allowed to obtain important insights regarding the mechanisms of interaction of dyes of different nature with the composts (Publication 1-3).

Deductions from pH studies and electrostatic forces. To understand the effect of pH on dye sorption and its relationship with the mechanisms of interaction, it must be remembered that solution pH controls simultaneously the net surface charge of the composts and the extent of dye ionization and therefore their charge. This was examined in detail in publication 2. In the case of DB151 and AR27, the dyes would be negatively charged at all the tested pH values, while CPB would be positively charged at pH 3, and negatively charged at pH 5 and 7, giving a plausible explanation to the maximal dye removal at pH 3. In turn, in the case of RV4, composts and dye would present net charges of opposite sign only for MSWC at pH 5.0 and 7.0; however, these were not the conditions producing the highest retention. Therefore, it is clear that electrostatic interaction cannot be the main -or at least not the only -mechanism involved in dye sorption by compost. In fact, in the case of BV10, the maximum sorption was found at pH 3.0, for which sorbent and sorbate have similar positive net charge, so that no electrostatic attraction could be expected and lower adsorption should have been observed, but this was not the case.

Overall, the fact that pH variations always influenced dye adsorption in the same direction, independently of the modifications of electric charge of sorbents and dyes caused by these pH variations, proves that electrostatic interaction cannot be the only or the main mechanism for the interaction between dyes and compost. Considering the complex structure of the dye molecules, the contribution of other mechanisms such as hydrophobic-hydrophobic and dipole-dipole forces should be envisaged to explain dye sorption under unfavorable charge conditions. Hydrophobic interaction between the organic dyes and organic matter-rich composts is possible and could explain the higher affinity of dyes toward CPB over all pH values, considering the much higher organic matter content of CPB with respect to MSWC. Similar results observed in the literature have been attributed to zwitterion aggregation, due to the attractive electrostatic interactions between the carboxyl and xanthene groups of different molecules, making large dimer clusters that reduce electrostatic interaction and cannot penetrate inside the pores of the sorbents (Yu et al., 2019; Hou et al., 2011).

Deductions from salinity studies and dimerization of dyes. In all cases it was observed that increasing the salinity had a favorable effect on dye removal by compost, as studied in detail in Publication 2. Once again this happened with independence of the variations in electric charge caused by the pH variations accompanying the modifications in ionic strength. The results reinforce the idea that electrostatic interaction is not the only or at least not the main mechanism involved in the retention of anionic dyes. For example, the highest sorption of BV10 by CPB was observed at 1.0 M KCl, when both CPB and BV10 carry net positive charge. In the case of AR27 and DB151, net charges of opposite sign existed for CPB but not for MSWC, so electrostatic interaction cannot explain why sorption always increased with salinity for both composts. Also for RV4, a dominant electrostatic interaction is not possible under any conditions, due to charges of similar sign in sorbate and sorbent.

This positive influence of salinity on the removal of anionic dyes from water has already been reported in the literature and attributed to the dimerization of dyes at high ionic strength, which reduces dye solubility and increases sorption as a result (Sunjuk et al., 2019). This dimerization can be due to an increase in intermolecular forces, such as dipole–dipole, ion–dipole or Van der Waals dispersion forces at high salinity, which produce a reduction of the repulsive interaction between dyes (Al-Degs et al., 2008; Fedoseeva et al., 2010). In summary, as already stated when discussing the effect of pH, hydrophobic interactions or dipole-dipole forces are likely mechanisms that can contribute to dye sorption under unfavorable charge conditions.

FTIR analysis. Studying the FTIR spectra of the dye-loaded composts helped to elucidate the interaction mechanisms, by evidencing structural changes in the composts after dye sorption. Publications 1 and 2 presented FTIR spectra before and after dye uptake by composts. The main modifications observed include reductions in the bands at 1600 cm^{-1} (corresponding to C=C bonds in lignin) and at 3000-3500 cm^{-1} (O-H bonds in alcohol and carboxylic acid groups), showing interaction of dyes with different functional groups of the organic matter. The detection of the band characteristic of azo bond in the region of 1400–1500 cm^{-1} indicates the presence of –N=N– on the surface of the sorbents (Hu et al., 2003), excluding dye degradation. The high reduction in the band interval 2000-2300 cm^{-1} (C=C stretching) for CPB is attributed to hydrophobic-hydrophobic interaction between dyes and this compost. Finally, reductions in the intensity of the 1000-1100 cm^{-1} band for MSWC, but not for CPB, are likely due to interaction of dyes with the inorganic components of MSWC (that are absent in CPB), since this band corresponds to Al-O bonds in clay minerals and Fe-O in oxides.

Overall, these results prove that surface functional groups, like carboxylic acids, are involved in adsorption and that, in general, electrostatic interaction is an important mechanism of interaction for both cationic and anionic dyes, but not the only one, with a relevant contribution of hydrophobic-hydrophobic forces in the sorption process.

4.3 PERSPECTIVES AND FUTURE RESEARCH

Besides agricultural uses of compost, increasing attention is being paid to its applications in environmental remediation, including removal of textile dyes from wastewaters (Anastopoulos and Kyzas, 2014). In this thesis, composted organic residuals have been investigated as a potential natural material for dyes removal from solution (Publications 1-4). From these studies, it is deduced that adsorption of dyes by composts derived from pine bark and municipal solid wastes is a promising methodology for removing dyes from effluent streams, due to advantages such as high efficiency, ease of application, adaptability and economic viability, as shown in Table 4.4. The results derived from this Thesis indicate a good performance of composts for removing different classes of dyes, with higher affinity for cationic dyes compared to anionic ones (Publications 1-4).

The advantages and disadvantages of using compost materials are summarized in Table 4.4. The comparison considers the cost of adsorbent, S/L ratio, solution pH, application of column adsorber, recycling of exhausted adsorbent, rate of sorption rate, multiuse, reducing waste dumping in landfills, and removing capacity for all classes of textile dyes.

Table 4.4. Advantages and disadvantages of compost application for removing dyes from textile water, based on the data obtained in this work.

Factor	Advantage	Disadvantage	Publication
Price	The price of the composts examined is very low compared to natural silicate minerals, activated carbon and processed organic materials. The prices of local Jordanian compost (which showed high affinity for direct blue 171) is around 10-15$/m^3. Commercial Spanish compost is produced with a cost of 20-30 $/m^3	Not all composts can be used as dye adsorbent. Only those of low agronomical value, as those of low N-P-K value and high salinity, are more profitable as dye adsorbers.	1 & 2
Affinity for different classes of dyes	Our research proved the applicability of composts for the adsorption of basic and direct dyes, with affinity comparable to other substrates. The good affinity of composts for reactive dyes is another advantage of this type of adsorbents.	At the best sorption conditions (low pH and high salinity), the uptake of reactive & acid dyes was not high. However, composts could be modified to adsorb these classes of dyes. Table 4.3	2
S/L ratio	Using S/L ratios of 0.45 and 1.1 g/100mL, compost adsorbents showed excellent performance toward basic and direct dyes, respectively.	High S/L ratios were necessary to remove reactive and acid dyes, 3.0 and 2.3 g/100mL, much higher than the S/L ratios of 1.0 and 0.5 g/100ml used for the removal of reactive dyes by other organic and inorganic adsorbents, respectively. Table 4.3	1-3
pH and salinity	Composts derived from pine bark and municipal solids are efficient for removing all classes of dyes at acidic pH (3.0) and in saline solutions; this is an advantage as textile wastewaters are saline.	Compost derived from mushroom was more effective for removing Basic Red 18 at alkaline pH (9.0) and this requires adding NaOH for better dye uptake. Table 4.3	1-3
High sorption rate	In general, compost derived from pine bark and municipal solid wastes can remove all classes of dyes in a shorter time (3-5 hr), compared with inorganic adsorbents (20-25 hr). Hence, composts are more practical than inorganic adsorbents.	Our survey showed that compost derived from mushroom needed a long contact time (8-10 hr) for removing most dyes from solution and this may retard the retention when using this material in column adsorber. Table 4.3	2

Factor	Advantage	Disadvantage	Publication
Usability in column	Most compost adsorbents have low density (0.3-0.4 g/ml), hence filtration through composts is rather quick and can be used in filtration (or column) systems and at moderate pressure. This gives compost more chance to be applied in filtration systems compared to inorganic adsorbents which have high density of low filtration quality. Our research on column adsorption indicated that more than 50% of ultimate capacity was achieved in column. More research is going on in our laboratory on this issue. Table 4.4	Running column adsorption is not efficient for mushroom-derived composts, which have slow rates for dyes uptake. Table 4.4	3, 4
Recycling	Very few studies were reported on recycling of composts. With 25% regeneration, recycling of reactive dye-composts was achieved and seems to be promising.	Unfortunately, only 10% regeneration of composts loaded with basic, direct and acidic dyes was reported. More research is going on in our laboratory on this issue.	1-4
Multiuse	Perhaps what distinguishes compost from other materials is its multiple uses in addition as being good adsorbent material Unlike other adsorbents, compost materials may have many applications in addition to water adsorbents. Compost can be used as soil amendment and conditioner, fertilizer, and as mulching to prevent soil erosion.	Dumping of dye-loaded composts should be addressed by environmental scientists. More research is needed in this line.	1-4
Reducing waste/ landfilling	The production of compost greatly reduces the organic wastes that could otherwise be accumulated in the environment. This point makes compost more advantageous than another classical organic adsorbent and many inorganic adsorbent.	The researchers believe that there is no disadvantage for this point, as reducing waste and dumping in landfills is essential for the local environment.	1-4

As happens with all the research works, these experimental results present limitations and could be expanded to better understand the application of composts for dye removal from wastewater. In this sense, several recommendations can be made to improve our knowledge of the process of adsorption.

First, acid and reactive dyes (like AR27 and RV4) do not show high sorption by compost compared to other classes, although published research is still scarce. In order to eventually confirm these trends and obtain more information, two actions can be envisaged: a) testing compost to remove more types of acid and reactive dyes, and b) testing different composts for adsorption of weakly interacting dyes.

A possible line of research would deal with potential modifications of the compost to increase their performance. These could include washing to remove excessive amounts of soluble organic matter, which can negatively affect the dye removal process (Toptas et al., 2014), temperature-mediated activation by boiling (Paradelo et al., 2009a), or charring (Yang et al., 2016). In particular, surface modification may improve the affinity of composts for dyes (including reactive and acid dyes), and this can be achieved by: a) activation by chemical treatment with acids or bases, or washing with water to remove soluble ions, and b) physical treatment by direct heating to improve surface area and porosity. Another possibility in this sense is using dry milling technology to prepare nano-size compost which will improve its adsorbent properties in solution. Another option is mixing compost with other adsorbents, such as clays, to improve their sorption performance.

Future research in this topic should also be oriented towards producing further information for practical application at real scale. This should involve studies about the influence of the presence of other pollutants typical of textile wastewaters, such as heavy metals, in the efficiency of dye removal. Also, testing the simultaneous removal of more than two dyes and studying the performance of composts with real textile wastewaters of different composition and properties.

Finally, research on sorbent regeneration and reuse should also be performed, studying different substances as eluents, as well as the effect of their concentration or other physicochemical parameters on dye desorption.

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5 CONCLUSIONS

The most important conclusions from this thesis can be summarized as following:

- Composts prepared from municipal solid wastes, pine bark or green waste are stable enough in suspension to be used as solid adsorbent for textile dyes.

- Among the three composts tested, pine bark compost was the most efficient for dye removal.

- In general, composts showed higher affinity for basic and direct dyes compared to acid and reactive dyes. The decreasing adsorption trend would be as follows: basic >> direct > reactive > acid. Dye adsorption at the equilibrium was adequately described by the Langmuir model, what allows to estimate maximum retention capacities by the composts. At the best operation conditions in each case, these ranged between 3.9 mg g^{-1} for Acid Red 27 and 876 mg g^{-1} for Basic Blue 9.

- Kinetics of dye adsorption by composts was best presented by pseudo-first order model. Adsorption rates increased in the following order: Reactive Violet 4 > Acid Red 27 > Basic Violet 10 > Direct Blue 151 > Direct Blue 71 > Basic Blue 9, with values ranging between 0.007 h^{-1} for Reactive Violet 4 and 3.6 h^{-1} for Basic Blue 9.

- Co-existence of several dyes in solution reduced their removal due to competition for adsorption sites, both in batch and column conditions. Dye removal was reduced in continuous flow columns with respect to batch conditions due to lower contact time.

- In most cases, dye removal by the composts increased at acidic pH and high salinity. Adsorption increase at acid pH is likely due to modification of charges of the dyes and higher electrostatic attraction, whereas the effect of salinity is attributed to a dye aggregation mechanism at high ionic strength.

- The study of the influence of these factors and the FTIR spectra of the adsorbents showed that both electrostatic forces and hydrophobic-hydrophobic forces contribute to adsorption.

- The adsorbents could be regenerated using ethanol as eluent, thus enabling reuse in the practical application of compost for textile dye removal.

- The results of this Thesis prove that composts can be successfully used for the removal of dyes from wastewaters, in particular in the case of basic dyes.

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7 PUBLISHED WORKS

7.1 UTILIZATION OF COMPOSTS FOR ADSORPTION OF METHYLENE BLUE FROM AQUEOUS SOLUTIONS: KINETICS AND EQUILIBRIUM STUDIES

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Contribution:
Khaled Al-Zawahreh: methodology, Validation, formal analysis, investigation, writing, review and editing.

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7.2 COMPARISON OF THE SORPTION CAPACITY OF BASIC, ACID, DIRECT AND REACTIVE DYES BY COMPOST IN BATCH CONDITIONS

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Khaled Al-Zawahreh: Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Project administration.

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7.3 OPTIMIZATION OF DIRECT BLUE 71 SORPTION BY ORGANIC RICH-COMPOST FOLLOWING MULTILEVEL MULTIFACTOR EXPERIMENTAL DESIGN

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Khaled Al-Zawahreh: Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Project administration.

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7.4 COMPETITIVE REMOVAL OF TEXTILE DYES FROM SOLUTION BY PINE BARK-COMPOST IN BATCH AND FIXED BED COLUMN EXPERIMENTS

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Al-Zawahreh, K., Barral, M.T., Al-Degs, Y., Paradelo, R., 2022. Competitive removal of textile dyes from solution by pine bark-compost in batch and fixed bed column experiments. Environmental Technology & Innovation, 27, 102421; https://doi.org/10.1016/j.eti.2022.102421

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With the objective of finding low-cost adsorbents for organic dye removal from textile wastewater, the performance of a municipal solid waste compost, a pine bark compost and a green waste compost has been tested towards different dyes: Basic Blue 9, Basic Violet 10, Acid Red 27, Reactive Violet 4, Direct Blue 71 and Direct Blue 151. Adsorption was studied in batch and column conditions; the influence of contact time, solution pH, salinity and competition with other dyes were assessed, whereas the recycling of adsorbents was evaluated by studying desorption. The mechanism of the interaction between the dyes and the composts was also investigated. The results show that composts can be successfully applied for dye removal from wastewater, and that they would be more effective with basic cationic dyes than other types.