The removal and kinetic study of Mn, Fe, Ni and Cu ions from wastewater onto activated carbon from coconut shells

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Abstract Activated carbon from coconut shells (ACCS) was synthesised and used for the removal of metal ions (manganese, iron, nickel and copper) from aqueous solutions. Two different adsorption models were used for analysing the data. Adsorption capacities were determined: copper ions exhibited the greatest adsorption on activated carbon obtained from coconut shells because of their size and pH conditions. Adsorption capacity varied as a function of the pH. Adsorption isotherms from aqueous solutions of heavy metals on ACCS were determined and were found to be consistent with Langmuir's adsorption model. Adsorbent quantity and immersion enthalpy were studied. The results were compared with other adsorbents used in a prior study.

Keywords Activated carbon · Immersion enthalpy ·
Adsorption · Heavy metals · Coconut shell

1 Introduction

At present, adsorption is widely accepted in environmental treatment applications throughout the world. Liquid–solid adsorption systems are based on the ability of certain solids to preferentially concentrate specific substances from solutions onto their surfaces. This principle can be used for the removal of pollutants, such as metal ions and organic compounds, from wastewater (Netzer and Hughes 1984; Ngah et al. 2002; Wang and Xing 2002; Keith and Gordon 2005). Extensive research has been carried out during the last ten years to find low-cost, high capacity adsorbents for the removal of metal ions. A wide range of adsorbents have been developed and tested, including several activated carbons (Cheung and Venkitachalam 2000; Rao et al. 2002; Yildiz 2004; Gray and Schwab 1993). In addition a number of low-cost agricultural wastes, such as mud, tyre rubber and fly ash, have been used for the removal of a range of metal ions. Other minerals and materials with a potential for exchange adsorption with cadmium, copper and zinc have been tested, amongst which are sodium calcium bentonite and bone char (Keith and McKay 2008; Purevsuren et al. 2004; Wilson et al. 2003; Jiang 2001; Wu et al. 2005; Nasiruddin et al. 2007; Liu et al. 2007; Pattanayak et al. 2000; Moreno-Piraján and Giraldo 2010a, 2010b, 2003, 2008; Moreno-Piraján et al. 2010a, 2010b; Li et al. 2007). Several natural resources have also been studied including tree fern, peat coal and chitosan.

The pollution of water resources due to the indiscriminate disposal of heavy metals has been causing worldwide concern over the last few decades. It is well known that some metals can have toxic or harmful effects on many forms of life. Metals, which are highly toxic to human beings and ecological environments include chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), manganese (Mn), cadmium (Cd), nickel (Ni), zinc (Zn) and iron (Fe). This problem has received a considerable amount of attention in recent years. One primary concern is that marine animals, which can readily absorb those heavy metals in wastewater and directly enter the human food chain, present a high health risk to consumers. Wastewater from many industries, such as metallurgical, tannery, chemical manufacturing, mining and battery-manufacturing industries contains one or more

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of these toxic heavy metals. Industries carrying out operations like electroplating, metal/surface finishing and solid-state wafer processing, generate wastewater contaminated with hazardous heavy metals. The concentrations of some of the toxic metals like Cr, Hg, Pb and arsenic (As) are higher than permissible discharge levels in these effluents. It, therefore, becomes necessary to remove these heavy metals from these wastewaters by appropriate treatment before releasing them into the environment.

In the present work, the adsorption of manganese (Mn), iron (Fe), nickel (Ni) and copper (Cu) ions from aqueous solutions onto activated carbon obtained from coconut shells in agitated batch absorber vessels was studied (Moreno-Piraján and Giraldo 2010a, 2010b, 2003, 2008; Moreno-Piraján et al. 2010a, 2010b; Li et al. 2007; Garg 2007; Kavitha 2007; Ofomaja and Ho 2007; Chojnacka et al. 2006; Chen et al. 2006; Giraldo and Cubillos 2005; Gregg and Sing 1982). The main goal of this study was to examine the ability of this material to adsorb ions from an aqueous solution and compare it with other results already published by us for the same ions using a different adsorbent (Moreno-Piraján and Giraldo 2010a, 2010b, 2003, 2008; Moreno-Piraján et al. 2010a, 2010b; Li et al. 2007), and therefore evaluate its potential for use in wastewater treatment systems.

2 Experimental section

2.1 Adsorbent: activated carbon from coconut shell

The dry coconut shell was initially scraped with a knife to remove all fibres present on the surface and was then crushed using a crushing mill (Retsch, Germany) of type Planetary ball mill PM 100. The resulting recovered product was washed several times with distilled water to eliminate water soluble impurities and then oven dried at 105 °C. 450 g of the small pieces from this material were mixed with 50 mL of concentrated phosphoric acid. The mixture was placed in a vertical local construction furnace in an inert atmosphere at 700 °C for 12 hours. The sample was then removed from the furnace and cooled in a desiccator. After cooling, the sample was rinsed several times with distilled water until the flushing water was obtained within a pH range of 6 and 7. The wet sample was dried at 105 °C for 24 hours, and was then crushed and filtered. Only the particles of sizes ranging from 0.5 to 0.2 mm were recovered. ACCS represents the activated carbon obtained from the coconut shell.

The apparent density of the sample was measured by a mercury intrusion porosimeter (PoreSizer-9320, Micromeritics). Proximate analysis was carried out by a thermogravimetric analyser (TA-50, Shimadzu). The characteristics of the starting material are shown in Table 1.

Table 1 ACCS physical and chemical properties

Property	Value
Ash %	11%
pH_{zpc}	6.4
Acidity (mmol/g)	1.75
Basicity (mmol/g)	0.55
Apparent density (kg/m^3)	0.42
S_{micr} ($m^2 \cdot g^{-1}$)	995
L_0 (nm)	0.85
BET area ($m^2 \cdot g^{-1}$)	1150
V_{meso} ($cm^3 \cdot g^{-1}$)	
V_t ($cm^3 \cdot g^{-1}$)	1.27
V_0 ($cm^3 \cdot g^{-1}$)	1.02

Notes: V_t: total pore volume, V_0: total volume of micropores, L_0: average pore size, S_{mic}: microporous surface area, S_{BET}: apparent BET area, V_{meso}: volume of mesopores, pH_{zpc}: point charge zero.

N_2 adsorption isotherms at 77 K were carried out in a volumetric system (Autosorb-3b, Quantachrome). The BET surface area was calculated from the isotherms by using the Brunauer–Emmett–Teller (BET) equation (Dubinin 1975). The cross-sectional area of the nitrogen molecule was assumed to be 0.162 nm. The Dubinin–Radushkevich (DR) equation was used to calculate the micropore volume, from which the micropore surface area was then determined (Barrett et al. 1951). The pore size distribution was determined using the BJH model (Dubinin 1966). The Dubinin–Radushkevich equation was used to calculate the characteristic energy of adsorption, E_0 (Boehm 1966) and with this the parameter L_0 is calculated. The acidic and basic surface groups were determined according to the method of Boehm (Teixeira et al. 1998). One gram of carbon sample was placed in 50 ml of 0.05 N solutions of either sodium hydroxide or hydrochloric acid. The vials were sealed and shaken for 24 h and then 5 ml of each filtrate was pipetted and the excess of base or acid was titrated with HCl or NaOH, as required. The numbers of acidic sites of various types were calculated under the assumption that NaOH neutralises all acidic groups (carboxylic, phenolic and lactonic groups) and HCl reacts with all basic groups.

2.2 Adsorbates: metal ions

Analytical grade manganese(II) nitrate ($Mn(NO_3)_2$), iron(II) sulphate ($FeSO_4 \cdot 7H_2O$), nickel(II) nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) and copper(II) nitrate ($Cu(NO_3)_2 \cdot 5H_2O$) reagents from J.T. Baker were used in the experiments. Stock solutions of metal ions were prepared using deionised water. Metal ion solution concentrations were determined by atomic absorption spectrometry (AAS).

2.3 Adsorption equilibrium isotherm

Batch adsorption experiments were conducted using 100 mL aliquots of the test solution, which was pH adjusted, and which contained 100 mg·L^{-1} of each of the following ions: Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} in monocomponent systems placed in 250 mL amber closed bottles. A known quantity (0.01–0.15 g) of ACCS was added to each bottle. Solutions were stirred at 200 rpm for periods of between 5 and 110 minutes at 298 ± 1 K. The ACCS was removed by filtration and Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} molar concentrations were measured by atomic absorption spectroscopy (in a Perkin Elmer Analyst equipment) at the end of each period of time. Blank solutions were also prepared and analysed. The solution pH changes as the metal ion concentration changes during the adsorption process. A previous investigation was carried out to determine the solution pH which produces the maximum adsorption. The pH value of each metal ion solution was adjusted using solutions of either 0.01 N NaOH or 0.01 N HNO$_3$ and employed volumes will be registered to calculate the final solution volume. To avoid the oxidation of Fe^{2+} to Fe^{3+} in the aqueous solutions and according to Pourbaix, the electric (electrode) potential was adjusted to between -0.5 and 0.8 volts with a nitrogenous base. Potentials were measured with an Orion 960 Autochemistry System, the recorder output of which was connected to an IBM® personal computer running an acquisition program, via a DGH Corporation 1121 module analogue-to-digital converter (Manchester, UK). An Orion 90-02 double junction silver-silver chloride reference electrode containing a 15% (w/w) solution of KNO$_3$ in the outer compartment and a Fluka ISE 16811 electrode body, were used for of measurements of potentials (Lagergren 1898).

The Fe-selective and reference electrodes were immersed and the potential of each sample iron solution was directly measured. The measured potentials were then registered; the potential of the solution was adjusted by the addition of the nitrogenous base, when it was not within the proper range to avoid oxidation of Fe^{2+} ion. This procedure in this research was conducted sporadically, because the potential was within the range.

2.4 Immersion enthalpy

Immersion enthalpies of ACCS were determined in solutions of Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} with concentrations ranging from 20 to 100 mg·L^{-1} for the maximum adsorption pH of 5.8. Immersion enthalpies were also determined for 100 mg·L^{-1} solutions at all pH values studied. This determination was performed in a heat conduction microcalorimeter with a stainless steel calorimetric cell (Gregg and Sing 1982). 30 mL of the solution to be used was pre-heated to 298 K and then placed in the cell. A sample of approximately 0.5 g of ACCS was weighed and placed inside the calorimetric cell in a glass ampoule. The microcalorimeter was then assembled. When the equipment reached a temperature of 298 K, potential readings were registered after a period of approximately 15 minutes, with readings every 20 seconds. The glass ampoule was broken and the thermal effect generated was registered. Electric potential readings continued for approximately 15 minutes more, and at the end of the experiment the equipment was electrically calibrated.

3 Results and discussion

3.1 Effect of activated carbon dosage on adsorption

Figure 1 shows the removal of Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} as a function of ACCS added to an aqueous solution of pH 5.8. ACCS granular dosage ranged from 0.01 to 0.08 g for the 100 mL of Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} test solutions and were equilibrated for 120 minutes. It can be seen that the maximum removal, expressed as a percentage, was between 88% and 99% from Mn to Cu at dosages between 0.001 g and 0.017 g of ACCS. Ion removal increased quickly at ACG dosages from 0.01 g to 0.02 g and reached a maximum at 0.03 g ACCS. This fact may be associated with the Mn^{2+} ion availability at pH 5.8. From pK_h values, it can be concluded that, at pH 5.1, Mn^{2+} ions have a concentration 1500 times greater than that of Cu^{2+} ions (Moreno-Piraján et al. 2010b; Li et al. 2007; Garg 2007; Kavitha 2007). On the other hand, hydrated Mn^{2+} ions have a volume almost 30% larger than hydrated Cu^{2+} ions. Consequently Mn^{2+} ions are more likely to be in solution than adsorbed. The observed constancy in the percentage of ion removal beyond 0.04 g/100 mL may be indicative of a very weak interaction between the adsorbent and adsorbate. This interaction appears weaker with Mn^{2+} ions than with Cu^{2+} ions. Ion solution concentration seems to attain a steady state with adsorbed species and, so no matter the quantity of adsorbent present, there will be a residual concentration of ions in solution. This fact determines a specific relation between ion concentration and adsorbent quantity.

Adsorption of metal ions on these types of materials is generally attributed to weak interactions between the adsorbents and adsorbates. Surface charges on substrates as well as softness or hardness of the solutes are mostly responsible for the intensity of the interaction. Coulombic interaction can be observed for the ionic interexchange of cationic species with anionic sites in the materials and is determined by their surface areas.

Comparing these results with others obtained from our work, the adsorption of ions is more efficient in this case with lesser amounts of adsorbate. This is directly related to the textural characteristics of the porous solid adsorbent. On the other hand, it is necessary to highlight that the adsorption capacity depends on the concentration of ions.
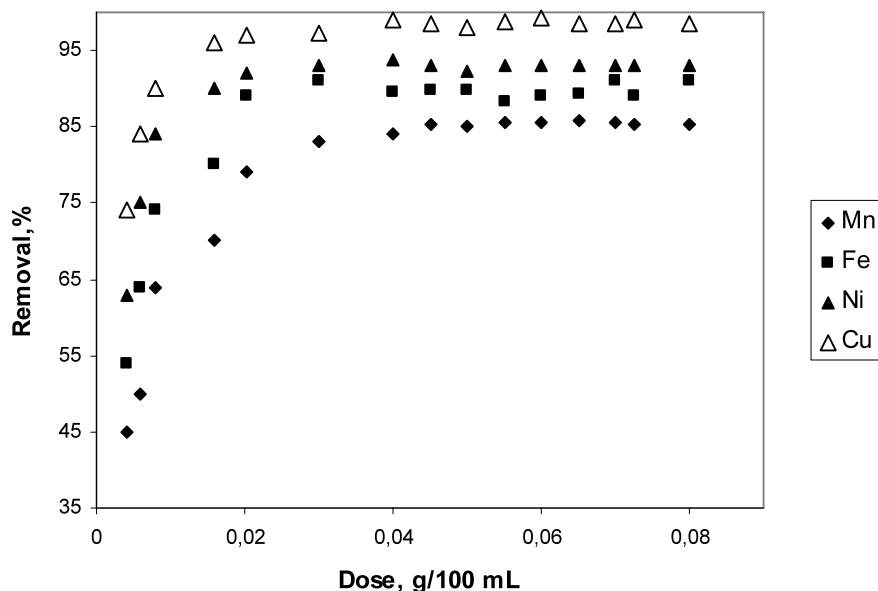
3.2 Effect of contact time

Figure 2 shows the effect of contact time on the ACCS removal of 20 $mg \cdot L^{-1}$ Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+}. Removal increases with time and reaches a maximum after 8 minutes of agitation. Nevertheless, the order of the affinity to the adsorbate is maintained: $Mn^{2+} < Fe^{2+} < Ni^{2+} < Cu^{2+}$. This is associated with the size of the ion and the pore development in activated carbon granular. The time obtained for the adsorption of the studied ions is very low with respect to other published research (Moreno-Piraján and Giraldo 2003; Li et al. 2007).

To analyse the adsorption rates of Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} ions onto the ACCS, two simple kinetic models were tested.

3.2.1 Pseudo-first-order model

The pseudo-first order rate expression, popularly known as the Lagergren equation, is generally described by the following equation (Lagergren 1898; Ho and McKay 1998):

$$\frac{dq}{dt} = k_{ad}(q_e - q) \tag{1}$$

where q_e is the amount of metal ions adsorbed at equilibrium per unit weight of sorbent (mg/g) and q is the amount of metal ions adsorbed at any time (mg/g). Furthermore, k_{ad} is the rate constant (min^{-1}). Integrating and applying boundary conditions, $t = 0$ and $q_t = 0$ to $t = t$ and $q = q_t$, (1) takes the form:

$$\ln(q_e - q_t) = \ln q_e - k_{ad}t \tag{2}$$

However, if the intercept does not equal the natural logarithm of the equilibrium uptake of metal ions, the reaction

is not likely to be of first-order, even if this plot has a high correlation coefficient with the experimental data (Ho and McKay 1998; Horsfall and Spiff 2004; Pearson 1997). Correlation coefficients were found to be between 0.9357 and 0.9858. The correlation coefficients are shown in Table 2 together with the Lagergren rate constants calculated from the slope of (2) (Ho and McKay 1998).

In order to obtain rate constants, straight-line plots of ln $(q_e - q_t)$ against t (time) were made (not shown here). This gave fairly straight lines for all four metal ions on the ACG. The intercept of this plot should give ln q_e.

3.2.2 Pseudo-second-order model

The adsorption data was also analysed in terms of a pseudo-second order mechanism given by (Pearson 1997):

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

where k_2 is the rate constant ($mg \cdot g^{-1} \cdot min^{-1}$). Integrating the above equation and applying boundary conditions, i.e., $t = 0$ for $q = 0$ and $t = t$ for $q = q_t$, gives:

$$\frac{t}{q_t} = \frac{1}{h_0} + \frac{1}{q_e}t \tag{4a}$$

where, h_0 is the initial adsorption rate. If second-order kinetics is applicable, the plot of t/q against t in (4a) should give a linear relationship from which the constants q_e and h_0 can be determined (plot not shown here). The linear model gave a good fit to the experimental data. This means that the adsorption can be described by a pseudo-second order rate equation, hence q_e and h_0 were evaluated and presented in Table 2. R^2 values are approximately the same for all four

Fig. 2 ACCS contact time effect on Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} removal. Conditions: C_0, 20 mg·L^{-1}; ACCS dose, 0.02 g; pH 5.8 and temperature 298 K
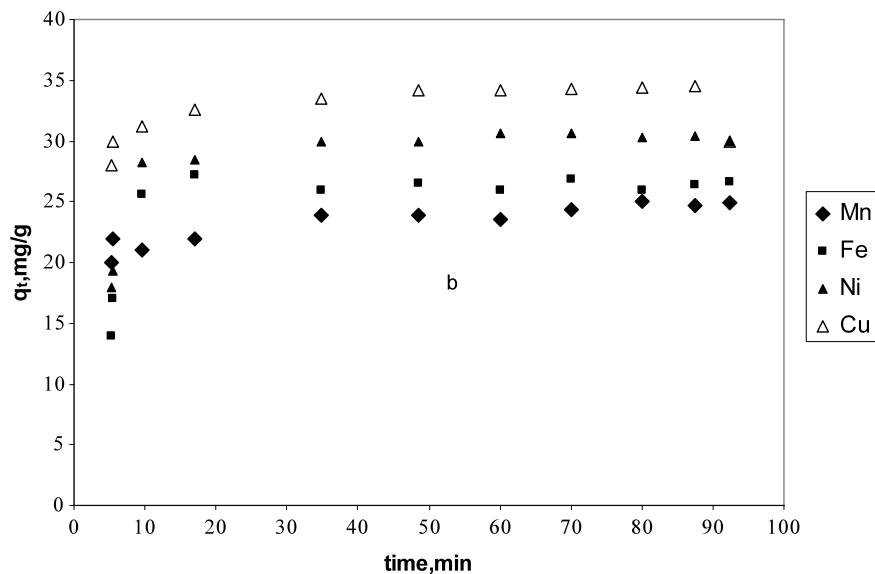

Table 2 Lagergren rate equation constants and pseudo second-order rate equation constants for Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} adsorption on ACG

Metal ions	Lagergren rate equations constants		
	$k_{ad} \times min$	$q_e \times (g \cdot mg^{-1})$	R^2
Mn^{2+}	0.025	7.5	0.9568
Fe^{2+}	0.022	8.5	0.9847
Ni^{2+}	0.019	11.6	0.9858
Cu^{2+}	0.013	13.5	0.9357
	Pseudo second-order rate equation constants		
	$h_o \times (min \cdot g \cdot mg^{-1})$	$q_e \times (g \cdot mg^{-1})$	R^2
Mn^{2+}	825.5	21.6	0.9992
Fe^{2+}	1645.7	27.7	0.9995
Ni^{2+}	1655.5	30.5	0.9999
Cu^{2+}	1744.7	32.1	0.9999

metal ions on ACG with a value of 0.9999. In the limit at initial adsorption time, h_0 is defined as (Ho and McKay 1998; Chong and Volesky 1995):

$$h_0 = k_2 q_e^2 \qquad (4b)$$

k_2 was calculated for the four metal ions and is shown in Table 2. The results obtained are similar to previous studies (Moreno-Piraján and Giraldo 2010a, 2010b, 2003, 2008; Moreno-Piraján et al. 2010a, 2010b; Li et al. 2007; Chong and Volesky 1995).

$$M^{2+} + H_2O \rightarrow MOH^+ + H^+$$

$$MOH^+ + H_2O \rightarrow M(OH)_2 + H^+$$

$$M^{2+} + 2H_2O \rightarrow M(OH)_2 + 2H^+$$
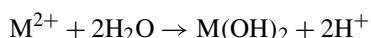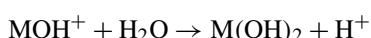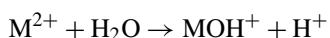
It can be seen that metal ions are easily adsorbed when the hydrated ionic size decreases. Ionic sizes of the heavy metals

used change in the order of $Mn^{2+} > Fe^{2+} > Ni^{2+} > Cu^{2+}$ (Table 3). Since the ACG used is a microporous adsorbent (Chong and Volesky 1995), metals penetrate easily into these pores when the ionic size is small (Langmuir 1918). According to the order above, Mn^{2+} must be the least adsorbed and Cu^{2+} must be the most easily adsorbed. This is compatible with our experimental results. On the other hand, high spin, transition metal complexes exhibit stabilities according to the Irving-Williams series. Studied systems agree with this behaviour, suggesting that a metal complex with the adsorbent may play an important role in adsorption processes.

3.3 Effect of pH

Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} uptake as a function of hydrogen ion concentration was determined for pH values from 2 to 14 (Fig. 3). Below 5.8, hydrogen ions are likely to compete with manganese, iron, nickel and copper ions. At pH

Table 3 Hydrolysis constants and ionic volumes of metals ions

Heavy metals ions	Mn^{2+}	Fe^{2+}	Ni^{2+}	Cu^{2+}
pK_h	10.7	10.1	9.40	7.53
Hydrated volume ($cm^3 \cdot mol^{-1}$)	189.6	174.5	147.8	147.8

values above 8, manganese, iron, nickel and copper might precipitate as hydroxides. pH effects at equilibrium are presented in Fig. 3. Maximum adsorption was observed at about pH 5.8. In general, the results indicated that adsorption is highly pH dependent. Similar results have been reported in the literature. When comparing the results obtained in this study with respect to pH, i.e. q_e quantity falling off after pH $= 5.1$, then the fall is more subdued and again this is related to the volume and pore diameter of the adsorbent.

pH values affect species of heavy metals in aqueous solutions and heavy metal removal increases as the pH value rises, reaching a maximum at around 5.8. The pH of the solution also has effects on the adsorbent and the surface charge of the ACG changes. Calculations from solubility products (K_{sp}) predict that the formation of $Cu(OH)_2$ occurs at a pH value of 6. Precipitation occurs at pH 6, along with a q_e of 26.7 mg·g^{-1}. On the other hand, the q_e has a value of 32 mg·g^{-1} when the initial pH is 5.8 (final pH of 2). This means that the removal of copper ions from the solution also contributes to a modification in pH. However, at low initial pH values, below 4, the influence of adsorption is the only effect responsible for the reduction of copper and nickel ions in the solution. This suggests that the process is a suitable application for heavy metal removal because of its neutral and clean effluent.

3.4 Adsorption isotherms from aqueous solution

When the initial metal concentration rises, adsorption increases while the binding sites are not saturated. The linear Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constants, and is performed by the following equation.

$$\frac{c_{eq}}{q} = \frac{1}{q_{max}b} + \frac{c_{eq}}{q_{max}} \tag{5}$$

Linear plots of c_{eq}/q vs c_{eq} (not shown) were used to calculate the parameters of the Langmuir isotherm, by means of linear regression equations. From these regression equations and the linear plots, the values of the Langmuir constants were calculated and are shown in Table 4. The q_{max} and b were obtained from the slope and intercept of the plots. The essential characteristic of Langmuir isotherms can be expressed in terms of a dimensionless constant separation

factor or equilibrium parameter, R_L, which is defined as (Pearson 1997):

$$R_L = \frac{1}{(1 + bc_0)} \tag{6}$$

where b is the Langmuir constant and c_0 is the initial concentration of the metal ions. The R_L value indicates the shape of the isotherm. R_L values between 0 and 1 indicate favourable adsorption (Langmuir 1918; Ahalya et al. 2005; Mckay et al. 1982; Freundlich 1907; Kardivalu and Namasivayan 2000; Juang et al. 1999). R_L equal to 0 indicates irreversible adsorption, $R_L = 1$ is linear and $R_L > 1$ is unfavourable. From our study, R_L values for Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} ion adsorption ranged from 0.005 to 0.006. This is for an initial metal ion concentration of 600 mg·L^{-1}. Therefore, the adsorption process is favourable.

The Freundlich isotherm was chosen to estimate the adsorption intensity of the adsorbent towards the adsorbate. It is represented by the equation (Kardivalu and Namasivayan 2000).

$$q = K_F c_{eq}^{\frac{1}{n}} \tag{7}$$

Where c_{eq} is the equilibrium concentration (mg·L^{-1}), q is the ion amount adsorbed (mg·g^{-1}) and K_F and n are constants incorporating all parameters affecting the adsorption process such as adsorption capacity and intensity, respectively. A linear form of the Freundlich adsorption isotherm was used to evaluate the adsorption data and is represented as (Ahalya et al. 2005; Juang et al. 1999):

$$\ln q = \ln K_F + \frac{1}{n} \ln c_{eq} \tag{8}$$

The linear regression equation for the Freundlich adsorption isotherm is shown in Table 4. Values of K_F and n were calculated from the intercepts and slopes of the Freundlich plots respectively and are shown in this table. Adsorption is favourable for values $0.1 < 1/n < 1.0$ (Hsisheng and Chien-To 1998). Freundlich's equation frequently gives an adequate description of adsorption data over a restricted range of concentrations, even though it is not based on any theoretical background. Apart from a homogeneous surface, Freundlich's equation is also suitable for a highly heterogeneous surface and an adsorption isotherm lacking a plateau, indicating multi-layer adsorption (Periasamy and Namasivayam 1995). Values of $1/n$ less than unity are an indication that significant adsorption takes place at low concentrations but the increase in the amount adsorbed with concentration becomes less significant at higher concentrations and vice versa (Gabaldon et al. 1996). The magnitude of K_F and n shows that it is possible to perform an easy separation of heavy metal ions from aqueous solutions and achieve a high adsorption capacity. Also, as the K_F value increments so

Fig. 3 pH effect on ACCS adsorption of Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+}. Conditions: C_0, 20 mg/L; ACG dose, 0.02 g; contact time, 20 min and temperature 298 K
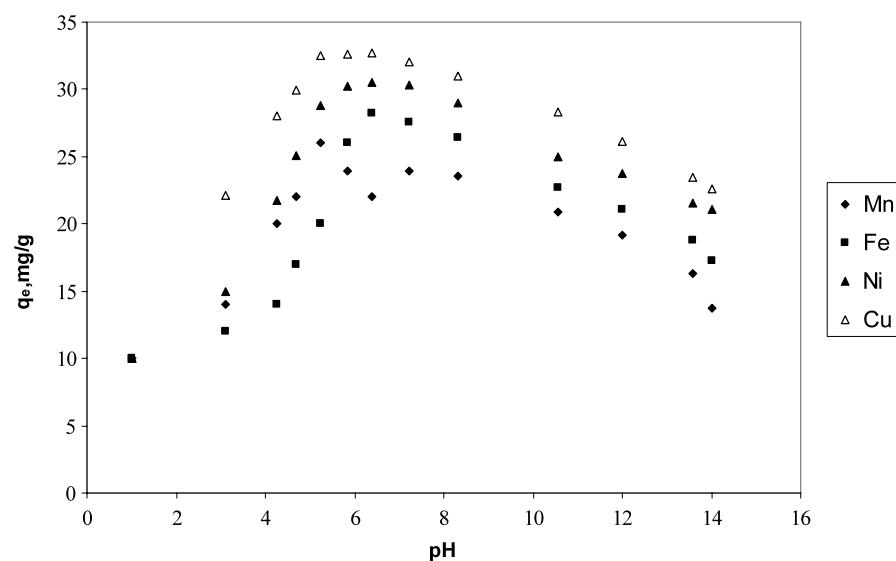
Table 4 Isotherm parameters of Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} adsorption on activated carbon granular from coconut shell (ACCS)

	Linear K_D (L/g)	Freundlich model			Langmuir model			
		K_F	$1/n$	R^2	q_{max} (mg/g)	b (L/g)	R_L	R^2
Mn^{2+}	6.06	1.633	0.365	0.9654	75.65	0.010	0.088	0.9979
Fe^{2+}	6.55	3.484	0.501	0.9674	81.89	0.016	0.065	0.9984
Ni^{2+}	7.43	5.820	0.791	0.9456	83.16	0.005	0.025	0.9976
Cu^{2+}	8.56	10.678	0.787	0.9182	86.01	0.983	0.010	0.9995

does the adsorption intensity. Therefore, K_F values, which are higher for the Cu^{2+} ions, confirm that the adsorption capacity of Cu^{2+} is greater than that of the others ions, according to this model. On the other hand, a relatively high R^2 value indicates that this model is adjusted more confidently. This parameter is shown in Table 4. According to the obtained values, the Langmuir model better fits the experimental data of the present study (Fig. 4).

3.5 Immersion enthalpies

Results show that immersion enthalpies are constant at low initial concentrations. Initial concentrations above 50 mg·L^{-1} exhibited a steady increment up to 80 mg·L^{-1}. The highest value of enthalpy was obtained for the immersion of activated carbon granular in copper ion solution, while the lowest value of immersion enthalpy was obtained for the immersion of activated carbon granular in the solutions of manganese. Enthalpy values were between -110 J·g^{-1} (Cu^{2+}—ACCS) and -70 J·g^{-1} (Mn^{2+}—ACCS), as shown in Fig. 5. This behaviour agrees with the textural characteristics of activated carbon granular and the sizes of the ions under study. It should be noted that the behaviour of immersion enthalpies in the solid prepared in this work are very similar to that of an isotherm.
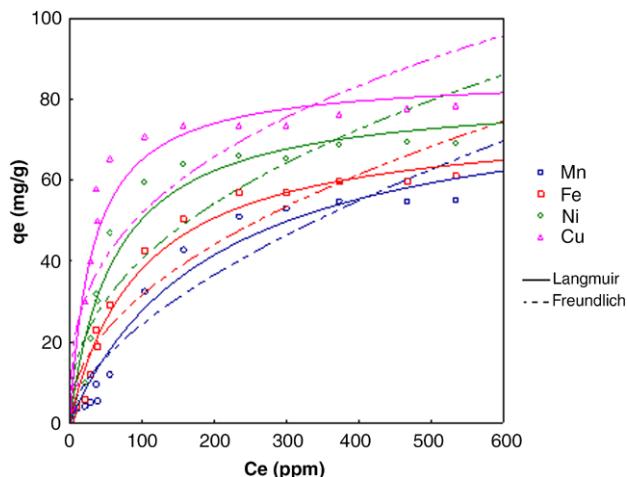
Fig. 4 ACCS adsorption isotherm removal of Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} from aqueous solution. Langmuir and Freundlich models

The enthalpy values obtained in this study are higher than those obtained by our research group using another adsorbent. This is explained by the microporosity of the activated carbon synthesised, which makes immersing the carbon in the different solutions of ions generate a high heat value since the diffusivity in its interaction with the walls is strong for its diameter.
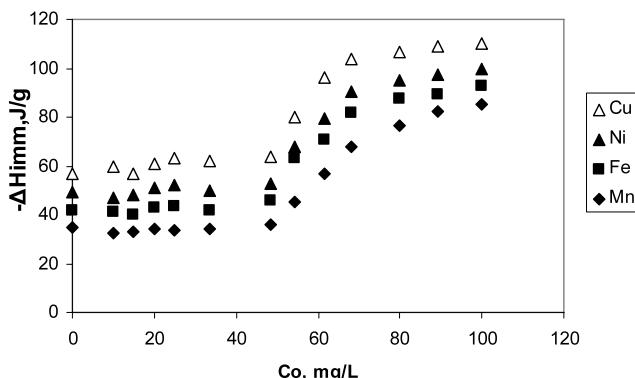
Fig. 5 Immersion enthalpies for Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} aqueous solution ion concentration at pH 5.1. Temperature = 298 K

3.6 Removal of Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} from wastewater

Just as an approximation for an application to a real problem, we tested an industrial wastewater sample. For that purpose, we chose waste from an electrochemical industry for which the content of studied metals was determined. Samples were carefully treated with the aim of performing an analysis of each one of the ions of interest, and we evaluated the adsorption capacity as the sole comparison parameter. They were analysed one by one in order to avoid a multicomponent system generation, which could produce bias in the obtained results.

Wastewater samples collected in our research laboratory from an electrochemical industry were found to contain more than 800 mg·L^{-1} of Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+}, among other organic and inorganic components. Six samples were treated with nitric acid, followed by a pH adjustment and adsorption with ACCS under the optimised conditions described earlier. Metal ions were analysed at each time by atomic absorption spectrometry, using a complexing agent to avoid interference of ions different from those analysed. Assays for manganese, iron, nickel and copper in the final effluents indicated 87.0% maximum removal of the ions originally present in the samples. The minimum removal was 64% for Mn(II). The mean standard deviation was 0.5%. These results show that ACCS is an adequate material to be used in the removal of these ions. However, these findings should be analysed carefully because, in spite of procedures employed to avoid interference in the assays, the sample complexity does not assure confidence in the results. Additionally, this study shows that textural characteristics play an important role for adsorbents, since this carbon has a higher adsorption capacity compared to others we have used.

3.7 Mechanism of adsorption

Figure 3 shows the effect of pH on the removal of Cu(II), Ni(II), Fe(II) and Mn(II) by adsorption onto activated carbon granular. Adsorption increases with an increase of pH from 2 to 5.8. Adsorption of metallic ions is efficient for the concentrations studied below the precipitation pH. One of the conventional methods of removing metals from aqueous solution is the precipitation of metal hydroxides using an alkali. This method has some demerits in that the complete removal of metals is not possible due to the solubility products of metal hydroxide. The ions investigated at this pHs, are removed by both adsorption as well as precipitation. Removal of metals was strongly dependent on the pH of the solution and removal increased from 10 to 34 mg/g at pHs between 1 to 5. The increase in metal ion removal as the pH increases can be explained on the basis of a decrease in competition between protons (H$^+$) and positively charged metal ions at the surface sites and by a decrease in positive charge, which results in a lower repulsion of the adsorbing metals ions. The removal efficiencies of metal ions are affected by the initial metal ion concentration with the removal decreasing as the concentration increases at a constant pH. This can be explained as follows. At low metal/carbon ratios, metal ion adsorption involves the high energy sites. As the metal/carbon ratio increases, the higher energy sites are saturated and adsorption begins on the lower energy sites, resulting in a decrease of adsorption efficiencies. pH curves are shifted to alkaline regions, as has been previously reported by several authors (Hsisheng and Chien-To 1998; Periasamy and Namasivayam 1995; Gabaldon et al. 1996). In the pH range 5–6, maximum removal was observed which might be due to partial hydrolysis that might be due to the formation of the hydroxides studied. Low solubilities of hydrolysis metal ion species may be another reason for maximum adsorption. The above statement agrees with earlier reports (Hsisheng and Chien-To 1998; Periasamy and Namasivayam 1995; Gabaldon et al. 1996).

The mechanism of metal ion adsorption may also be explained based on an ion exchange model. In activated carbon, carbon–oxygen complexes are present. The surface oxygen complexes hydrolysed water molecules as shown below:

$$2COH + M^+ \rightarrow (CO)_2M^+ + 2H^+$$
$$COH_2^{2+}M^+ \rightarrow COM^{2+}M^+ + 2H^+$$
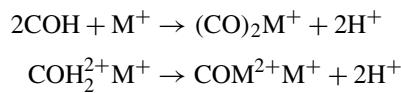
4 Conclusions

From the experiments, it can be concluded that the activated carbon obtained from coconut shells has an excellent ability to retain Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^2 metal ions from aqueous solutions at studied concentrations. Removal of heavy metals (manganese, iron, nickel and copper) from aqueous

solution was possible using an activated carbon from co-conut shells (ACCS). Adsorption was seen to take place in 10 minutes for the concentration levels of the four metals studied. Under our experimental conditions, the pH plays an important role in the adsorption process, particularly on the adsorption capacity. Solution pH has a great influence on the adsorption capacity for the studied heavy metals. The selected pH for an optimal rate of adsorption was 5.8 for all the ions investigated. It was shown that ACG has a relatively high adsorption capacity for these heavy metals. The quantities adsorbed per gram of ACCS at equilibrium (q_e) were 51.23 mg·g^{-1} for Mn^{2+}, 58.76 mg·g^{-1} for Fe^{2+}, 67.56 mg·g^{-1} for Ni^{2+} and 76.66 mg·g^{-1} for Cu^{2+}. This adsorption is described by an isotherm of type I and is fully verified by the Langmuir isotherm. The kinetics of the manganese, iron, nickel and copper adsorption on the ACCS was found to follow a pseudo-second-order rate equation. This method is advantageous as it can be applied to countries where the residue of coconut is a problem.

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