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# Adsorption of zinc(II) from an aqueous solution onto activated carbon

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#### Abstract

Adsorption isotherms were measured experimentally for Zn(II) adsorption from aqueous solution onto commercial activated carbons C, F-400, F-300 and Centaur HSL in a batch adsorber. The effects of carbon type and solution pH on adsorption isotherms were evaluated in this work. Nearly three times as much Zn(II) adsorbed onto C carbon as on the other three carbon types. The adsorption isotherm for Zn(II) was dependent on solution pH since Zn(II) did not adsorb to carbon below pH 2, and the adsorption isotherm increased as pH increased from 3 to 7. The adsorption isotherm of Zn(II) on C carbon was temperature independent while on F-400 the isotherm showed unusual behavior as temperature increased. © 2002 Elsevier Science B.V. All rights reserved

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# 1. Introduction

In 1978, the United States environmental protection agency (USEPA) prepared a list of 129 organic and inorganic pollutants found in wastewater that constitute serious health hazards. This list, known as the Priority Pollutants List, includes the following thirteen metals: antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc [1]. Unlike organic compounds, metals are non-biodegradable and, therefore, must be removed from wastewater.

Zinc is present in the air, soil, water and almost all food. Zinc is naturally released into the environment, although industrial activities are mostly responsible for zinc pollution. Mining and foundry activities, zinc, lead and cadmium refining, steel production,

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carbon combustion and solid waste incineration contribute most significantly to environmental zinc pollution [2]. Water reservoirs are contaminated by the run-off from these industries. Zinc is commonly used to coat iron and other metals for prevention of oxidation. Various zinc salts are used industrially in wood preservatives, catalysts, photographic paper, accelerators for rubber vulcanization, ceramics, textiles, fertilizers, pigments and batteries [2].

Several processes are currently used in industry for the removal of heavy metals from aqueous solutions. Ion exchange, adsorption, reverse osmosis, chemical precipitation and sedimentation, filtration, electrodialysis and air flotation are among those methods most commonly employed [3]. Chemical precipitation, though the most widely used process for removal of heavy metals, produces a large amount of sludge that must then be contained in toxic waste landfills. Also, the precipitated metal is economically unrecoverable. The development of processes to simultaneously remove and recover metals from aqueous solutions would allow metal recycling in industrial activities, combining environmental and economical benefits to both industry and society.

Over the past 30 years, adsorption onto activated carbon has been successfully applied for treating municipal and industrial wastewater and drinking water. Successful removal of heavy metals from aqueous solutions using activated carbon has recently been demonstrated [4]. Carbon adsorption is considered the best available technology for eliminating non-biodegradable and toxic organic compounds from aqueous solutions [5]. Activated carbon is considered the universal adsorbent because its inherent physical properties, large surface area, porous structure, high adsorption capacity and extensively reactive surface, make it extremely versatile [4].

Current research describes Zn(II) adsorption from aqueous solutions onto several organic and inorganic adsorbents. Among the different adsorbents that have been tested are lignite [6]; synthetic goethite [7]; microbeads [8]; peat [9]; oxidized anthracite [10]; natural and activated bentonite [11,12]; charcoal [13]; and activated carbon [14,15].

Few studies assess Zn(II) adsorption from aqueous solutions onto different commercial, granular and powdered activated carbons [15,16], or on activated carbons manufactured from different sources such as olive stones, almond shells and peach stones [14]; anthracite [10]; lignin [16]; and wood [13]. Zn(II) adsorption onto activated carbon was reported to be highly dependent upon solution pH. The mass of Zn(II) adsorbed was negligible below pH 2, increased substantially from pH 3 to 5, and remained essentially stable for pH > 7.

Published reports describing the effect of temperature on Zn(II) adsorption isotherms on activated carbon state that the influence of temperature depends on the type of carbon used. For carbons produced from agricultural residues, the adsorption isotherm decreased with increased temperature [14], while for some other carbons, the adsorption isotherm increased as temperature increased [15].

Although the mechanism of Zn(II) adsorption onto activated carbon is incompletely understood, the Langmuir and Freundlich adsorption isotherms have been used to model experimental adsorption equilibrium data [13,14]. Marzal et al. [15] applied the surface-complex formation, triple-layer model to interpret Zn(II) adsorption onto activated carbon. This model assumes that adsorption occurs by a chemical complexing reaction and Coulombic attractions caused by the electrostatic interactions between the ions in solution and the surface complexes. Additional information describing interactions between the surface and the Zn(II) species in solution is required to explain adsorption isotherm behavior in response to changes in the temperature, solution pH and carbon type.

The aim of this work is to study Zn(II) adsorption from aqueous solutions onto different commercial activated carbons and the effects of solution pH, temperature and carbon type on the adsorption isotherm. Moreover, the interactions between the carbon surface and Zn(II) ions in solution are investigated to better understand the adsorption mechanism of Zn(II) onto activated carbon.

# 2. Materials and methods

Commercially available, activated carbons used in this study were C, Centaur HSL, F-300 and F-400. The C carbon from Carbones Mexicanos, is prepared from wood waste (sawdust), and calcined at a high temperature using phosphoric acid as a catalyst. Centaur HSL carbon is produced from a bituminous carbon according to a patented process by Calgon Carbon Corp. F-300 and F-400 carbons are also manufactured by Calgon Carbon Corp. using bituminous carbon and are activated at temperatures between 800 and 1100 °C. The total surface areas for C, Centaur HSL, F-300 and F-400 carbons were determined by the N<sub>2</sub>-BET method using a Micromeritics ASAP 2010 surface analyzer.

All activated carbons were sieved to a uniform particle size, washed several times with distilled water, dried in an oven at  $110 \,^{\circ}$ C for 24 h and kept in closed containers. All standard Zn(II) solutions were prepared from Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and the solution pH was adjusted with either 0.1 or 0.01 M HNO<sub>3</sub> and NaOH solutions.

Activated carbons were oxidized with HNO<sub>3</sub> by adding 40 g of carbon and 200 ml of 50% (v/v) concentrated HNO<sub>3</sub> solution in a flask. The solution was heated to 50 °C for 2 h and then allowed to cool to room temperature. The acid solution was drained and the carbon was rinsed with deionized water until the pH of the rinsing water remained constant. The oxidized carbon was dried in an oven at 110 °C for 24 h and stored in a closed container. Acidic and basic sites on both plain and oxidized carbons were determined by the acid–base titration method proposed by Bandoz et al. [17].

The concentration of Zn(II) in aqueous solution was determined by atomic absorption spectroscopy [18] using a Varian, double beam, atomic absorption spectrophotometer, model SpectrAA-20. The Zn(II) concentration of a sample was estimated using a calibration curve (absorbance versus concentration) prepared using standard concentration Zn(II) solutions. Calibration curves were prepared for each of the different pH values tested since the curves varied with pH.

The solution containing the adsorbate was introduced into a 500 or 1000 ml Erlenmeyer flask that served as the experimental batch adsorber. Granular activated carbon was added to a Nylon mesh basket and placed inside the adsorber. The adsorber was partially submerged in a constant temperature water bath placed over a magnetic stirrer and the solution was stirred continuously with a Teflon coated stir bar.

Activated carbon was pretreated prior to performing the adsorption experiments to eliminate air present in the carbon pores so that the entire carbon surface area would be in contact with the solution and available for adsorption. A known mass of carbon was introduced into a Nylon basket that was subsequently placed in a flask with distilled water, heated to boiling for 30 min, and allowed to cool to room temperature. The basket containing the carbon remained in the water until it was added to the adsorber.

Experimental adsorption isotherm data were obtained in the batch adsorber by contacting 1 or 2 g of pretreated carbon with 480 ml of an aqueous solution of known initial Zn(II) concentration. The carbon-containing basket was completely submerged in the continuously stirred solution within the adsorber. Solution pH was measured periodically with a pH meter and kept constant by adding 0.01 N HNO<sub>3</sub> or NaOH solution as required. The solution was sampled at predetermined time intervals, and the concentration of Zn(II) was determined for each sample. The carbon was left in contact with the solution until equilibrium was reached between 5 and 7 days, when the concentration of two successive samples remained constant. The equilibrium of Zn(II) uptake was calculated by performing a mass balance.

Determination of the surface charge of activated carbon particles was carried out using a Malvern zetameter, model Zetasizer4, that measures particle mobility by laser velocimetry. The surface charge was determined using 0.001 M aqueous solutions of constant ionic strength at different pH values prepared by mixing different proportions of 0.001 M HNO<sub>3</sub>, NaNO<sub>3</sub> and NaOH solutions. A small amount (0.01 g) of carbon was ground with an agate ball mill to a particle size passing through 400 mesh. The carbon was placed in a volumetric flask, filled to the mark with the 0.001 M solution at the different pH values and left for 5 days while the carbon and solution remained in contact. The pH then was measured for each of the solutions, and the surface charge was determined by the zetameter.

## 3. Results and discussion

#### 3.1. Adsorption isotherms

Experimental adsorption data were fitted to the Langmuir and Freundlich isotherm models. The isotherm parameters were evaluated by a least-squares method based on an optimization algorithm and are shown in Table 1 along with the average absolute percent deviation (D%). The isotherm best fitting the experimental data was assumed to be that having the lowest average absolute percent deviation. Of the 12 isotherm cases shown in Table 1, 7 were best fit to the Langmuir and 5 to the Freundlich isotherm.

#### 3.2. Effect of carbon type

Adsorption isotherms for Zn(II) onto C, Centaur HSL, F-300 and F-400 activated carbons at pH = 7 and T = 25 °C are exhibited in Fig. 1. The adsorption isotherms for Zn(II) onto Centaur HSL, F-300 and F-400 were very similar. An average of three times more Zn(II) adsorbed on C carbon than on the other three carbons, and maximum Zn(II) uptake on C was 19.9 mg/g. This value compares reasonably well with maximum uptakes reported for other carbons and adsorbents. For example, a maximum Zn(II) uptake of 6.65 mg/g was reported for an activated carbon prepared from almond shells [14] and of near 26.0 mg/g for a natural bentonite [12].

The total surface areas of the different carbons were calculated as  $768 \text{ m}^2/\text{g}$  for C,  $803 \text{ m}^2/\text{g}$  for Centaur HSL,  $863 \text{ m}^2/\text{g}$  for F-300 and  $987 \text{ m}^2/\text{g}$  for F-400. F-400 carbon

Table 1	
Freundlich and Langmuir isotherm parameters	

Carbon type	<i>T</i> (°C)	рН	Langmuir			Freundlich		
			$q_{\rm m} K  ({\rm l/g})$	<i>K</i> (l/mg)	D <sup>a</sup> (%)	$\frac{k (l^{1/n})}{mg^{(1-1/n)} g^{-1}}$	n	D <sup>a</sup> (%)
C	25	7	26.06	1.406	16.1	10.05	5.54	19.2
		6	16.56	2.251	17.4	4.392	5.11	8.14
		4	1.978	0.493	7.85	2.022	5.47	8.84
	35	7	62.58	3.572	21.3	11.58	7.12	12.6
	15	7	35.85	1.964	4.46	10.59	6.75	6.63
F-400	25	7	0.393	0.037	26.3	1.022	2.05	18.6
		6	0.460	0.085	9.48	0.901	2.40	20.4
		4	0.170	0.054	28.9	0.329	1.96	25.8
	35	7	1.207	0.172	13.3	1.854	2.99	25.8
	15	7	1.682	0.142	20.3	2.876	2.84	11.7
F-300	25	7	1.074	0.178	7.07	1.827	3.38	15.8
Centaur HSL	25	7	0.403	0.040	21.9	0.807	1.82	30.0

<sup>a</sup>  $D(\%) = \left(\frac{1}{N}\sum_{i=1}^{N} \left| \frac{q_{\exp}-q_{cal}}{q_{\exp}} \right| \right) \times 100\%.$ 

has the greatest surface area, yet a comparatively low capacity for Zn(II) adsorption, while C carbon has the smallest surface area and the largest capacity for Zn(II) adsorption. This indicates that Zn(II) adsorption is specific and dependent on the concentration of specific active sites on the activated carbon surface rather than the total surface area available.



Fig. 1. Adsorption isotherms for Zn(II) onto different types of activated carbon at pH = 7 and  $T = 25 \,^{\circ}$ C.

Carbon type	Plain carbon		Oxidized carbon		
	Acidic sites (meq./g)	Basic sites (meq./g)	Acidic sites (meq./g)	Basic sites (meq./g)	
С	1.364	0.140	1.875	0.041	
F-400	0.050	0.337	1.014	0.141	

 Table 2

 Concentration of active sites for plain and oxidized carbons

The concentrations of active sites for C and F-400 carbons with and without  $HNO_3$  oxidation are shown in Table 2. Plain (unoxidized) C carbon contains close to 27 times more acidic sites than F-400, while F-400 has nearly three times more basic sites than C. Furthermore, oxidation of the carbons with  $HNO_3$  caused the expected increase in acidic and decrease in basic sites [19]. Following oxidation, the acidic sites of C carbon increased only 37% while those for F-400 increased drastically 20-fold (2000%).

The adsorption isotherms of Zn(II) onto plain and oxidized F-400 carbons are illustrated in Fig. 2. The Zn(II) adsorption capacity of F-400 carbon increased nearly 2.5 times following HNO<sub>3</sub> oxidation. Assuming that all the acidic sites were involved in Zn(II) adsorption and that one ion of Zn(II) is adsorbed on two acidic sites, oxidation should have increased adsorption capacity by 10, since the concentration of total acidic sites for this type of carbon increased by 20. This observation indicates that Zn(II) is adsorbed onto specific acidic sites on F-400 carbon.

The oxidation of C carbon caused an increase in the acidic sites but did not increase the Zn(II) adsorption capacity of C carbon for concentrations of Zn(II) < 4 mg/l, and the



Fig. 2. Adsorption isotherms for Zn(II) onto F-400 carbon without and with oxidation by HNO<sub>3</sub>, pH = 7 and  $T = 25 \,^{\circ}$ C.

increase in adsorption capacity was relatively small for greater concentrations. The likely explanation is that Zn(II) adsorbs specifically onto certain, but not general, types of acidic sites on C carbon.

#### 3.3. Effect of pH

The effect of solution pH on the adsorption isotherms for Zn(II) on F-400 and C activated carbons is displayed in Figs. 3 and 4, respectively. The Zn(II) adsorption onto activated carbon was significantly affected by the pH. No Zn(II) was adsorbed below pH 2 and maximum Zn(II) adsorption occurred at pH 7. The adsorption isotherm of Zn(II) increased markedly as the solution pH rose from 2 to 7, and Zn(II) started to precipitate as Zn(OH)<sub>2</sub> at pH > 7. Marzal et al. [15] reported similar results.

Throughout the adsorption experiments, solution pH changed as Zn(II) adsorption progressed, necessitating addition of 0.01 N HNO<sub>3</sub> or NaOH solutions to keep the pH constant. The solution pH increased during adsorption of Zn(II) onto F-400 carbon and decreased during adsorption onto C. Therefore, Zn<sup>+2</sup> and H<sup>+</sup> ions were being adsorbed simultaneously onto the surface of F-400 carbon and both ions were probably competing for the same sites. For C carbon, Zn<sup>+2</sup> ions were being adsorbed while H<sup>+</sup> ions were being desorbed from its surface. This last phenomenon is known as ion exchange and it is likely that H<sup>+</sup> was desorbed from a surface site where Zn<sup>+2</sup> could then be adsorbed.

The effect of pH on the adsorption isotherm was attributed to interactions between ions in solution and complexes formed at the adsorbent surface. The fact that Zn(II) in aqueous solution can form different species whose presence depends on the solution pH is well documented [20]. The speciation diagram for Zn(II) can be obtained using the following



Fig. 3. Effect of pH on the Zn(II) adsorption isotherm onto F-400 activated carbon at  $T = 25 \,^{\circ}$ C.



Fig. 4. Effect of pH on the Zn(II) adsorption isotherm onto C activated carbon at  $T = 25 \,^{\circ}$ C.

reactions and equilibrium constants [21]:

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$$Zn^{2+} + H_2O \Leftrightarrow Zn(OH)^+ + H^+, \quad pK_1 = 8.96$$
  

$$Zn^{2+} + 2H_2O \Leftrightarrow Zn(OH)_2 + 2H^+, \quad pK_2 = 7.94$$
  

$$Zn^{2+} + 3H_2O \Leftrightarrow Zn(OH)_3^- + 3H^+, \quad pK_3 = 11.50$$
  

$$Zn^{2+} + 4H_2O \Leftrightarrow Zn(OH)_4^{-2} + 4H^+, \quad pK_4 = 12.80$$

The speciation diagram for Zn(II) has been reported by several authors [16]. Accordingly, the predominant ionic species is  $Zn^{2+}$  for pH < 7, whereas Zn(II) is present mainly as  $Zn^{2+}$  and Zn(OH)<sub>2</sub>, and in lesser quantities as Zn(OH)<sup>+</sup> for pH between 8 and 9. Since all the experiments were carried out at a maximum pH of 7, the predominant Zn(II) species found in solution and adsorbed on the carbon surface was Zn<sup>2+</sup>.

#### 3.4. Reversibility of Zn(II) adsorption onto C and F-400 carbons

Reversibility was investigated by carrying out desorption experiments consisting of saturating activated carbon with Zn(II) in an adsorption experiment at a constant pH 7, then removing the activated carbon from the Zn(II) solution and placing it inside a solution without Zn(II) and at pH 7. Solution pH was kept constant throughout the desorption experiment. In preliminary runs, it was found that 7 days were enough for the desorption experiment to reach new equilibrium.

Fig. 5 shows Zn(II) adsorption data for C carbon as well as the corresponding desorption data at pH 7 and 25 °C. Zn(II) adsorbed on C carbon did not desorb since the mass of Zn(II)



Fig. 5. Reversibility of Zn(II) adsorption from aqueous solution onto C activated carbon, pH = 7 and  $T = 25 \,^{\circ}\text{C}$ .

adsorbed remained essentially constant during the Zn(II) desorption experiment. Zn(II) adsorption on C carbon was thus irreversible.

Zn(II) adsorption on F-400 carbon at pH 7 was reversible for concentrations <12 mg/l, but irreversible above this concentration, although not completely. Some of the Zn(II) was adsorbed reversibly onto F-400 carbon while another portion of the Zn(II) was adsorbed irreversibly. Thus, Zn(II) adsorption on F-400 carbon occurred by two mechanisms, one that is reversible and the other irreversible.

#### 3.5. Adsorption mechanism

The surface charge of carbon particles depends on solution pH. The surface is positively charged when the solution pH is below the isoelectric point (IEP), negatively charged at pH above the IEP and neutral when the pH is equal to the IEP. The surface charges of C and F-400 carbons are graphed in Fig. 6 and their respective IEP's of 1.9 and 3.2 are shown.

As shown in Fig. 6, the shape of the potential–pH curve for F-400 carbon is different from that for C carbon, and this difference can not be ascribed to experimental procedure since both curves were obtained using the same procedure. The potential–pH curve for F-400 carbon has plateau regions at low and high pH, whereas that for C carbon has no plateau regions. However, both of these potential–pH curve shapes have been described for activated carbons [22]. The scatter in the data for F-400 carbon, observed in the plateau regions, is very similar to scatter reported in other studies [23], and probably is associated with experimental error or to the fact that the surface of activated carbon is heterogeneous.

At pH below the IEP, adsorption of Zn(II) is nearly zero, since the carbon surface is positively charged causing a mutual repulsion between  $Zn^{2+}$  and the carbon surface. If adsorption occurs at all, it is not due to an electrostatic attraction, but to a chemical interaction with sufficient energy to overcome the surface–ion repulsion. When the solution pH is



Fig. 6. Surface charge for C and F-400 activated carbons at I = 0.001 M.

above the IEP,  $Zn^{2+}$  is attracted to the negatively charged carbon surface. This condition favors  $Zn^{2+}$  accumulation onto the activated carbon surface, and adsorption can occur by electrostatic or chemical interactions, or a combination of both. Adsorption of Zn(II) onto C carbon must, therefore, occur by chemical adsorption since Zn(II) is adsorbed irreversibly onto this activated carbon.

#### 3.6. Effect of temperature

The effect of temperature on adsorption was investigated by determining the adsorption isotherms at 15, 25 and 35 °C. The isotherm of Zn(II) onto C carbon either was independent of temperature or the effect of temperature was so minimal as to be masked by experimental error. For F-400 carbon, the adsorption isotherm decreased as temperature increased for concentrations <30 mg/l. At greater concentrations, the isotherm increased as temperature was increased from 15 to 25 °C, and it remained constant or increased only slightly as temperature was increased from 25 to 35 °C. This unexpected behavior could be explained by assuming that Zn(II) adsorption onto F-400 carbon was occurring by two mechanisms, one of which is favored while the other is inhibited by the increase in temperature.

## 4. Conclusions

Zn(II) adsorption onto C carbon is on the average three times greater than adsorption measured on F-300, F-400 and Centaur HSL carbons. Despite the fact that this carbon

has the smallest surface area of the four carbons, C carbon has more acidic sites than the other carbons tested making it more efficient for Zn(II) adsorption. The solution pH plays a very important role for Zn(II) adsorption onto activated carbon. At pH < 2, Zn(II) did not adsorb, the adsorption isotherm increased drastically as the pH was increased from 2 to 7, and maximum adsorption uptake was achieved at pH 7. The effect of pH on the isotherm is attributed to interactions between ions in solution and complexes formed on the carbon surface.

According to the speciation diagram,  $Zn^{2+}$  was the predominant Zn(II) species found at pH < 7, and since all the adsorption experiments were performed within this pH range, Zn(II) adsorbed onto the activated carbon as  $Zn^{2+}$ .

When the pH was lower than the isoelectric point (IEP), repulsion between the  $Zn^{2+}$  ions and the carbon surface interfered with adsorption. If adsorption occurred at all at low pH, it was due not to electrostatic, but to chemical attractions. When the solution pH exceeded the IEP,  $Zn^{2+}$  was attracted by the negatively charged carbon surface, favoring the accumulation of  $Zn^{2+}$  on the surface and, thus, promoting adsorption.

The adsorption isotherm of Zn(II) onto C carbon was not dependent on temperature while on F-400 temperature changes produced an unusual adsorption response, first increasing, then remaining stable as temperature increased.

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