Simultaneous Adsorption of Pb(Ii)-Cd(Ii), Pb(Ii)-Phenol, and Cd(Ii)-Phenol by Activated Carbon Cloth in Aqueous Solution

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Abstract

The aim of the present work was to determine the effect of the simultaneous adsorption of lead(II)-cadmium(II), lead(II)-phenol, and cadmium(II)-phenol by activated carbon cloths (ACCs). Three commercial ACCs were characterized and tested for individual metal adsorption, and competitive adsorption experiments were carried out with the best ACC (AW1104). The specific surface areas of all ACCs were >1000 m^2/g, yet only AW1104 presented a high content of acidic

sites (1.0 meq/g). Competitive adsorption experiments indicate that cadmium uptake is strongly affected by the presence of lead. This can be attributed either to a more favorable hydroxyl complexation of Pb(II) (that adsorbs strongly),or to the smallest hydrated radius of the Pb(II) molecule (that more easily diffuses). On the contrary, lead uptake was not considerably decreased in the presence of an equimolar cadmium concentration, indicating that AW1104 is more selective for Pb(II) than for Cd(II). Also, the presence of phenol causes a decrease in the heavy metal adsorption capacity, especially for cadmium (40 %). The former might be due to adsorbed phenol, which creates steric hindrance for cations to adsorb on specific oxygenated groups on the ACC. On the other hand, when heavy metals adsorb on the ACC surface, they stabilize the repulsive forces on the surface of the ACC for phenol adsorption, resulting in an increase of the adsorption capacity.

1. Introduction

It is well known that heavy metals are toxic when present in aquatic systems; they are responsible for several diseases due to ingestion of water contaminated with these compounds (Tiffanycastiglioni et al. 1989; Baldwin and Marshall 1999). Among the heavy metals, lead and cadmium are very toxic (Johri et al. 2010; LopezCarrillo et al. 1996; Markus and McBratney 2001); their intake has been related to sterility, renal dysfunction, blood damage, cancer, etc. Hence, their removal from aqueous

solutions is of utmost interest.

There are many reported methodologies for the removal of heavy metals from water, such as precipitation (Feng et al. 2000; Matlock et al. 2002), coagulation-flocculation (Charerntanyarak 1999), and membrane process (Feng et al. 2000; Abd El-Rehim et al. 2000). In recent years, there has been great interest in the removal of heavy metals by adsorption. Studied materials for heavy metal removal from aqueous solutions include zeolites (Perić et al. 2004; Wang and Peng 2010; Turan et al. 2005; Payne and Abdel-Fattah 2005), red mud (Gupta et al. 2001), waste biosorbents (Gupta and Ali 2004; Saeed et al. 2005; Velazquez-Jimenez et al. 2013), chitin and chitosan (Rangel-Mendez et al. 2009), and carbon nanotubes (Andrade-Espinosa et al. 2009; Perez-Aguilar et al. 2010). Activated carbons are the most widely employed adsorbents for water treatment because they represent an easy and economical option compared to other materials. Activated carbon cloth (ACC) is an innovative form of activated carbon that has garnered attention in recent years due to its high surface area, microporous structure (Le Cloirec et al. 1997), low pressure drop, and easy operation (Pastor et al. 1999). Also, these materials are composed of thin fibers on the order of 10 μ in diameter, leading to greater adsorption rates and, hence, contributing to the minimization of the reactor size (Ayranci and Duman 2009, 2010; Duman and Ayranci (2010a, b)). This makes it an interesting material for heavy metal removal from aqueous solution. ACCs can be prepared from various raw materials such as, cellulose, phenol resins, viscous rayon, and polyacrylonitrile (PAN) (Motoyuki 1994; Faur-Brasquet et al. 2002; Duman and Ayranci 2006), and their particular activation methodologies confer them different adsorptive properties.

The removal of the heavy metals Pb and Cd by ACCs has been studied by several authors, demonstrating that those materials have good adsorption capacities (Faur-Brasquet et al. 2002; Babić et al. 2002; Goyal and Bhagat 2010; Moreno-Castilla et al. 2004; Leyva-Ramos et al. 2005; Harry et al. 2006; Zaini et al. 2010; Leyva-Ramos et al. 2011; Rangel-Mendez and Streat 2002). However, most of these studies have been carried out in single adsorption experiments. It has been demonstrated that the presence of other compounds in a solution may change the selectivity and adsorption

capacity of the target compound, and this change strongly depends on the selected adsorbent. Nevertheless, few studies have reported multicomponent and simultaneous adsorption of heavy metals on ACC. The available reports correspond to other binary metal systems such as Cu(II)-Pb(II) (Faur-Brasquet et al. 2002) or Co(II)-Pb(II) (Saha et al. 2009). To the best of our knowledge, the simultaneous adsorption of Cd(II)-Pb(II) has not yet been studied on activated carbon cloths.

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The presence of organic compounds in solution during heavy metal uptake is another issue in which adsorption studies have rarely focused. Its inclusion might enhance or decrease the uptake of metals by adsorbents. Phenol is a pollutant commonly found in aqueous effluents that might be released with heavy metals. Hence, the study of how this organic compound affects the adsorption capacity of heavy metals (and vice versa) on ACC is of utmost importance in the design of water treatment systems.

The objective of the present work is to study the simultaneous adsorption of the systems Cd(II)-Pb(II), Cd(II)-phenol, and Pb(II)-phenol on ACC and to analyze how their presence affects the adsorption capacity of the ACCs. Those effects are explained utilizing the chemistry associated with ACC surface groups and the species in solution. Three commercial ACCs were selected and characterized; depending on their physicochemical properties and adsorption capacity, the ACC with the highest capacity for heavy metal removal was selected for simultaneous adsorption experiments.

2. Materials and Methods

2.1. Materials and Reagents

The selected commercial ACCs were polyacrylonitrile (PAN)-based AW 1104 provided by KoTHmex and rayon-based FM 70/700 and FM 10/700, which were provided by Calgon Co. The ACCs were washed with double-deionized water and dried at 100 °C in order to remove all impurities. All chemical reagents used were reagent grade (SIGMA-ALDRICH). Lead and cadmium solutions were prepared from $Pb(NO_3)_2$ and $Cd(NO_3)_2 \cdot 4H_2O$, respectively.

2.2. Material Characterization

2.2.1. Specific Surface Area and Pore Volume Determination

Specific surface area and pore volume of ACCs were determined in an ASAP 2020 (Micromeritics) instrument. The specific surface area was calculated by using the BET isotherm, and the total pore volume was determined by single adsorption point at $P/P_0 > 0.98$. Degasification temperature and pressure were 105 °C and 10^{-5} Torr, respectively.

2.2.2. Surface Charge Distribution and Point of Zero Charge

Charge distribution and point of zero charge (pH_{PZC}) were obtained in a Metler Toledo (PL 70) automatic titrator according to the protocol used by Arcibar-Orozco et al. (2012), which is as follows: 50 mg of ACC were immersed in a solution containing 50 mL of 0.1 M NaCl and 1.5 mL of 0.1 M HCl. The container was saturated with N_2 gas for 3 min and then stirred for 12 h in order to guarantee that equilibrium was reached. The solution was then titrated with 0.1 M NaOH under a nitrogen atmosphere to avoid CO_2 interferences. Control experiments were conducted without the addition of material. The ion released (IR) was calculated according the procedure described in the Supplementary Information.

The pH_{PZC} is the pH at which the overall sum of positive and negative charges is zero and corresponds to the intersection of the x-axis on the charge distribution chart.

2.2.3. Elemental Analysis and Ash Content

Elemental analysis of the ACCs was carried out in an elemental combustion system ECS 4010 from Costech instruments operated in semi-micro mode. The oven temperature was 80 °C and the sample mass was 2 mg. The inner and sample furnace temperatures were 1020 °C and 620 °C, respectively. Helium and oxygen fluxes were kept constant at 100 and 30 mL/min, respectively. The sample packed column was a Costech 051081. The retention times of N_2, C, and H were 1.5, 2.3, and 8 min, respectively, and the oxygen content was obtained by calculating the difference minus the

ash content.

Ash content was determined in a CAHN VersaTherm Analyzer in which the ACC were heated from room temperature up to 900 °C under a constant flow of 100 mL/min of air and with a heating rampage of 10 °C/min. The content of inorganic compounds is defined as the percentile ratio between starting and final masses.

2.2.4. Determination of Acid Active Sites

The determination of active acidic sites was carried out according to the acid-base titrations proposed by Boehm (2002). Briefly, 1 g of ACC was put into contact with 50 mL of 0.1 M NaOH, Na_2CO_3, or $NaHCO_3$. The solutions were bubbled with N_2 gas for 5 min in order to remove all CO_2 interferences and then hermetically closed. The solutions were maintained at 25 °C for 5 days, which was enough time to reach equilibrium. Next, the solutions were decanted, and 10 mL of the remaining solution was titrated with 0.1 M HCl. The titration with NaOH reveals the concentration of all acidic groups (carboxylic, lactonic, and phenolic groups); the Na_2CO_3 neutralizes the carboxylic and lactonic sites, while the $NaHCO_3$ neutralizes only the carboxylic sites. The same procedure was applied for the quantification of the basic sites with HCl 0.1 M as neutralizing agent.

2.3. Adsorption Experiments

Experimental adsorption data were obtained in batch reactors. The ACCs were immersed in double-deionized water and heated at 60 °C before the adsorption experiments were carried out. This is in order to remove the air trapped in pores and make them available for the adsorption process. Adsorption experiments were carried out as follows: 40 mL of a known equimolar concentration of Cd(II), Pb(II), and/or phenol were placed in a glass vial and then 0.1 g of ACC was added. The solution pH was kept constant by the addition of 0.1 M NaOH or 0.1 M HNO_3. The equilibrium criteria was established when the solution concentration was constant for 2 days. Once the adsorption equilibrium was reached (7–10 days), the solution was centrifuged and decanted. The concentration of the remaining solution was determined, and the amount adsorbed was calculated

according to the mass balance (Eq. 1):

$$qe = \frac{C_i V_i - C_e (V_i + V_a)}{m}$$

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Where q_e is the mass adsorbed at the equilibrium per mass of adsorbent, C_i and C_e are the initial and equilibrium concentration of the adsorbate, V_i is the initial volume of adsorbate, V_a is the volume added of NaOH or HNO_3, and m is the adsorbent mass. All experiments were carried out in duplicate, and standard deviations are described in the figure captions.

Concentrations of lead (II) and cadmium (II) solutions were determined by atomic absorption spectroscopy in a PerkinElmer AAnalyst 400. Phenol determination was carried out by UV adsorption in a Thermo Spectronic Helios at a wavelength of 269 nm.

2.4. Adsorption Isotherm Models

Adsorption experiments were fitted by the Langmuir (Langmuir 1916, Eq. 2) and Freundlich (Freundlich 1906, Eq. 3) equations:

$$q = \frac{q_m K_L C_e}{1 + K_L C_e}$$

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$$q = k_F C_e^{1/n}$$

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Where q (mmol/g) is the adsorption capacity at the equilibrium concentration C_e (mmol/L), K_L is the Langmuir constant in L/mmol, q_m is the maximum adsorption capacity (mmol/g), k_F is the Freundlich constant ($L^{1/n}$ mmol$^{1-1/n}$ g^{-1}), and n is the surface heterogeneity constant.

The best fit model was chosen according to its absolute percentage deviation (%D) defined as

$$\%D = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{q_{obs} - q_{cal}}{q_{obs}} \right| * 100$$

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Where N stands for the number of experiments, q_{obs} is the calculated adsorption capacity, and q_{cal} is the predicted adsorption capacity.

3. Results

3.1. Activated Carbon Cloth Characterization

Adsorptive properties of ACCs depend on their pore properties, their chemical surface, and their elemental composition. These properties were utilized in selecting the best ACC for competitive experiments. Specific surface area and pore volume of the three ACCs are summarized in Table 1. The specific surface area of all ACCs was higher than 1000 m^2/g, and the highest corresponds to the PAN-based AW 1104 (1198 m^2/g). Total pore volume was very large (>0.5 cm^3/g), and average pore diameter (d_p) was about 2 nm, indicating that the three ACCs are composed of a large number of micropores. The results indicate that there are subtle differences in the pore properties of the three ACCs. Therefore, it is likely that any difference in the adsorption performance can be attributed to their surface chemistry rather than their pore properties.

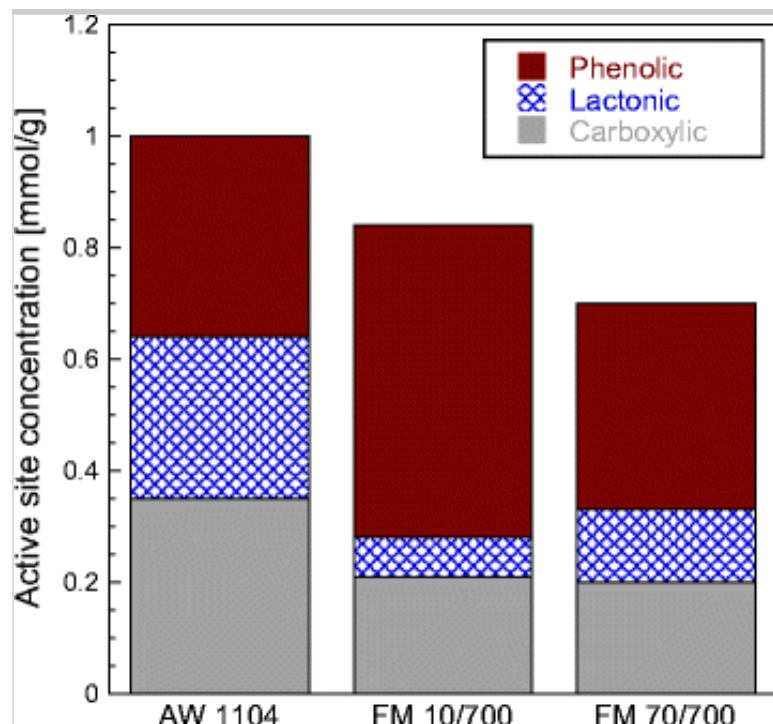**Table 1**

Specific surface area and pore volume of the ACCs

ACC	S_{BET} [m^2/g]	V_t [cm^3/g]	d_p [nm]
AW 1104	1198	0.59	1.94
FM 10/700	1099	0.52	1.94
FM 70/700	1154	0.60	2.10

The chemical properties were determined by evaluating the concentration of acidic active sites on the ACCs; the results of Boehm titration are reported in Fig. 1. It can be seen that AW 1104 has a great number of total active sites (1 meq/g) (which agrees with previously studied PAN-based ACCs (Leyva-Ramos et al. 2011)) and also has the highest number of carboxylic and lactonic groups. FM 10/700 has less total active sites but the greatest number of phenolic groups (0.56 meq/g); meanwhile, FM 70/700

has the lowest amount of total groups and the same number of carboxylic groups as FM 10/700 (0.2 meq/g). The basic sites in the ACC were 0.33, 0.30, and 0.31 meq/g for the AW 1004, FM 10/700, and FM 70/700, respectively.
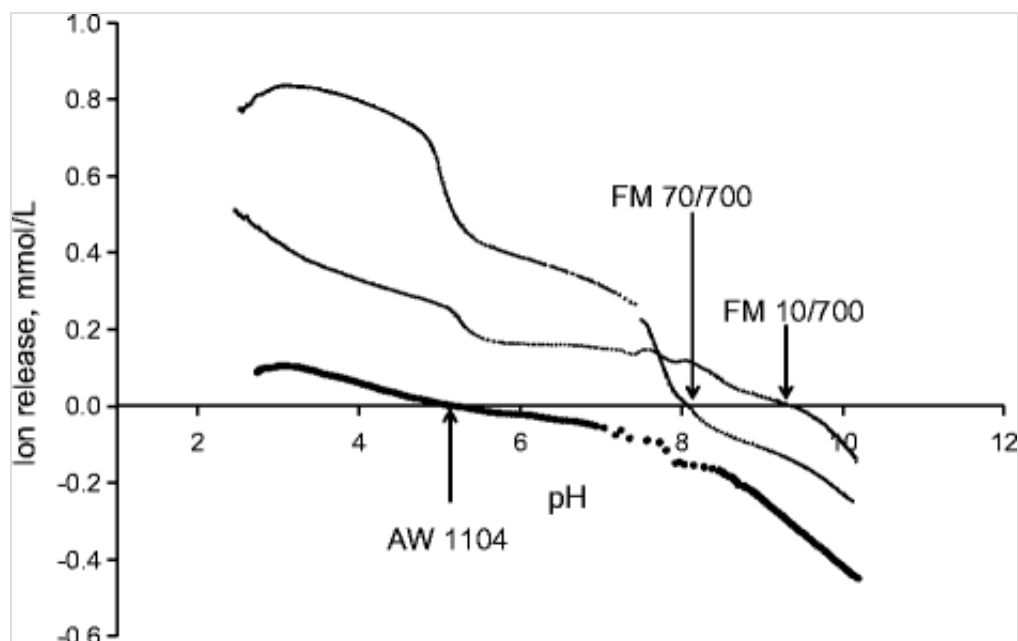
Fig. 1

Acidic groups present in the ACCs

The presence of several groups on the ACCs, along with their capacity to adsorb protons, confers a charge distribution in the carbonaceous materials (Fig. 2). The pH_{PZC} of AW 1104 is 5.1 (acidic) attributed to its high content of acidic groups (carboxylic and lactonic) as aforementioned. Since FM 10/700 and FM 70/700 have less content of acidic moieties, their surface charge distribution is more basic, yielding a pH_{PZC} of 9.3 and 8.1, accordingly.

Fig. 2

Surface charge distribution, arrows show the pH_{PZC} of each ACC

As can be seen in Table 2, nitrogen content is low in all ACCs (<3 %), indicating that most of their functionalities might be attributed to oxygen groups. In agreement with the acidic group quantification, oxygen content in AW 1104 is the highest, followed by F10/700 and FM 70/00. It is noteworthy that PAN-based carbon has a low ash content (<1 %) due to its synthetic precursor that is an important property in water treatment applications.

Table 2

Elemental composition of the ACCs

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ACC/content [%]	N	C	H	O	Ash
AW 1104	2.28	74.71	ND	22.46	0.55
FM 10/700	2.96	71.29	ND	20.79	4.96
FM 70/700	2.19	80.14	ND	9.34	8.33
ND not detected					

3.2. Single Adsorption Experiments

In order to select which of the three ACCs was more suitable for competition experiments, single adsorption experiments of heavy metals

were carried out. These experiments were conducted at pH 7 for cadmium and pH 5 for lead since at these pH the metals are soluble mainly as 2+ species (speciation diagrams are available in Supplementary Information). At pH values higher than those used, the precipitation of metals as hydroxides might interfere the ACC uptake.

The single adsorption isotherms for Pb(II) and Cd(II) are provided in Fig. S3 of the Supplementary Information. The Freundlich and Langmuir parameters and their absolute percentage deviation are shown in Table 3. In summary, the adsorption capacities of Cd(II) and Pb(II) at an arbitrary chosen value of 0.7 mmol/L are presented in Table 4. AW 1104 showed the highest adsorption capacity for both heavy metals. This can be attributed to its negative surface, and its high content of oxygen groups, especially carboxylic groups. These groups have been reported (Kadirvelu et al. 2000) as being responsible for the uptake of heavy metals from aqueous solution. This can be corroborated by the comparable adsorption capacities of FM 10/700 and FM 70/700, which also have a similar content of carboxylic groups and charge distribution. Based on the above, AW 1104 ACC was selected to perform competitive adsorption experiments.

Table 3

Langmuir and Freundlich parameters of cadmium, lead, and phenol in single and simultaneous adsorption on AW 1104 at 25 °C

System	Compound	pH	Freundlich parameters			Langmuir parameters		
			k_F [mmol$^{1-1/n}$ L$^{1/n}$/g]	n	%D	q_m [mmol/g]	K_L [L/mg]	%D
Single	Cadmium	7	0.20	3.84	6.0	0.16	46.2	18.7
Single	Lead	5	0.17	3.94	13.3	0.14	65.7	18.4
Single	Phenol	5	0.44	3.66	35	0.31	66.9	7.4
Single	Phenol	7	0.42	3.52	35.8	0.30	55.7	10
Single	Cadmium	5	0.060	3.1	2.9	0.06	7.9	4.1
Cd-Pb	Cadmium	5	0.094	0.58	26.3	194.5	0.0003	71

Cd-Pb	Lead	5	0.24	2.14	13.1	0.3	2.96	20.5
Cd-Phenol	Cadmium	7	0.14	3.1	8.9	0.13	10.4	7.1
Cd-Phenol	Phenol	7	0.84	2.14	7.0	0.57	12.9	11.8
Pb-Phenol	Lead	5	0.16	3.8	1.8	0.13	25.6	7.8
Pb-Phenol	Phenol	5	0.84	2.10	7.5	0.54	13.89	5.8

Table 4

Cadmium and lead adsorption capacities at $Ce_eq = 0.7$ mmol/L and 25 °C

ACC	Metal	pH	Adsorption capacity [mmol/g]
AW 1104	Cadmium	7	0.184
FM 10/700	Cadmium	7	0.100
FM 70/700	Cadmium	7	0.091
AW 1104	Lead	5	0.160
FM 10/700	Lead	5	0.056
FM 70/700	Lead	5	0.073

3.3. Simultaneous Adsorption of Cd(II)-Pb(II).

Simultaneous adsorption of Cd(II)-Pb(II) was carried out at pH 5, and to compare these results, the single adsorption isotherm of Cd at pH 5 was obtained. Figures 3 and 4 show the single and competition adsorption isotherms of Cd(II) and Pb(II); for the sake of comparison, the single adsorption isotherms are also included.

Fig. 3

Cadmium adsorption isotherms for the AW1104 at 25 °C. The *lines* represent the Freundlich equation
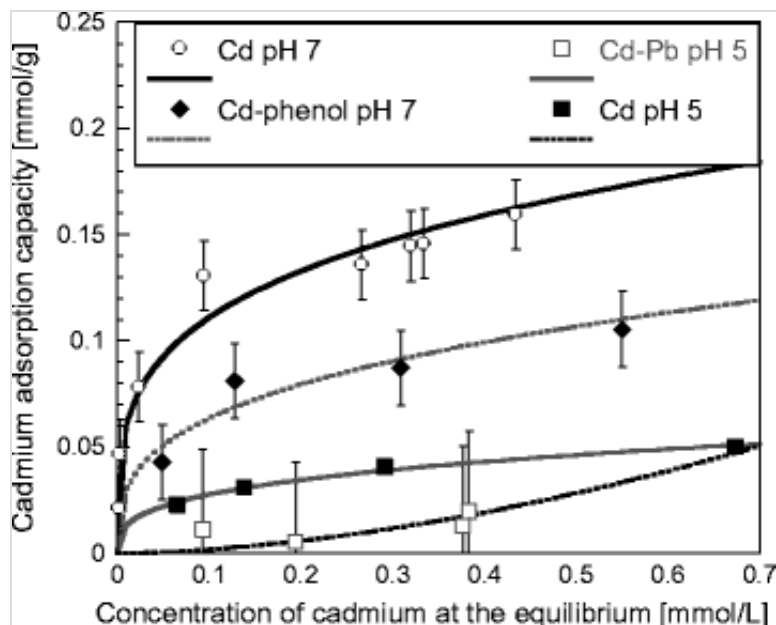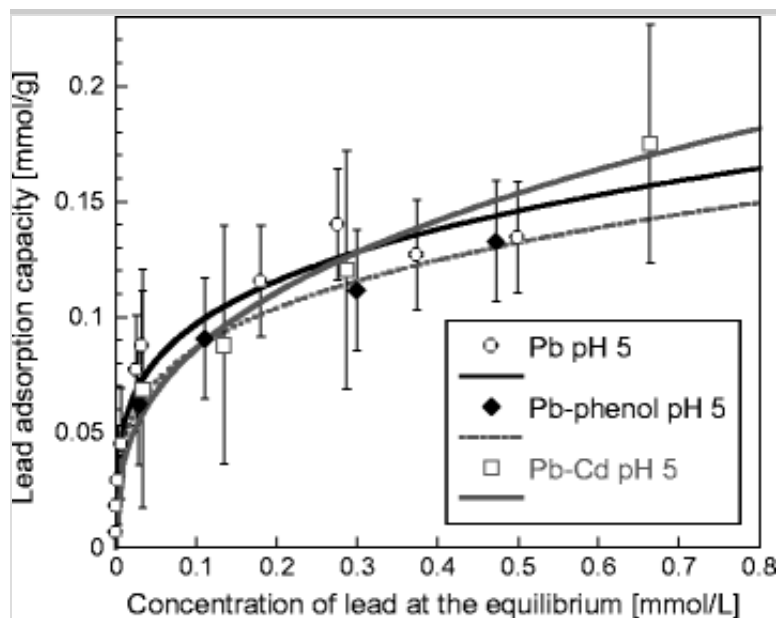
Fig. 4

Adsorption isotherms for lead experiments of AW 1104 at pH 5 and 25 °C. The *lines* represent the Freundlich equation

Competitive adsorption experiments were adjusted with both models, in the figures is shown the Langmuir or Freundlich equation as corresponds (parameters and %*D* are provided in Table 3).

At pH 5, the AW 1104 hasd a higher adsorption capacity (about 10 times at 0.4 mmol/L) for Pb(II) than for Cd(II). When both components are present at equimolar concentrations in the starting solution, the Cd(II) adsorption

capacity was decreased, especially at low concentrations (decreased 3.4-fold at C_e <3 mmol/L). As the concentration increased, the adsorption isotherms converged at a similar adsorption value. On the other hand, the lead adsorption capacity ~~is~~was not considerably affected by cadmium, since both single and competitive adsorption isotherms are closely related, and they have the same adsorption capacity. Those results indicate that AW1104 has more adsorption capacity and selectivity for lead than for cadmium adsorption.

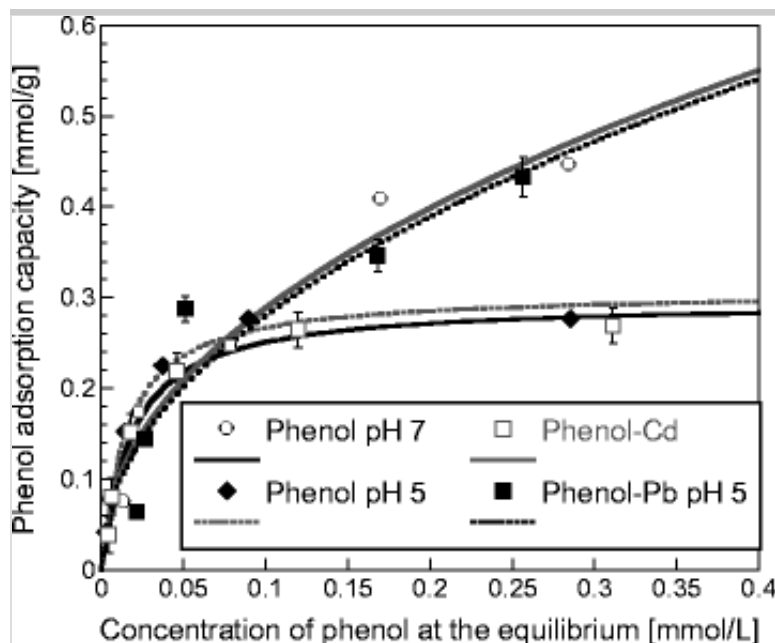## 3.4. Simultaneous Adsorption of Cd(II)-Phenol

Simultaneous adsorption experiments for the system phenol-Cd(II) were carried out at pH 7. Since at this pH the adsorption capacity was higher than at pH 5, the cadmium is entirely present as free Cd^{2+} ions. The results of the phenol-Cd(II) isotherms of AW 1104 are shown in Fig. 3. When phenol was present in the starting solution, a remarkable decrease was observed in the cadmium adsorption capacity. At a Cd(II) equilibrium concentration of 0.3 mmol/L, the adsorption capacity of the AW1104 was 0.146 mmol/g; however, in the presence of phenol, the capacity decreased to 0.088 mmol/g (a decrease of 40 %). As a result of this decrease, the Freundlich constant changes from 0.2 to 0.13, indicating a decrease of the adsorbent capacity to accept cadmium molecules.

Interestingly, an increase of the phenol adsorption capacity was noticed when Cd was present in the starting solution. In Fig. 5, the increase in the phenol adsorption capacity was observed when the equilibrium concentration surpassed 0.05 mmol/L. At an equilibrium concentration of 0.3 mmol/L, the phenol adsorption capacity increases about 160 %. Also, there is a change in the adsorption isotherm shape; while single adsorption experiments were better correlated for the Langmuir equation, the competitive adsorption experiments were better correlated for the Freundlich isotherm. This suggests the formation of multilayers in the competitive experiments.

Fig. 5

Phenol adsorption isotherm in single and metal competition at 25 °C. The *lines* represent the Langmuir isotherm in the single adsorption experiments

and the Freundlich equation for the systems phenol-Cd and phenol-Pb

3.5. Simultaneous Adsorption of Pb(II)-Phenol.

For this system, the decrease in Pb(II) adsorption capacity caused for the phenol presence is lower than for Cd(II). At an equilibrium concentration of 0.3 mmol/L of Pb(II), the single lead adsorption capacity is 0.125 mmol/g (interpolated from the Freundlich equation) and in the phenol-Pb(II) system is 0.116 mmol/g (7 % less) at the same pH. Similar to the cadmium adsorption, the phenol uptake is enhanced by the presence of lead (Fig. 5). At the same pH value of 5, at an equilibrium phenol concentration, the adsorption capacity increases by about 140 %. The metal-organic system (of either Cd-phenol or Pb-phenol) indicates that when the compounds are present in equimolar concentrations in the starting solution, the adsorption capacity for the retention of the organic compound is enhanced by the presence of the heavy metal, while the adsorption capacity of the metal is decreased.

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4. Discussion

The simultaneous adsorption of the studied systems involves various uptake mechanisms. In the case of heavy metals, it has been reported that

the main adsorption mechanism occurs by electrostatic attraction between positively charged ions and the negative surface of the ACC (Kadirvelu et al. 2000). In this case, the most important groups are carboxylic, that are dissociated at the adsorption pH. Both Cd(II) and Pb(II) are attracted and bonded to the ACC surface by means of this mechanism. When these two heavy metals are present in the starting solution, the Cd(II) adsorption capacity is decreased to a greater extent than that of Pb(II). Therefore, AW 1104 selectively favors lead over cadmium ions. This effect was observed by Sheela and Nayaka (2012) for the adsorption of lead and cadmium by NiO nanoparticles at pH 6. The authors attributed the favorable selectivity for lead ions to the lower hydrolysis constant of the hydroxyl complexes (see Figure S1 and S2 in Supplementary Information); therefore, the formed $Pb(OH)^+$ complex adsorbs stronger than the free Cd^{2+}. At pH 5, both cations are present as free 2^+ cations, and no hydrolyzed ions are formed; however, the creation of microenvironments of pH, due to the deprotonation of surface groups on the ACC, might result in the creation of instantaneous complexes of MOH^+. These complexes adsorb strongly on the ACC. Since Pb might form hydrolyzed ions with less change in pH than cadmium, its adsorption is favored over the cadmium.

Also, the selectivity of the ACC might be linked to the hydrated ionic radius of the Pb^{2+} (0.401 Å), which is smaller than Cd^{2+} (0.426 Å). This leads to less steric hydrance and pore restriction of Pb^{2+} to adsorb onto active sites of the ACC. Also, the increase in the selectivity might be linked to the higher spontaneous adsorption of lead over cadmium, as reported by Sheela and Nayaka (2012).

On the other hand, the adsorption mechanism of phenol is governed by non-specific dipole attractions and pi-interactions between the benzene ring and the graphitic layers of the ACC (Mattson et al. 1969). It has been reported that phenol might also adsorb onto carbonaceous materials by means of π-π interactions of the aromatic ring and carbonyl groups in the carbon (Bansal and Goyal 2010). However, the low concentration of these groups might render this contribution insignificant. This effect can be observed in Fig 5, since a change of two units in the adsorption pH causes a small decrease in the phenol adsorption capacity.

The phenol presence strongly decreased the adsorption uptake of both heavy metals (especially cadmium (II)) by AW1104. This can be attributed to steric hindrance caused by phenol adsorption on the graphitic layers of the ACC. As a result of this effect, when phenol is present, a decrease of about a 40 % in the Cd(II) adsorption capacity was noticed.

Some authors have reported that when an organic compound is added to a solution containing heavy metals, there is an increase in the metals adsorption capacity. For example, Faur-Brasquet et al. (2002) studied the adsorption of Cu^{2+} and Pb^{2+} onto ACC in the presence of benzoic acid, observing an increase in the adsorption capacities of metals. This increase was attributed to the formation of organic-metal complexes that enhance the metals' adsorption capacity. Later, this observation was corroborated by Moreno-Castilla et al. (2004) in a system that contained a mixture of metals and tannic acid. However, in those studies, the formed complexes were due to the dissociation of the organic molecule that allows their interaction with charged ions. In this study, since phenol is not dissociated, the metal-organic complexes cannot be formed, and therefore, the phenol presence lessened adsorption sites for metal bonding, instead of enhancing them. This result indicates that when the organic compound is non-dissociated in a solution containing ions, the metal adsorption capacity decreases.

On the other hand, the presence of the metals strongly increases the phenol uptake. At the adsorption pH 5 and 7, the carboxylic groups are dissociated; however, the presence of the phenolate anion is too low to promote electrostatic adsorption of phenol (phenolate pK_a = 10, Bartok et al. 1962). It has been reported that the acidification of the carbonaceous surface brings a decrease in the capacity of the materials for adsorbing phenol; this is caused by the repulsive forces of acidic oxygen groups and the phenol molecule (Bansal and Goyal 2010). It is possible that when Pb(II) or Cd(II) adsorb on negatively charged carboxylic groups in the ACC, they stabilize the ACC surface. This effect counteracts repulsive forces that phenol must overcome to become adsorbed. Additionally, the presence of the metals in the hydrophilic site will allow the phenol to interact more easily with the surface of the ACC enhancing the π-π

interactions. These two effects result in an increase of the phenol adsorption capacity (Diaz-Flores et al. 2009). It is important to notice that single and simultaneous isotherms were compared on the same basis (in an equimolar concentration), and not by changing the concentration of one compound, while keeping the concentration of the other constant (a normal procedure in multicomponent adsorption isotherms). This was in keeping with the objective of the current research, which was to study the effect of an organic compound that is not dissociated during heavy metal uptake in ACC.

5. Conclusions

The simultaneous adsorption of cadmium-lead, phenol-cadmium, and phenol-lead was studied on a PAN-based ACC (AW 1104). The ACC was selected from a set of three commercial ACCs due to its higher adsorptive properties for heavy metal uptake. Isotherms are correlated with the Freundlich equation that best fitted the experimental data. At the same pH value, the ACC has a higher adsorption capacity for lead than for cadmium. Equimolar simultaneous experiments demonstrate that ACC is more selective for Pb than for Cd, which might be attributed to the ease of hydroxide complexation by Pb, and also to the smallest hydrated ionic radius of the Pb ion. On the other hand, ACC has a higher affinity for phenol than for the heavy metals, as evidenced by phenol-Cd and phenol-Pb experiments. It is hypothesized that since phenol adsorbs non-specifically on the carbon surface graphitic layers, its presence diminishes adsorption sites for heavy metal uptake. The presence of phenol affects to a higher extent the cadmium uptake, even at the best pH conditions for the removal of Cd, which might be attributed to the steric hindrance of Cd molecules to adsorb on the ACC surface. Furthermore, the adsorption of heavy metals stabilizes the adsorbent surface charge, increasing the phenol adsorption capacity of the ACC during competition experiments. The results presented herein demonstrate that when an organic compound, such as phenol, is not dissociated in a solution containing Cd and Pb, the adsorption capacity of lead(II) and cadmium(II) by a rayon-based ACC decreases and the uptake of the organic compound increases.

Acknowledgments

6. Electronic Supplementary Material

Below is the link to the electronic supplementary material.

ESM 1

(DOCX 80 kb)

References

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