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Equilibrium Studies of Mn(II), Pb(II) and Cr(III) in Bone Char

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The present work aimed to investigate the removal process of Mn (II), Pb(II) and Cr (III). Equilibrium isotherms were obtained at 25, 30 and 40 ^oC considering solutions with a pH range between 5 and 6. Langmuir and Freundlich models were tested. Langmuir model seems to best fit the lead and chromium isotherms while Freundlich were best fit to manganese isotherms. The thermodynamic parameters were also estimated. The selectivity sequence s $Pb^{2+} \approx Cr^{3+} > Mn^{2+}$ at 25 ^oC, $Pb^{2+} > Cr^{3+} > Mn^{2+}$ at 30 and 40 ^oC were obtained. Chromium sorption seems to be exothermic while manganese and lead isotherms provided an endothermic process.

1. Introduction

Metal ions such as manganese, chromium and lead in wastewaters represent a significant environmental and health problem. There has been investigated many different technologies to treat wastewaters contaminated with such heavy metals. Adsorption is one of the most promising ones when these heavy metals are found in diluted concentrations.

Bone char is mainly produced by the carbonization of bones. Structurally, the calcium phosphate in bone char is in the hydroxyapatite form (Hassan et al., 2008; Choy et al., 2004). Recently results for removal of metal ions from wastewaters have also been reported (Chen et al., 2008; Keith et al., 2005) although investigation of the removal mechanism has been scarcely published (Hassan et al., 2008). In fact, chemisorption and even ion exchange seems to be the main operating mechanism for cation removal from aqueous solution (Bennet and Abram, 1967). The hydroxyapatite may be responsible for such behavior, which is comparable to the ion exchange sites of the zeolitic framework (Choy and McKay, 2005). Then, after the ion exchange monolayer, the adsorption process may be relevant due to the attraction of anions and other cations (Shibata and Seff, 1997). Therefore, the physisorption process should not be totally neglected. Moreover, solution pH as well as temperature plays an important role in such process (Chen et al., 2008; Schneider et al., 2007) due to the adsorption itself, ion speciation and cation dehydration process related to increasing temperatures.

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In order to design commercial adsorption systems it is necessary to develop design models, which must define the solid– liquid equilibrium relationships. In terms of the capacity of an adsorbent, the equilibrium data are usually expressed in the form of an isotherm equation. Therefore, the main objective of the present work is to construct equilibrium isotherms at three different temperatures, 25, 30 and 40 °C for the Mn(II), Pb(II) and Cr(III). The experimental data can be used to provide the thermodynamic parameters enthalpy of adsorption (ΔH^o), free energy of adsorption (ΔG^o) and entropy (ΔS^o) allowing the determination of cation selectivity and the estimation of the maximum amount of cation in bone char samples.

2. Experimental

The reagent-grades $CrCl_3.6H_2O$, $PbCl_2$, $MnCl_2.4H2O$ and $MnSO_4.H_2O$ were mixed with distilled water to prepare 18 mg/L solutions for single metal removal with pH 5-6. pH adjustment was fulfilled by adding 0.1 mol/L HCl or 0.1mol/L NaOH into the solutions always when necessary. The bovine bone char with average particle size less than 200 mesh. The adsorbent was characterized through N_2 adsorption, Infrared spectrophotometry (FTIR) and Scanning electron microscopy (SEM). Zero point charge (ZPC) was obtained based on Park and Regalbuto (1995).

A series of batch experiments 25, 30 or 40 °C were conducted to study the adsorption isotherms. Procedure was described in Barros et al., 2009. After six hours of contact time the flasks were removed from the constant temperature bath the liquid phase rapidly separation through a filtration process. The cation concentration in the beginning solutions or after equilibrium time was determined through a Varian 50B atomic absorption spectrophotometer. Then the cation retained (q_e) was plotted against the concentration in the fluid phase (C_e).

The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogenous adsorbent surface. The Langmuir parameters were q_{max} is related to the monolayer capacity (meq/g) and b is related to the energy of adsorption (L/meq). The Freundlich expression is an exponential equation and therefore assumes that as the adsorbate concentration increases so too does the concentration of adsorbate on the adsorbent surface. The Freundlich parameters are K_F and n.

The thermodynamic parameters such as standard Gibb´s free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) were estimated to evaluate the feasibility and nature of the adsorption process as described in Schneider et al. (2007).

3. Results and Discussion

Analysis of adsorption/desorption of N_2 showed that bone char powder sample was predominantly mesoporous with BET area of 100 m^2/g, which is a typical value for this kind of solid material (Hassan et al., 2008). Due to such feature and considering the size of the cations here investigated, it may be supposed that the diffusional resistance may be neglected. SEM results reveal heterogeneity morphology of particles and channels as it can be seen in Figure 1. ZPC occurs at pH 7.9, a value higher than those of the single cationic solutions (pH = 5-6). It is believed that removal process may not occur predominantly though attraction of the opposite charges as the adsorbent surface is positively charged. Therefore, it may be supposed that ion exchange process plays an important role in the cation removal. In fact, the hydroxyapatite compound (CaHOAP), which is the main component of bone char, was reported to adsorb metal ions by adsorption and ion exchange (Hassan et al., 2008). The FTIR spectrum of adsorbent presented in Figure 2 shows a characteristic band at 1380 cm^{-1} attributed to $^{v}NO_3$ group beside bands at 3450 cm^{-1}, 603 cm^{-1} due to –OH group vibration, band at 1640 cm^{-1} due to $CO_3^{\ 2-}$ and a band at 1038 cm^{-1} attributed to the molecular vibration of PO_4^{3-}, similar to the FTIR of camel bone charcoal (Hassan et al., 2008). Such superficial groups may be responsible for chemisorption process as well. Besides the superficial groups that may be related to the chemisorption process, the carbon structure (C) in the bone char act as "physical" sorption sites for the metal ions.

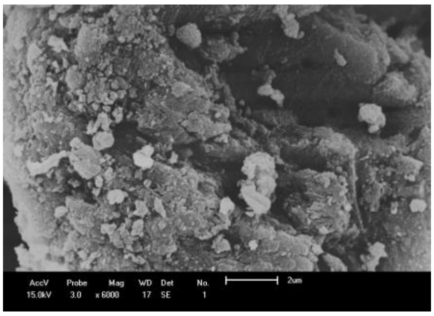

Figure 1: Micrograph obtained by SEM fro bovine bone char

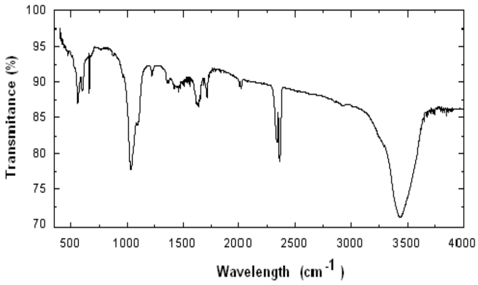

Figure 2: FTIR Spectrum of the bone char sample

The isotherm results provided by the equilibrium data as well as the isotherm model that best fit are depicted in Figure 3. The model adjustments will be discussed later in Table 1. Figure 3a shows the lead isotherms. It can be observed a pronounced plateau, characteristic of very favorable isotherms originated from a monolayer of Pb^{2+} ions mainly at 30 and 40 °C. It may be supposed that at higher temperatures the isotherm will form an irreversible shape characterized by a horizontal line since the beginning. At 25 °C Pb^{2+} ions are not as much more evidenced than $Pb(OH)^+$, $Pb_2(OH)^{3+}$, $Pb_3(OH)_4^{2+}$ and $Pb_4(OH)_4^{4+}$. Then, the ion exchange process with H^+ presented in the CaHOAP will depend on the charge of the lead species. On the other hand, as temperature increases, there should be a dehydration process and some of these species may be replaced by the Pb^{2+} ion itself. This increases the possibility of a monolayer formation in the ion exchange process evidenced through the pronounced plateau. The manganese isotherms shown in Figure 3b are quite different from the previous ones and they may be classified as *Lmx* according to Giles et al. (1960). The first part of the isotherm has a smooth favorable curvature that may be related to the partial hydrolysis of Mn^{2+} ions resulting in the formation of $MnOH^+$ and some $Mn(OH)_2$ besides Mn_2OH^{3+}, $Mn_2(OH)_3^{\ +}$, $Mn_2(OH)_4^{2-}$ at pH = 5 – 6. It is also observed a fall in slope that occurs after the first inflection. This is probably due to association of the metal ions in solution, ie., with increase in concentration the Mn^{2+} -Mn^{2+} attraction begins to increase more rapidly than the adsorbent – Mn^{2+} attraction. The maximum is more pronounced at 40 °C ($q_e \approx 0.6$

meq/g). Then, all three isotherms go to a minimum ($q_e \approx 0.4$ meq/g) and the curves thereafter rise again, finishing part one. A typical multilayer adsorption commonly observed at high solution concentration is observed in part two. Therefore, concerning manganese removal, it can be concluded that both phenomena (ion exchange and adsorption) may not be neglected. The ion exchange mechanism followed by an adsorption process has already been reported for other ion exchangers such as zeolites (Barros et al., 2009).

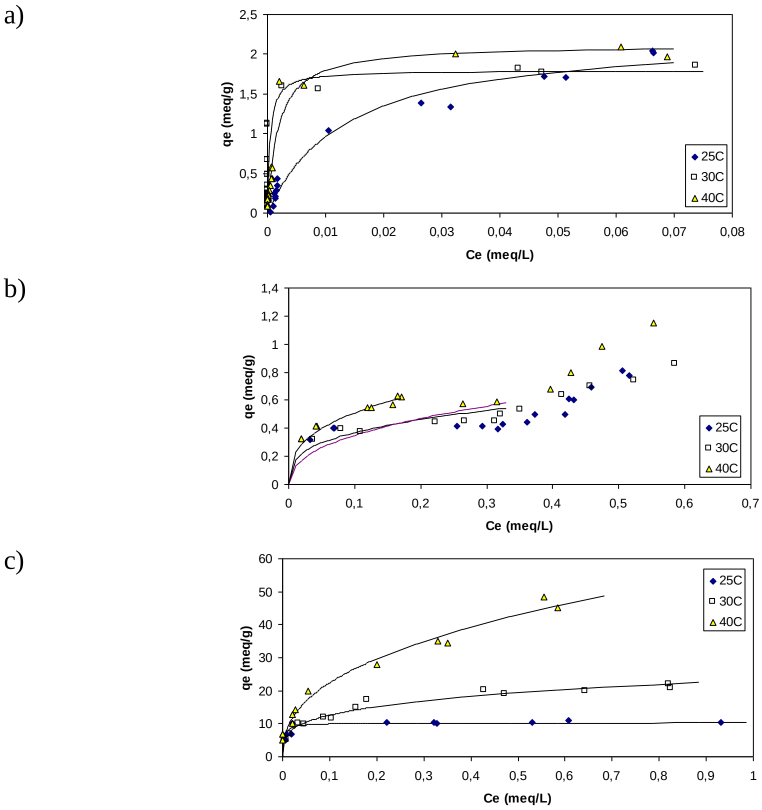

Figure 3: Isotherms at different temperature: a) Pb^{2+} ions, b) Mn^{2+} ions, c) Cr^{3+} ions

At first it is weird to have some huge differences in shape when Pb^{2+} and Mn^{2+} isotherms are compared. Pb^{2+} isotherms are more sensitive to changes in temperature and may reach a maximum amount of ions retained close to 2 meq/g, much more than 0.6 meq/g reached by manganese isotherms. As Mn^{2+} ion is less electronegative (1.5 eV) than Pb^{2+} (1.8 eV), there is a less attraction to the ion exchange sites. These may explain, besides the speciation, the different removal mechanisms followed by the divalent cations. The chromium isotherms presented in Figure 3 show a pronounced plateau, almost an irreversible shape at 25 ^{o}C (q_{max} = 10 meq/g). This is by far, the highest retention from the ions here considered. This is due to the significant electro negativity (1.6 eV) besides the trivalent charge, which means more attraction to CaHOAP. At pH solution between 5 – 6 there is Cr^{3+} and $Cr(OH)_2^{+}$ and a significant amount of $CrOH_2^+$. Therefore, as temperature increases, besides the ion exchange monolayer, there is a multiplayer formation probably due to this speciation, which facilitates the accommodation of the in-going cations up to the solid phase. In Figure 3 there are also presented some models that were chosen according to the higher R^2 shown in Table 1. For Pb^{2+} it was applied the Langmuir isotherm as it best fits the experimental data. For Mn^{2+} isotherms, Freundlich model was also used but only in part one. Finally, chromium isotherm was fit to Langmuir at 25 °C and Freundlich at 30 and 40 °C.

Table 1: Isotherm parameters

Ion	T(°C)	**Langmuir**			**Freundlich**		
		q_{max}	b	R^2	K	1/n	R^2
Pb^{2+}	25	2.25 ± 0.13	75.2 ± 15.2	0.98	7.97±0.80	0.500±0.030	0.98
	30	1.80± 0.23	2331±2905	0.52	3.38±0.66	0.196±0.048	0.87
	40	2.12 ± 0.10	557 ± 89.4	0.95	5.00±0.81	0.297±0.037	0.84
Mn^{2+}	25	0.63±0.070	20.3 ± 13.1	0.35	0.77±0.09	0.324±0.103	0.50
	30	0.91 ±0.17	5.57 ±2.95	0.63	0.93±0.09	0.435±0.079	0.80
	40	0.92 ±0.10	15.0±6.34	0.65	1.14±0.096	0.350±0.054	0.80
Cr^{3+}	25	10.3±0.5	294±104	0.87	11.3±0.6	0.104±0.020	0.79
	30	21.5±1.0	20.3±4.3	0.94	23.3±0.7	0.267±0.02	0.97
	40	48.0 ±4.6	12.0 ±4.3	0.92	56.8±2.4	0.404±0.03	0.98

The thermodynamic parameters can be seen in Table 2. Due to the negative value of the free energy, it is possible to assure that all sorption processes are favorable. Moreover, an increase in temperature makes the process more favorable for the divalent ions, a consequence of the endothermic change. From a consideration of ΔG^0 values the selectivity sequence should be written as: Pb2+ ≈ Cr3+ > Mn2+ at 25 °C, Pb2+ > Cr3+ > Mn^{2+} at 30 and 40 °C. It is important to observe a high change in entropy for the Pb2+. It may be a consequence of the high degree of disorder in the system. As there is some relevant Mn^{2+} association in solution, $\Delta S^{0,}$ in this case, is lower. When chromium ions are considered, it is noted an exothermic process accompanied by a decrease in the entropy changes. Negative entropy changes of ion exchange processes are possible to occur and were already evidenced for chromium removal (Barros et al., 2004).

4. Conclusion

It was concluded that removal of such ions may efficiently occur in bone char systems. Moreover, an increase in temperature favors the removal process, which is an indication that the ion exchange phenomenon has a relevant importance. Cations with higher charge are preferred attracted to the sorption sites. Moreover, when cations with the same charge are considered, electronegativity seems to play an important role in the sorption process. Therefore, more electronegative ions are more attracted to the sorption sites. Lead and manganese sorptions are endothermic process while chromium sorption may occur exothermically. In all cases it was observed a favorable process with the selectivity sequence $Pb^{2+} \approx Cr^{3+} > Mn^{2+}$ at 25 °C, $Pb^{2+} > Cr^{3+} > Mn^{2+}$ at 30 and 40 °C.

Table 2: Thermodynamic parameters

Ion	T(°C)	ΔG^o (kJ/mol)	ΔH^o (MJ/mol)	ΔS^o (J/molK)
Pb^{2+}	25	-11.2	67.10	800
	30	-19.9		
	40	-24.0		
Mn^{2+}	25	-2.81	15.4	182
	30	-2.89		
	40	-5.40		
Cr^{3+}	25	-10.3	-11.5	-95.4
	30	-9.44		
	40	-8.81		

Removal of chromium ions may also stabilize the fluid phase providing a decrease in entropy change.

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