

The application of diffusion–reaction mixed model to assess the best experimental conditions for bark chemical activation to improve copper(II) ions adsorption

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Abstract Natural sorbents have been thoroughly assessed to determine their adsorption capabilities to remove pollutants from industrial wastewaters. Among them, pine bark has demonstrated potential for carrying out the removal of contaminants, particularly heavy metals, at the level of traces present in dissolved state. Nevertheless, to move towards the wastewater treatment implementation at large scale, the handling and processing requirements of pine bark to optimise the adsorption of heavy metals must be fully assessed. This research study presents a new mathematical model to evaluate the impact of acid pre-treatment of pine bark on heavy metals adsorption at different pine bark-aqueous solution pulp densities. A diffusion–reaction mixed model was developed and applied to the case study of copper(II) adsorption onto pine bark. The low binding energy inferred from analysing the adsorption isotherms suggested that a diffusive mechanism is governing the whole process. The mixed diffusion–reaction kinetic model indicated that the activation increases the rate at which metal ions are adsorbed, but it reduces the

maximum achievable adsorption which in turn restricts its usefulness to relatively high pulp densities (above 10 g/L). The latter constitutes the first step towards optimising the use of bark pine for treating wastewater polluted with heavy metals and for establishing rules for scaling-up the process.

Keywords Adsorption kinetics · Heavy metals · Wastewater treatment · Pine bark · Chemical activation

Introduction

The treatment of wastewaters containing heavy metals is of particular interest for the environmental research as it is commonly required at large scale operations related to industrial activities such as mining and metallurgical processes (Bourke and Kemp 1979; Martins et al. 2009; Huang et al. 2007). Nowadays, classic pathways for wastewater treatment such as precipitation and filtration are widely implemented (Peters et al. 1985; Diels et al. 2002; Islamoglu et al. 2006). Nevertheless, the increasingly strict legislation reduces the maximum allowable concentration of heavy metals present in industrial effluent streams make such paths for wastewater treatment expensive or impractical. In most cases, regardless the amount of alkali added to an aqueous solution, the complete removal of heavy metals is virtually impossible to achieve since precipitation will always leave a small amount of soluble metal in solution raised from the respective specie solubility (Kim et al. 2002). This situation is worse in cases where heavy metals at high pH values generate soluble oxide anionic species which will inevitably remain in dissolved state, e.g. zinc (Hisaindee et al. 2011) turning the pollutants removal fruitless.

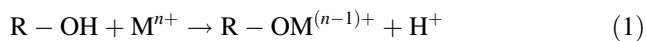
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Instead, the use of adsorption techniques overcomes this problem leaving aqueous solutions with heavy metal concentrations typically in the order of parts per billion (Saeed et al. 2005).

For many years, several natural products have been comprehensively assessed as possible sorbents for heavy metal ions from aqueous solutions (Tiwari et al. 1999; Vazquez et al. 1994; Randall et al. 1974; Zhou and Haynes 2012; Zawierucha et al. 2013; Martin-Lara et al. 2013). Some examples of sorbents are sugar maple (Watmough and Hutchinson 2003); mulch (Jang et al. 2005); papaya wood (Saeed et al. 2005); tea industry wastes (Cay et al. 2004); sawdust (Taty-Costodes et al. 2003); and pine bark (Montes et al. 2005, 2006, 2009; Nehrenheim 2011; Khokhotva 2010). It has been proved that the governing mechanism for the adsorption of cationic heavy metals is ionic exchange reactions (Martin-Dupont et al. 2006) which occurs throughout the removal of protons present in the different bark molecular structures (Eq. 1),



where R is the organic structure of the sorbent, M^{n+} is the heavy metal ion in solution. The ion-exchange mechanism may coordinate one or more adsorption sites and the charge of the metallic ion can be totally or partially compensated by the surface charge of the biosorbent. Several mathematical models have been applied to understand the adsorption of heavy metals onto pine bark. On one hand, the thermodynamics of the adsorption process is usually described using adsorption isotherms, such as the Langmuir and/or the Freundlich isotherms, and, more precisely, their linearised forms, widely applied in these case studies (Table 1).

Where $q_{e,i}$ represents the volume (mol) of adsorbate adsorbed in standard conditions ($i = \text{L}$: Langmuir; $i = \text{F}$: Freundlich), C_e is the equilibrium concentration of the adsorbate in the solution (mol/L), K_L is the Langmuir isotherm constant or binding energy, S_m is the amount of adsorbate required to fully cover the sorbent surface, K_F is the Freundlich empirical constant usually referred to as the sorption capacity, and n represents the sorption intensity.

On the other hand, the adsorption kinetics of heavy metals onto natural sorbents has been studied using simple kinetics equations. The specific surface is usually

unknown; therefore, all the information is gathered into one parameter associated with the equilibrium concentration of the adsorbate in solution, and the specific rate constant.

The pseudo-first- and pseudo-second-order kinetics involving an equilibrium state in its integrated form can be expressed as Eqs. (2) and (3), respectively.

$$\ln \frac{(q_e - q_t)}{q_e} = -k_1 t \quad (2)$$

where

k_1 is the pseudo-first-order rate constant that can be written as $k_{\text{ads}}C_s + k_{\text{des}}$, being C_s the adsorbent concentration in solution.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where k_2 is the pseudo-second-order rate constant. Furthermore, the kinetic models are not restricted to reaction-driven mechanisms. The intraparticle diffusion model derived by Weber and Morris (1963) represents the initial rate observed when the system is governed by this mechanism (Eq. 4).

$$q_t = k \times \sqrt{t} + T \quad (4)$$

where k_{id} is the intraparticle diffusion rate constant and T is a parameter usually related to the thickness of the boundary layer. Argun and Dursun (2008) applied this model to heavy metals adsorption onto natural adsorbents finding some general agreement between heavy metal adsorption data with film diffusion models similar to that of a pseudo-first-order kinetics.

From an experimental standpoint, there is a number of sorbent pre-treatment reported in the literature aiming at improving the adsorption efficiency. For example, it has been claimed that the best adsorption results can be achieved by carrying out a sorbent pre-treatment named “chemical activation”. This pre-treatment consists of immersing the pine bark into diluted acid media at slightly high temperatures such as 50–70 °C (Al-Asheh et al. 2000; Teles de Vasconcelos 1997) before performing the adsorption tests. The adsorption pH range at which the effect of pine bark chemical activation is the highest is narrow and it significantly depends on the nature of the heavy metal to be adsorbed and pulp density to be used (Celik and Demirbas 2005). Another low-cost pre-treatment postulated consists of just washing the pine bark with water which may favour the removal of tannins and other soluble species which, if not removed, could irreversibly pollute the streams.

The aim of this research work is to assess the effectiveness of bark chemical activation on the adsorption kinetics of heavy metals onto pine bark. Adsorption results will be correlated with common models and a newly built diffusion–reaction mixed model. In addition, possible

Table 1 Adsorption isotherms of Langmuir and Freundlich and their linearised forms (Jang et al. 2005; Argun and Dursun 2008)

Isotherm type	Original form	Linearised form
Langmuir	$q_{e,L} = \frac{S_m K_L C_e}{1 + K_L C_e}$	$\frac{1}{q_{e,L}} = \frac{1}{K_L S_m C_e} + \frac{1}{S_m}$
Freundlich	$q_{e,F} = K_F C_e^{1/n}$	$\ln q_{e,F} = \ln K_F + \frac{1}{n} \ln C_e$

consequences regarding the overall process of wastewater treatment will be analysed.

Materials and methods

Materials

Pinus radiata D. Don (*Pinus sylvestris*) was used as sorbent to carry out the batch tests. Synthetic solutions of 100 mg Cu(II)/L were prepared using cupric sulphate pentahydrate (p.a.). The pH of the pulp was kept constant using 0.5 M NaOH solution. All reagents used were high purity.

Methods

Pine bark size reduction

Pine bark was originally obtained in the form of irregular pieces peeled off during the wood processing. The material was ground using a laboratory mortar and wet sieved to standardise the material used in adsorption experiments. Dry sieving was difficult to implement due to the low specific gravity of the material and, therefore, wet sieving was implemented. All the material passed the 16# Tyler. The particle size distribution was found close to a unimodal distribution with a P_{80} around 0.65 mm.

Batch adsorption isotherm experiments

Preliminary adsorption experiments revealed that the best pH conditions for copper(II) ions adsorption is close to pH 5 which is in agreement with previous research studies (Gaballah and Kilbertus, 1998). The adsorption isotherm was obtained after 48 h adsorption, at 10 g/L pulp density and 20 °C, departing from different concentrations of copper(II) ions. In this article, the isotherm with the washed material is presented. The isotherm of the activated pine bark has been already published elsewhere (Gaballah et al. 1997).

Batch adsorption kinetics

Batch adsorption experiments were carried out to determine the adsorption kinetics of copper(II). Two experimental conditions were assessed: (1) washed bark and (2) chemically activated bark with 1 M solution of sulphuric acid at 50 °C keeping a solid/liquid ratio equal to 1:10. Batch experiments consisted of a conditioning stage of 2 h followed by the adsorption tests. In the case of acid pre-treatment, once the activation was finished, the bark was thoroughly washed with double-distilled water until reaching neutral pH.

Adsorption tests were performed at 20 °C (± 2 °C) for different 1, 3, 5, 10 and 20 g/L pulp density. The pH of the

pulp was 5 and it was kept constant by adding drops of 0.5 M NaOH solution. During adsorption tests the liquid was sampled after several times and subsequently analysed to determine the amount of metal remaining the aqueous solution. Atomic absorption spectrophotometry (AAS) using the equipment Perkin Elmer Model 2380 allowed determining the metal concentration in solution. The amount of metal adsorbed was calculated by difference between the copper initial concentration and its concentration in the samples obtained at different adsorption reaction times. The wavelength and slit used to perform the measurements were 324.7 nm and 0.5 cm, respectively. All experiments were performed in duplicate and the averages are reported. The results statistics exhibited variation of less than 5 % between repeats.

Results and discussion

Adsorption isotherm

Figure 1 presents the equilibrium concentration in solution and the specific adsorption of copper(II) ions using washed pine bark.

Two adsorption models were used to describe the data: Langmuir and Freundlich isotherms. Table 2 shows the parameters directly derived from applying the adsorption models, Fig. 2a (Langmuir) and b (Freundlich) as presented in Table 1.

From applying the Langmuir isotherm model it can be concluded that the binding energy is low. Thus, the physisorption is in agreement with other research works claiming that would be the governing mechanisms of the adsorption process. The complete surface coverage is still too high to be achieved under the experimental conditions tested in this work. From the application of the Freundlich isotherm model, the sorption capacity parameter reveals a

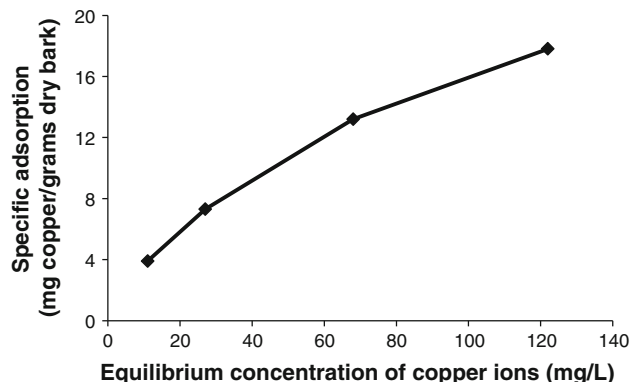


Fig. 1 Adsorption isotherm of copper(II) ions onto washed pine bark at pH 5, 10 g/L pulp density

Table 2 Adsorption parameters of the two adsorption isotherms: Langmuir and Freundlich

Adsorption model	Adsorption parameters
Langmuir	$K_L = 1.08$, $S_m = 38.46$
Freundlich	$K_F = 19.22$, $n = 1.57$

low value compared to the moles of copper(II) adsorbed, which indicates a more realistic behaviour of this model. The sorption intensity, though, is low and it follows the same trend found using the Langmuir model.

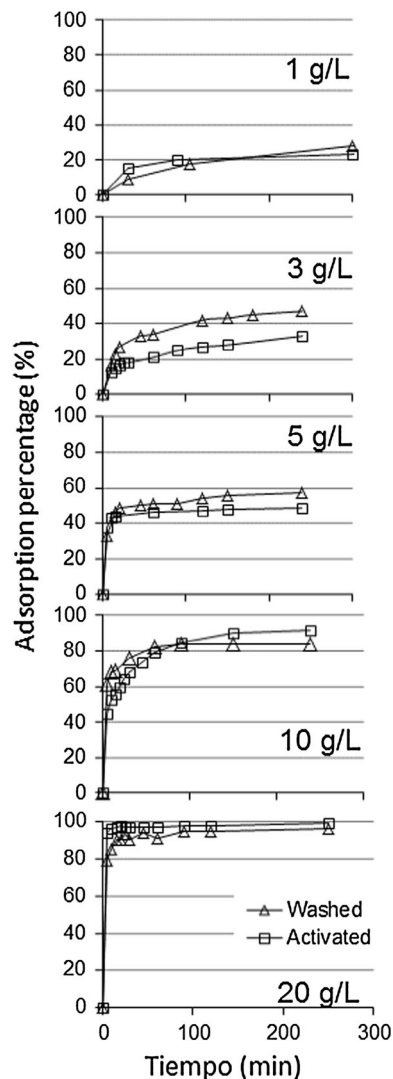
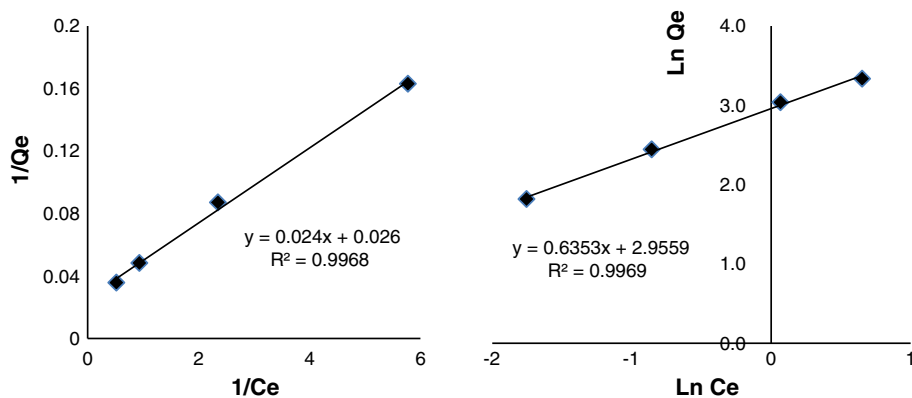
Adsorption kinetics

Figure 3 shows the adsorption percentage and the specific adsorption results obtained at different pulp densities with washed and activated pine bark.

As expected, the higher the number of sorbent surface sites available for adsorption (i.e. higher pulp densities), the higher the amount of metal removed from solution. The adsorption kinetic curves exhibit a classic increase of the adsorption percentage with time. The trends were found to be statistically relevant as the experimental points did not vary during repeats above 5 % (95 % confidence). Depending on the pulp density, the concentration of the heavy metal in solution and the contact time of the solution with the bark, the adsorption percentage may reach a plateau or maximum value. Such maximum value is usually referred to as “saturation” which might be misleading. Figure 4 presents the specific adsorption or adsorption capacity as function of time for the same experiments. It can be observed that the higher the pulp density, the lower the specific adsorption. At constant initial metal concentration, the increase of pulp density favour the adsorption process on bark surface sites that are easier to reach and to be replaced by a metal ion (high energy surface sites). In other words, the material is not being used at its maximum capacity.

Moving from the high-to-low pulp density values, the specific adsorption increases. This indicates that higher

concentrations of copper(II) ions activate sites. This is expected, given that the increase of copper(II) ions will shift the adsorption equilibrium constants of secondary

**Fig. 3** Kinetics of adsorption percentage (%) of copper(II) ions onto washed and activated bark**Fig. 2** Graphic correlations used to determine the adsorption parameters of Langmuir and Freundlich models

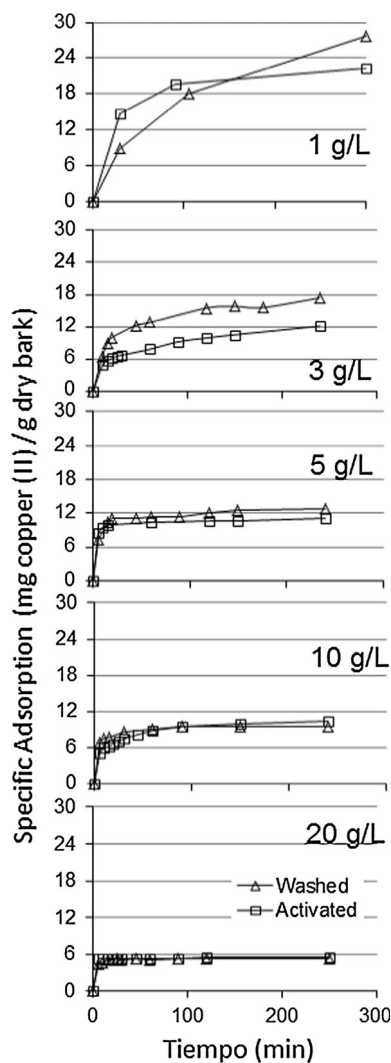


Fig. 4 Kinetics of specific adsorption (mg copper(II) ions/g dry bark) using washed and activated bark

reactions towards increasing the metal concentration in its adsorbed state. Indeed, the ion exchange mechanism (the main responsible for metal adsorption) occurs throughout many organic radicals with different acidity constants.

Figure 5 presents only some of the radicals and the equilibrium constants for hydronium ions ionisation. The structures that are easily ionised occur seldom in bark structure compared to the structures where ionisation is almost negligible. However, they can be activated if the concentration of the metallic ion in solution is high enough, which ultimately increases the specific adsorption.

Adsorption kinetics modelling

In the following section a classic analysis of the metal adsorption kinetics is performed. Pseudo order 1 (Eq. 2) and 2 (Eq. 3) kinetics will be separately applied. The ground pine bark expands when immersed into aqueous solution

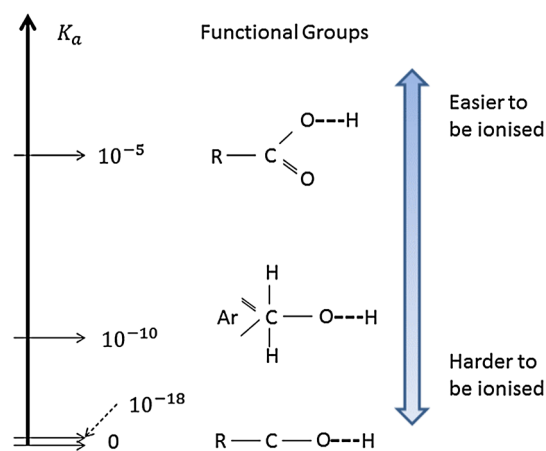


Fig. 5 Schematics of the organic groups, its relative proportion in the structure of bark, and radicals through which the ionisation could lead to heavy metals adsorption onto bark. K_a represents the acidity constant, C carbon, O oxygen, Ar aromatic structure (from Habibi-Yangjeh et al. 2005; Brown et al. 2009)

capturing water molecules within its fiber structures. This is expected to behave as an extra resistance to reach internal adsorption sites. That is the reason why the intraparticle diffusion model (Eq. 4) will also be applied.

The worst results, with the exemption of pulp densities of 1 and 3 g/L, were obtained for pure intraparticle diffusion mechanisms. Pseudo order 1 and 2 models exhibit a mostly equally good Pearson coefficient so any of them could be considered as a suitable model describing the adsorption kinetics. Nevertheless, it is possible to estimate the contribution of ion exchange and diffusion mechanisms to the overall adsorption process by defining a weigh factor, α , widely used in other fields of knowledge (Kelsall 1961) (Eq. 5).

$$q_t = q_R + q_D = \alpha q_e (1 - e^{-k_R t}) + (1 - \alpha)(k_D \sqrt{t} + T) \quad (5)$$

Table 3 shows the summary of the specific rate constants and coefficients. The minimisation protocol considered the following assumptions:

1. The adsorption specific rate constant does not depend on the concentration of copper(II) ions in solution nor on the amount of pine bark used in the experiments. Therefore, it will be considered as a constant for all experiments.
2. The diffusion constant will be considered as a constant, since it refers to copper(II) ions in solution and their approach to active sites.
3. All other parameters will vary with the experimental conditions. The restrictions for the other variables are: (1) $0 \leq \alpha \leq 1$, (2) $q_{max,exp} \leq q_e \leq 1.575$.

T was left unrestricted as in the research conducted by Sahu et al. (2008).

Table 3 Parameters of the reaction–diffusion mixed kinetic model (Eq. 5)

Pulp density (g/L)	Washed			Activated		
	Parameter	Value	R^2	Parameter	Value	R^2
1	q_e	0.46	0.761	q_e	0.39	0.984
	T	0.38		T	0.64	
	α	1.00		α	1.00	
3	q_e	0.74	0.985	q_e	0.52	0.951
	T	-0.03		T	-0.97	
	α	0.34		α	0.78	
5	q_e	0.97	0.995	q_e	0.77	0.999
	T	-0.03		T	-0.58	
	α	0.69				
10	q_e	1.58	0.994	q_e	1.58	0.984
	T	0.04		T	0.04	
	α	0.69		α	0.45	
20	q_e	1.58	0.997	q_e	1.56	0.998
	T	0.14		T	1.23	
	α	0.89		α	1.00	

The mixed model provided a good description of the data with exception of 1 g/L washed pine bark probably due to the significant scattering of the data. In general, the adsorption equilibrium parameter reaches higher values in the case of washed bark for pulp densities below 10 g/L. Passing from washed to activated pine bark, the reaction and diffusion specific rate constant increased from 0.35 and 0.5 to 0.48 and 0.1, respectively. The latter means that the bark activation increases the rate at which the adsorption occurs but it limits the use of the bark in the process. Probably, this effect is a result of the reduction of active sites due to the de-polymerisation of poly phenolic structures present in the pine bark (Gaballah and Kilbertus 1998; Selga and Torres 2005). Furthermore, it is important to highlight that the model was developed to copper(II) and, more generically, to a divalent metal with low binding energy when adsorbed to a pine bark as a substrate. Preliminary studies with other divalent metals such as Zn(II) exhibited similar results to those observed for Cu(II) which may be explained in terms of the similar affinity both metals have with respect to this type of natural substrates (Oh and Tshabalala 2007); nevertheless, further research is required to be performed to understand how metals interactions may change the single metal adsorption behaviour.

Conclusions

A thermodynamic analysis indicated that the adsorption of copper(II) ions is a low energy binding process. This suggests that diffusive mechanisms could be of significance.

Considering that the adsorption mechanisms are usually modelled as pseudo-first- or pseudo-second-order kinetics, a mixed reaction–diffusion model was suggested.

The activation of pine bark material increases the rate at which copper(II) ions are adsorbed and it simultaneously reduces the maximum achievable adsorption equilibrium. This limits its usefulness to relatively high pulp densities (above 10 g/L). The depolymerisation mechanisms suggested by other authors will only be significant above a certain specific pulp density (10 g/L for copper(II) ions). The increase of specific adsorption with the adsorbate concentration in solution is expected to lead to better use of the biosorbent in the process.

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