Heterogenous Lignocellulosic Composites as Bio-Based Adsorbents for Wastewater Dye Removal: ~~A~~ a Kinetic Comparison

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Abstract

Different lignocellulosic substrates consisting of modified barley husk, peanut shells and sawdust were entrapped in calcium alginate beads and used as adsorbents to remove dye compounds from vinasses. For comparative purposes, a biocomposite formulated with humus was also included in this work. Kinetic studies were carried out by applying ~~pseudo-first order, pseudo-second order,~~ pseudo-first-order, pseudo-second-order, Chien–Clayton and intraparticle diffusion models, observing a good agreement between theoretical and experimental results when the data were adjusted to ~~pseudo-second order~~ pseudo-second-order kinetic model. The results of this study show that ~~lignocellusosic based~~ lignocellulosic-based biocomposites could be used as an effective and low-cost adsorbent for the removal of dyes from aqueous solutions. Among the heterogeneous biopolymers evaluated, the biocomposite based on barley husk gave the best capacity for dye removal. Moreover, in all cases, it was found that there exists a direct relationship between the capacity of the biocomposites to remove dyes and the percentage of carbon contained in the lignocellulosic residues.

Keywords

- Peanut shell
- Barley husk
- Sawdust
- Alginate
- Dye adsorption kinetics

1. Introduction

Many lignocellulosic residues such as corncobs, globe artichoke leaves, coconut coir, bamboo waste, orange peel, rice husk, peanut shells, spent tea leaves or ~~weeds,~~ weeds have been proposed in literature for the production of activated ~~carbons;~~ carbons, although, in most cases, they have been submitted to different activation processes involving high temperatures or the utilization of alkalis or acids (Sanghi and Verma 2013; Angin 2014). Thus, Robinson et al. (2002) compared low-cost ~~pre-treated~~ pretreated residues consisting of barley husk, corncob and wheat straw, for the removal of dyes from an artificial effluent, observing a higher percentage of dye removal and a faster rate when samples were milled, except for barley husk, which had a higher percentage removal for the control.

Moreover, Gong et al. (2005) used powder prepared from peanut hull for the biosorption of three anionic dyes, Amaranth, Sunset Yellow and Fast Green FCF at initial pH ~~2;~~ 2, obtaining a ~~pseudo-first order~~ pseudo-first-order kinetic behaviour. In addition, Reddy et al. (2013) developed activated carbons from ~~bio-waste~~ biowaste materials like rice husk and peanut shell by various physicochemical activation methods, observing that the experimental data fitted well in the Langmuir isotherm model when activated carbons were used to remove methylene blue from water.

On the other hand, Pehlivan et al. (2012) used barley straw as a biosorbent material for the removal of copper (Cu^{2+}) ions

from aqueous solutions after treatment with citric acid, suggesting that the sorption process was dominated by adsorption, ion exchange, electrostatic attraction and chelation. Moreover, Ding et al. (2014) treated peanut hulls, soybean shells and grapefruit peels with sodium hydroxide and then copolymerized them with ~~epichlo-rohydrin~~ epichlorohydrin and ethylenediamine in order to remove Pb (II) from aqueous solution, finding that the adsorption followed a ~~pseudo-second order~~ pseudo-second-order kinetic model. Furthermore, Ibrahim et al. (2010) modified the surface of barley straw, using a cationic surfactant (hexadecylpyridinium chloride monohydrate) and then used it as an adsorbent to remove Reactive Blue 4 (RB4) from aqueous solutions, observing that the kinetic data yielded excellent fit to the ~~pseudo-second order~~ pseudo-second-order model. However, few studies exist in literature about the utilization of non-chemically oxidized lignocellulosic biomass in the treatment of wastewater or in the formulation of biocomposites based on lignocellulosic residues.

In previous studies, it has been demonstrated that heterogeneous biopolymers based on lignocellulosic biomass entrapped in calcium alginate beads can be used as potential adsorbents for the treatment of coloured wastewater as well as to remove micronutrients from water (Perez-Ameneiro et al. 2014a, b; Vecino et al. 2014). In these studies, the lignocellulosic residue, consisting of biodegraded grape marc, was submitted to spontaneous biodegradation in order to oxidize the organic matter and improve the capacity of this residue to remove dyes and micronutrients from vinasses (Perez-Ameneiro et al. 2014a, b). Biocomposites based on lignocellulosic residues have many advantages, since they are ~~eco-friendly, low-cost,~~ ecofriendly, low cost, biodegradable and abundant in comparison to non-renewable adsorbents.

On the other hand, peat is a porous and rather complex soil material with organic matter in various stages of decomposition that has been proposed by Vecino et al. (2013) to elaborate a biocomposite to remove dyes from vinasses.

The elimination of dye compounds from vinasses using lignocellulosic residues can involve several complex mechanisms, such as surface adsorption, ion exchange, complexation, complexation–chelation or microprecipitation (Chu and Chen 2002a, b).

In this work, a comparative study involving heterogeneous biopolymers based on lignocellulosic residues entrapped in calcium alginate beads was developed by evaluating the behaviour of the biocomposites as ~~eco-friendly~~ ecofriendly adsorbents for dye removal in wastewater treatments. Several kinetic models were considered to investigate the adsorption processes of dyes from vinasses onto the different biocomposites.

2. Materials and Methods

2.1. Substrates

Peanut shell, barley husk and eucalyptus sawdust were obtained from local ~~industries,~~ industries, whereas humus was supplied by Comporense S.L. (Ourense, Spain).

According to the providing company, commercial worm humus has a composition of 1.6–2.3 % in total nitrogen, 1.4–1.9 % in total phosphor, 1.4–1.9 % in total ~~potassium,~~ potassium and 1.3–6.9 % in calcium, pH 7–7.2, and a maximum moisture of 35 %; and nutrients such as magnesium, iron, sodium, copper, manganese and organic matter are also contained in this substrate.

In contrast to the other adsorbents, barley husk underwent a supplementary delignification process following the procedure described by De Abreu et al. (2012). In the mentioned study, antioxidants were extracted from barley husk using 3 % of H_2SO_4 at 130 °C during 15 min, in order to remove the hemicellulosic sugars, followed by a delignification process using 6.5 % of NaOH at 130 °C during 60 min (see Fig. 1).

Before formulating the biocomposites, peanut shell, barley husk and sawdust were milled and sieved up to a particle size of 0.5 mm, whereas humus was used as provided by the company without any other previous process.

2.2. Analytical Methods for the Characterization of Adsorbents

For the characterization of the adsorbents, substrates were sieved to 0.5 mm and homogenized. The samples were ~~air-dried~~ air dried and milled prior to carbon and nitrogen ~~analysis,~~ analysis and then decomposed by thermocatalysis. C, N, H and S were determined in a Fisons-EA-1108 CHNS-O element analyser (Thermo Scientific).

2.3. Vinasses

Vinasses were collected from local winery industries and kept at 4 °C until use. The initial concentration of coloured compounds, measured as equivalents of Amaranth dye, was set around 29 mg/L.

2.4. Biocomposite Formulation

Biocomposites were formulated by mixing 2 % of lignocellulosic substrate or humus, 2 % of sodium alginate and calcium chloride ($CaCl_2$) 0.58 mol/L, following the methodology used in previous works (Perez-Ameneiro et al. 2014b). Before adsorption experiments were carried out, the biopolymer was washed several times with distilled water at room temperature to remove excess $CaCl_2$.

2.5. Adsorption Studies

Adsorption experiments were carried out in ~~250 mL~~ 250-mL Erlenmeyer flasks at 25 °C and 112 rpm during 2 h. The ratio between the different adsorbents and vinasses was 1.5:1 ~~(v/v).~~ (*v*/*v*). Samples of vinasses were obtained at several times and the amount of dye compounds was evaluated.

The adsorption capacity q_e (mg/g) was calculated following Eq. 1.

$$q_e = \frac{(C_0 - C_e)\cdot V}{W} \quad (1)$$

where C_0 and C_e (mg/L) are the concentrations of coloured compounds in the winery vinasses before and after treatment, respectively; V (L) is the volume of the winery vinasses used during batch ~~experiments,~~ experiments; and W (g) is the mass of dry adsorbent ~~(i.e.,~~ (i.e. the amount of lignocellulosic biomass used in the formulation of the adsorbent composite).

2.6. Optical Images of Lignocellulosic Adsorbents

The macro views of the biocomposites composed of different lignocellulosic substrates and humus, entrapped in calcium alginate beads, were obtained with a regular digital camera (Sony optical SteadyShot) using an Optical Zoom 4X with ~~26 mm~~ a 26-mm wide-angle lens and 14.1 Megapixels.

2.7. Scanning Electron Microscope ~~(SEM)~~ Images of Lignocellulosic Adsorbents

In order to corroborate the adsorption of dyes onto the adsorbents, batch adsorption experiments were carried out using no entrapped lignocellulosic polymers in the same conditions that ~~those~~ were described above. Thus, samples of lignocellulosic biomass and humus powder were collected before and after adsorption experiments. After wastewater treatment, powder was washed with deionized water, filtered and ~~air-dried.~~ air dried. All samples were then covered with gold and directly observed using a JEOL ~~JSM-6700 F~~ JSM-6700F FEG scanning electron microscope (SEM) operating at an acceleration voltage of 10.0 kV for ~~secondary-electron~~ secondary electron imaging and ~~lower-electron~~ lower electron imaging (SEI/LEI).

2.8. Dye Analysis

Dyes in vinasses were evaluated in a double beam spectrophotometer (Jasco V-650). Colour measurements were analysed by considering the CIE 1976 ~~(L*, a*, b*)~~ (*L**, *a**, *b**) or CIELAB colour ~~system,~~ system as well as the colour index (CI). CIELAB system is widely accepted by both the scientific community and industry, as it is the most ‘perceptually uniform’ of the colour spaces (Berns 2000; Völz ~~2001),~~ 2001), whereas CI, which is described as the sum of the absorbance values of a sample at the wavelengths of 420, 520 and 620 nm, was used in previous works to measure the dye compounds in vinasses (Devesa-Rey et al. 2011; Vecino et al. 2012, 2013; Bustos et al. 2014).

Vinasses are composed of a mixture of dyes that have a peak of absorbance at the same wavelength (520 nm) than commercial Amaranth dye. In order to evaluate the colour reduction that occurred in the vinasses after treatment with biocomposites, the absorbance value at 520 nm of each sample was converted to equivalents of Amaranth dye. Thus, the amount of coloured compounds in vinasses was measured as equivalents of Amaranth dye, following the methodology used in a previous work (Perez-Ameneiro et al. 2014a).

Additionally, ~~pseudo-first order~~ pseudo-first-order (Lagergren 1898), ~~pseudo-second order~~ pseudo-second-order (Ho and McKay 1999), Elovich equation (Elovich and Larionov 1962a, b) modified by Chien and Clayton (1980) and intraparticle

diffusion models (Weber and Morris 1962) were used to study the behaviour of the adsorption process onto the bioadsorbents.

3. Results and Discussion

3.1. Elemental Analysis of the Adsorbents

In this work, several lignocellulosic residues were entrapped in calcium alginate beads in order to obtain a more manageable adsorbent. In Fig. 2, ~~it can be observed~~ the spherical surface and the size of the different ~~biocomposites,~~ biocomposites can be observed, whose diameters were between 3.0 ~~mm~~ and 4.0 mm. Sodium alginate is a linear ~~polysaccharide, natural~~ polysaccharide and a naturally occurring polymer composed of α-guluronate and β-mannuronate ~~residues,~~ residues, whereas lignocellulosic residues are composed of cellulose, lignin and hemicellulose in different concentrations depending on their origin. Table 1 includes the information related to the elemental composition of the lignocellulosic polymers used to formulate the ~~biocomposites,~~ biocomposites as well as the composition of the humic substrate. As it can be observed, barley husk gave the highest percentage of C, followed by peanut shell and ~~sawdust,~~ sawdust, whereas humus contained the lower amount of C. The high content of C in barley husk can be related with the concentration of the lignocellulosic fraction in the residue after the hydrolysis and the delignification process carried out to remove the hemicellulosic sugars and lignin (see Fig. 1). Regarding the nitrogen concentration, humus provided the highest percentage, followed by peanut ~~shell,~~ shell, while sawdust and barley husk are composed of a minor concentration of nitrogen. The treatment of barley husk reduced the nitrogen concentration of this residue from 10.68 ~~%~~ up to 0.29 %. Minor variations were observed in the percentage of carbon and hydrogen after the treatment of barley husk.

3.2. SEM Analysis of Lignocellulosic Adsorbents Before and After Adsorption

The adsorption capacity of the adsorbent is not only determined by its physical or porous ~~structure,~~ structure but also influenced by the chemical structure of its surfaces. A scanning electron microscope ~~(SEM)~~ was also applied to the samples. Figure 3 shows the morphology changes of unloaded and loaded non-entrapped substrates. Images revealed that unloaded non-entrapped substrates have a rough surface, with many fractures and small convex ~~protrusions;~~ protrusions, whereas after bioadsorption of dyes, the surface of lignocellulosic materials and humus becomes smoother and less porous, probably due to the entrapping and adsorption of the coloured compounds.

3.3. Kinetic Study

Table 2 shows the reduction in colour index, the increase in lightness and the reduction in colour pigments at the equilibrium in vinasses after being treated with the four different biocomposites. Based on the highest reduction in colour index, the highest values of lightness ~~(L*)~~ (L^*) as well as in the decrease of pigments achieved in water after treatment, it can be speculated that barley husk is the most suitable substrate when applying the biocomposite. In line with the foregoing, in terms of efficiency, barley ~~husk based~~ husk-based biocomposite showed the best performance, being able to remove the 98.41 % of coloured compounds in water, followed by peanut shell and sawdust (87.15 ~~%~~ and 84.71 %, respectively). On the contrary, the humic-based composite provided lower lightness values and lower pigment removal with percentage reductions about 83 ~~%;~~ %, measured as percentage of decolouration based on equivalents of Amaranth dye. These values are similar to those achieved by other authors using other techniques. Thus, Bocos et al. (2014) found that 90 % of dyes were decolorized during batch ~~electro-fenton~~ electro-Fenton treatment with Fe hydrogels after ~~two hours~~ 2 h of ~~treatment~~ treatment, and Álvarez et al. (2013) eliminated 60 % of textile dyes contained in industrial effluents using *Anoxybacillus flavithermus*.

On the other hand, the kinetic behaviour of the adsorbents is of great interest for any further work concerning ~~scaling-up.~~ scaling up. Thus, the adsorption of dyes onto the biocomposites was described using different kinetic models. Equation 2 shows the linear form of the ~~pseudo-first order model,~~ pseudo-first-order model:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \qquad (2)$$

where q_e (mg/g) and q_t (mg/g) are the concentration of adsorbed dyes at equilibrium and at a defined time t, respectively, and $k_{~~1~~}$ $_1$ (1/min) is the rate constant of ~~pseudo-first order~~ pseudo-first-order adsorption.

The kinetic coefficients obtained in this case showed that there is a clear difference between humus and the other lignocellulosic residues. Barley husk, peanut shell and sawdust gave theoretical capacity values between 0.46 ~~mg/g~~ and 0.45 ~~mg/g;~~ mg/g, whereas, by using humus, the capacity was only 0.23 mg/g. Among the lignocellulosic biocomposites that

showed better performance, it was observed that barley husk reached the highest value of ~~q_e~~ q_e (0.96 mg/g) when taking into account the experimental capacities. Figure 4a shows the correlation between the experimental data and the theoretical data when these were described by using ~~pseudo-first order~~ pseudo-first-order kinetic model. When comparing the theoretical values obtained to the experimental ones shown in Table 3, ~~it can be noticed~~ the huge variance between ~~them.~~ them can be noticed. This illustrates that none of the adsorption processes of the biocomposites ~~follow~~ follows a ~~pseudo-first order~~ pseudo-first-order kinetic model.

Moreover, sorption kinetics were also described using a ~~pseudo-second order~~ pseudo-second-order model following Eq. 3.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

where ~~k_2~~ k_2 (g/mg min) is the equilibrium rate constant of ~~pseudo-second order~~ pseudo-second-order adsorption. In this case, Eq. 3 does not have the problem of assigning an effective q_e. If the ~~pseudo-second order~~ pseudo-second-order kinetic equation is applicable, the plot of t/q_t against t should give a linear relationship, from which q_e and ~~k_2~~ k_2 can be determined from the slope and intercept of the plot, and there is no need to know any parameter beforehand.

Table 3 shows the kinetic parameters obtained after the treatment of the ~~data~~ data, and Fig. 4b shows the variation of the experimental data when they are adjusted to a ~~pseudo-second order~~ pseudo-second-order kinetic model. It was observed that barley husk gave the most favourable kinetic parameters for the removal of dye compounds from water, followed by peanut shell and ~~sawdust based~~ sawdust-based biocomposites, being the ~~humus based~~ humus-based biocomposite the adsorbent with the lowest capacity. In all of these cases, there is a close agreement between the experimental and theoretical capacities predicted by the model.

Furthermore, adsorption kinetics can also be adjusted to the Elovich equation, which, although firstly used to explain the adsorption kinetics of gases on solids, it has been successfully applied for the adsorption of solutes from a liquid solution (Eq. 4).

$$\frac{d\ q_t}{d\ t} = \alpha \exp\left(-\beta q_t\right) \tag{4}$$

Chien and Clayton proposed the simplification of Eq. 4 by assuming $\alpha\beta t$ ~~>>1,~~ >>1 and considering the boundary conditions $q_t = 0$ for $t = 0$ and $q_t = q_t$ at $t = t$. In the ~~Chien-Clayton~~ Chien–Clayton expression (Eq. 5),α (min mg/g) is the initial sorption ~~rate,~~ rate and β (g/mg) is related to the extent of surface coverage and activation energy for chemisorption.

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{5}$$

Regarding the kinetic parameters obtained after applying the Chien–Clayton kinetic model shown in Fig. 4c, it can be observed that α values predicted by this model are higher than those obtained using composted grape marc entrapped in calcium alginate beads, whose values were between 4.99 ~~mg/g min~~ and 6.66 mg/g min (Perez-Ameneiro et al. 2014a). Since α parameter determines the initial sorption rate, it can be speculated that the adsorption process is more favourable using calcium alginate biopolymers based on barley husk than using adsorbents based on peanut shell and sawdust. Moreover, it can be noticed that, although calcium alginate containing humus showed the highest value for α, the adsorption capacity for this adsorbent was lower than the capacity obtained using lignocellulosic-based biocomposites.

Finally, experimental data have been fitted to the ~~Intraparticle Diffusion~~ intraparticle diffusion model in order to determine whether the adsorption process is governed only by intraparticle diffusion or if it is more complex and involves more than only one diffusive resistance, as shown in Fig. 4d. The intraparticle diffusion model can be expressed using Eq. 6.

$$q_t = k_P t^{0.5} + C \tag{6}$$

where k_P is the intraparticle diffusion rate constant (mg/g min$^{0.5}$) and C is the intercept (mg/g), and it is related to the thickness of the boundary layer. The slope of the linear part of the curve of q_t vs $t^{0.5}$ ~~–~~ k_P ~~–~~indicates the rate of adsorption controlled by intraparticle diffusion. When the ~~intercept –~~ intercept, C ~~–~~, equals zero, then the intraparticle diffusion is the only controlling step. However, if C does not pass through the origin, it indicates that there are other processes involved in the rate of adsorption. In this case, the intraparticle diffusion model gave C values higher than 0, which indicates that there are other processes, apart from the intraparticle diffusion, involved in the rate of adsorption. These results are in concordance with those obtained in a previous work, where the performance of a lignocellulosic biocomposite based on composted grape marc was studied (Perez-Ameneiro et al. 2014a).

For all the kinetic studies regarding the lignocellulosic biocomposites, good correlation coefficients ~~(~~(r^2) were obtained with values between 0.93 and 0.99 (see Table ~~3);~~ 3), whereas when the kinetic adsorption of biocomposite based on humus was studied, the correlation coefficients ~~(~~(r^2) varied between 0.59 and 0.99. In this case, the best kinetic model that explained the adsorption process onto the humus biocomposite was the pseudo-second ~~order;~~ order, whereas the ~~first order~~ first-order kinetic model provided the lowest correlation coefficient. It can be stated, then, that pseudo-second order was the kinetic model that better explained the behaviour of the adsorption process for all the biocomposites evaluated ~~(~~(r^2 = 0.99). Intraparticle diffusion model yielded also remarkable correlation coefficients ~~(~~(r^2 = 0.99–0.85) for the studied bioadsorbents.

On the other hand, Fig. 5 shows the linear relationship between the capacity of the biocomposites based on lignocellulosic residues and the percentage of carbon. It was observed that those biocomposites with higher percentage of carbon showed higher capacities. However, no relationship was observed between the other elemental components included in Table 1 and the adsorption capacity of biocomposites.

In comparison with the biocomposite based on grape marc compost evaluated in a previous work to remove dyes from vinasses (Perez-Ameneiro et al. 2014a), it was observed that the barley husk, peanut shell and sawdust bioadsorbents showed similar performance and similar capacities than the composted grape marc biocomposite.

Some authors have used bioadsorbents based on different lignocellulosic materials to remove contaminants from water. However, in these cases, the adsorbents were not entrapped in any matrix and thermic or chemical methods were used to modify the composition of the lignocellulosic residue. In comparison with the current work, Hassan et al. (2014) prepared three adsorbents, calcium alginate beads, sodium hydroxide activated carbon based on coconut shells, and calcium alginate/activated carbon composite beads, observing that the adsorption of dyes follows a ~~pseudo-second order~~ pseudo-second-order mechanism. Thermodynamic studies show spontaneous and endothermic nature of the overall adsorption process. These results are in concordance with the kinetic data obtained in this work.

4. Conclusions

The results obtained from this study showed that biocomposites based on barley husk, peanut shell or sawdust in batch adsorption experiments were effective at removing dyes from winery vinasses, showing that the barley ~~husk based~~ husk-based bioadsorbent has the best performance. A direct relationship between the content in carbon of the substrates and their capability to remove coloured compounds from vinasses was found. Additionally, ~~pseudo-2nd order~~ pseudo-second-order kinetic model, Chien–Clayton kinetic model and ~~Intraparticle~~ intraparticle diffusion model were successfully applied to predict the kinetic of the adsorption, showing that the adsorption process for all the studied biocomposites follows a ~~pseudo-second order~~ pseudo-second-order kinetic model and that the intraparticle diffusion is not the only controlling step.

Acknowledgments

We are grateful to the Xunta de Galicia (project GPC, ref. ~~CN2012/277)~~ CN2012/277), and Vecino X. gratefully acknowledges the University of Vigo for her predoctoral contract.

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Figures:

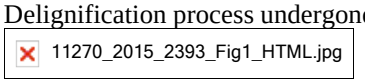
Fig. 1
Delignification process undergone by barley husk


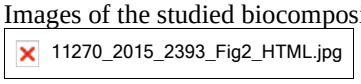
Fig. 2
Images of the studied biocomposites: **a** peanut shell; **b** sawdust; **c** barley husk; **d** humus


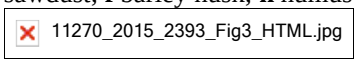
Fig. 3
SEM images, at different magnifications ~~x1000, x2500~~ ×1000, ×2500 and ~~x5000,~~ ×5000, of the compared non-entrapped substrates before adsorption: **a** peanut shell; **c** sawdust; **e** barley husk; **g** humus, and after adsorption: **b** peanut shell; **d** sawdust; **f** barley husk; **h** humus


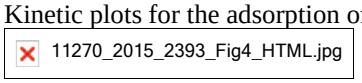
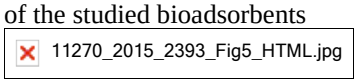
Fig. 4
Kinetic plots for the adsorption of coloured compounds onto the studied biocomposites


Fig. 5
Plot for the correlation between the composition in carbon of the different cellulosic substrates and the adsorption capacity of the studied bioadsorbents


Tables:

Table 1
Elemental analysis of the substrates used in the formulation of the biocomposites

	N (%)	C (%)	H (%)	S (%)			
Peanut ~~Shell~~shell		0.89 ± 0.04		48.34 ± 0.46	6.03 ± 0.09	<LD[a]	
Sawdust		0.20 ± 0.01		46.70 ± 0.18	6.04 ± 0.13	<LD[a]	
Barley ~~Husk~~husk		0.29 ± 0.04		51.0 ± 0.09	6.77 ± 0.22	<LD[a]	
Humus		1.95 ± 0.13		21.57 ± 1.55	3.12 ± 0.24		0.47 ± 0.07

[a] ~~LD: Limit~~ *LD* limit of ~~Detection~~detection

Table 2
Colour parameters at equilibrium

	CI (AU)	~~L*~~ *L** (CIELAB units)	C pigments (mg/L)
Initial	2.803	48.35	29.07
Peanut ~~Shell~~shell	0.428	90.04	3.79
Sawdust	0.536	87.99	4.51
Barley ~~Husk~~husk	0.063	98.57	0.47
Humus	0.839	87.25	4.97

Table 3
Comparison of kinetic parameters for ~~pseudo-first order, pseudo-second order,~~ pseudo-first-order, pseudo-second-order, Chien-Clayton and intraparticle diffusion kinetic models

Adsorbent	~~Pseudo—1st Order~~ Pseudo-first-order kinetic model				~~Pseudo—2nd Order~~ Pseudo-second-order kinetic model				Chien–Clayton kinetic model			Intraparticle ~~Diffusion~~ diffusion model		
	~~K~~K_1	~~q_e~~ q_e exp	~~q_e~~ q_e calc	~~r~~r^2	~~K~~K_2	~~q_e~~ q_e exp	~~q_e~~ q_e calc	~~r~~r^2	~~α~~α	~~β~~β	~~r~~r^2	~~K~~K_p	~~C~~C	~~r~~r^2

	(L/g min)	(mg/g)	(mg/g)		(L/g min)	(mg/g)	(mg/g)		(mg/g min)	(g/mg)		(mg/g $min^{0.5}$)	(mg/g)	
Peanut ~~Shell~~shell	0.0454	0.86	0.46	0.946	0.2897	0.86	0.88	0.998	6.69	10.36	0.979	0.1150	0.2100	0.993
Sawdust	0.0477	0.83	0.45	0.953	0.3091	0.83	0.85	0.998	7.51	10.82	0.975	0.1118	0.2093	0.992
Barley ~~Husk~~husk	0.0485	0.96	0.45	0.930	0.3482	0.96	0.98	0.999	19.47	10.19	0.987	0.1355	0.2597	0.987
Humus	0.0251	0.77	0.23	0.590	0.4796	0.77	0.76	0.996	~~13145.19~~13,145.19	23.68	0.955	0.0946	0.2888	0.854