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Improving the Adsorption of Heavy Metals from Water Using Commercial Carbons Modified with Egg Shell Wastes

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ABSTRACT: We introduce the application of hen egg shell waste to improve the adsorption capacities of heavy-metal ions using commercial carbons via the modification of their surface chemistry. Specifically, a calcium solution extracted from egg shell waste has been used as a low-cost activation agent to improve the adsorption properties of three commercial carbons. An orthogonal array of the Taguchi method has been applied to identify the optimal conditions for the adsorbent modification process using the Zn^{2+} batch adsorption, at 30 °C and pH 5, as the response variable. Our results show that maximum adsorption capacities of Cd^{2+}, Ni^{2+}, and Zn^{2+} ions, at 30 °C and pH 5, may increase up to 15 times, with respect to the results obtained using the commercial adsorbent without modification. The improvement of adsorbent performance may be related to the formation of calcium phosphate on the carbon surface. Finally, adsorption studies in binary metal solutions were performed to identify the competitive effects in multicomponent adsorption, using calcium-modified carbons.

1. INTRODUCTION

Wastewaters from several industrial activities are an important source of environmental pollution, because of their high content of heavy-metal ions. Heavy metals are biologically important, because of their toxicity for living organisms, including human beings. Currently, water treatment technologies for the removal of heavy-metal ions include chemical precipitation, membrane filtration, ion exchange, electrochemical processes, and adsorption.[1] Adsorption is one of the most important methods for wastewater treatment and offers several advantages for heavy-metal removal, especially when the metal concentrations are in the range of 1−100 ppm.

Until now, several studies have reported the application of different adsorbents for the removal of heavy-metal ions from aqueous solution.[2−11] In particular, activated carbon (AC) has been used for a long time to remove heavy metals from wastewaters,[4,12−16] and its performance depends on two important factors: (1) the textural parameters and (2) the surface functional groups.[13,15] The adsorption capacities of commercial carbons for heavy-metal ions are usually low (i.e., < 10.0 mg g^{-1}), since these adsorbents are produced in large scale and are synthesized using standard procedures, which have been developed for general applications. Therefore, an additional modification of the carbon surface chemistry is required to increase the adsorbed amount of these toxic pollutants. To date, many carbon surface modification methods have been introduced, including both chemical and physical treatments.[17] Specifically, chemical treatments are commonly used for improving the adsorption of heavy metals on carbons. For example, the modification of carbon surface by impregnation with anionic surfactants such as the sodium dodecyl sulfate, sodium dodecyl benzene sulfonate, or dioctylsulfosuccinate sodium is suitable to improve the removal of Cd^{2+} ions in aqueous solution.[18] Nadeem et al.[19] have also studied the adsorption of Cd^{2+} ions from aqueous solution using surfactant-modified carbons obtained from husk and pods of *M. oleifera*. These authors showed that the adsorption capacity of carbons can be significantly enhanced by modification with surfactants. In another study,[20] the carbon modification with tartrazine has been successfully applied to increase the adsorbed amount of Pb^{2+}, Cd^{2+}, and Cr^{3+} ions, while the modification of commercial coconut activated carbon using HNO_3 and NaOH for the selective adsorption of Cr^{6+} has been also reported.[21] Recently, some authors[22,23] have reported the chemical surface modification of commercial carbons using different oxidizing agents such as HNO_3, H_2O_2, and $Fe(NO_3)_3$. On the other hand, physical treatments are used to introduce specific compounds on the carbon surface. For instance, SO_2 gas can be used to introduce sulfur groups on the carbon surface for the selective adsorption of cadmium.[24]

Alternatively, both physical and chemical treatments can be simultaneously used in the preparation or modification of carbons, to enhance their adsorption properties. Some examples of these studies are activated carbons obtained by carbonization of bagasse impregnated with concentrated sulfuric acid, followed by a treatment with carbon dioxide at 900 °C for the removal of hexavalent chromium,[25] and activated carbons obtained from date pits using different activation methods for the removal of lead and cadmium.[26] However, a significant disadvantage of these approaches is that the reagents used in the carbon modification may imply a significant additional cost for the treatment process. Therefore, the use of wastes and industrial byproduct is an attractive alternative for developing low-cost activation reagents.

In the present study, an activation agent obtained from hen egg shells (HES) is proposed for the chemical treatment of three commercial carbons prepared from different precursors. HES are

Table 1. Chemical and Physical Properties of the Commercial Carbons Used in This Study

	Adsorbent		
parameter	coconut shell carbon, CC	bituminous carbon, BC	lignite carbon, LC
composition (%)			
carbon	93.45	87.3	77.71
hydrogen	1.22	0.84	1.40
nitrogen	1.43	0.56	0.78
sulfur	0.08	0.29	0.39
oxygen	4.15	3.48	6.10
BET surface area, S_{BET} (m^2 g^{-1})	399	961	658
total pore volume, V_{total} (cm^3 g^{-1})	0.172	0.529	0.697
micropore volume, V_{mic} (cm^3 g^{-1})	0.160	0.369	0.250
pore diameter, D_p (nm)	1.726	2.203	4.238

widely generated from the bakery industry, homes, and restaurants; because of their physicochemical properties, these wastes may have several applications in metallurgy, bioremediation, and materials science.[27] In the field of water treatment, HES wastes also have been applied as heavy-metal sorbents;[28,29] however, for some metallic ions, the raw HES adsorption capacities are considered low. In particular, the calcium content of HES (i.e., 94% of calcium carbonate)[30] can be used as an activation agent for improving carbon adsorption properties. Note that this cation is thought to play an important role in the removal of heavy metals through ion exchange and other mechanisms. Therefore, in this study, we introduce the application of HES wastes to improve the adsorption of heavy-metal ions on commercial carbons via modification of their surface chemistry. The commercial carbons selected for this work have a low adsorption capacity for heavy metals (i.e., < 1.0 mg g^{-1}) and they have been used as case study to illustrate the application of HES for developing new adsorbents to remove heavy metals from wastewaters. To identify the optimal conditions for the modification process of the selected commercial carbons, a Taguchi orthogonal array was applied, where the adsorption capacity of Zn^{2+} ions at 30 °C, pH 5, and batch conditions was defined as the response variable. In addition, the adsorption isotherms of Cd^{2+} and Ni^{2+} ions at 30 °C and pH 5 were obtained to determine the adsorption capacity of the modified carbons in comparison with those obtained using the raw commercial carbons. Finally, adsorption studies in binary solutions of these metal ions were performed to identify the competitive removal effects in multicomponent solutions of heavy metals using calcium-modified carbons.

2. EXPERIMENTAL METHODOLOGY

2.1. Description and Characterization of Commercial Carbons. In this study, three types of commercial carbons provided by Clarimex Company (Mexico) were used. For the selection of these commercial carbons, two considerations were made: (1) carbons must be prepared from different precursors and (2) all of them were previously subjected to a physical activation process (i.e., using water steam). Thus, the selected commercial adsorbents are coconut shell carbon (CC), bituminous carbon (BC), and lignite carbon (LC). Table 1 provides the chemical and physical properties of these commercial carbons. In our study, these carbons were milled and sieved to retain the 18−20 mesh fractions. These carbon particles were washed with deionized
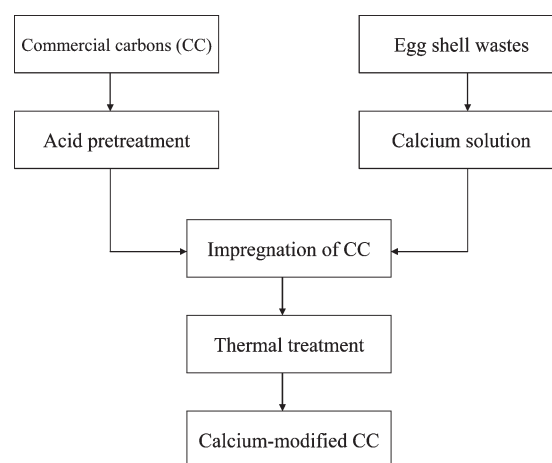

Figure 1. Experimental procedure for the surface modification of commercial carbons using a calcium solution extracted from egg shell wastes.

water until pH was constant and, finally, they were dried at 70 °C for 24 h. These samples were used to perform the modification of carbon surface chemistry and the adsorption experiments.

With respect to the characterization of commercial adsorbents, the content of carbon, hydrogen, nitrogen, and sulfur in the carbons was obtained with a LECO Model CHNS-932 elemental analyzer and the oxygen content with a LECO Model VTF-900 system. Carbon samples were heated at 815 °C under an air atmosphere for 1 h (UNE 32004 standard) to determine their inorganic fraction contents (i.e., ash content). The obtained ashes were analyzed by X-ray diffraction (XRD). Diffraction patterns were recorded in a Bruker Model D8 Advance diffractometer equipped with a Cu Kα X-ray source, operated at 40 kV and 40 mA. A single Göbel mirror configuration was used to monochromatize and focus the X-rays on the sample, attaining highly efficient parallel beam geometry. Diffraction data were collected by step scanning with a step size of 0.02° 2θ and a scan step time of 5 s. Finally, the textural parameters were calculated from the N$_2$ adsorption isotherms at −196 °C, using a Micromeritics TriStar II 3020 volumetric adsorption system. Prior to measurement, samples were outgassed overnight by heating at 523 K under vacuum. The experimental points of the nitrogen isotherms were analyzed using suitable methods for microporous and mesoporous materials.

Table 2. Experimental Layout Using the L9 Taguchi Orthogonal Array for the Chemical Modification of Commercial Carbons Using Egg Shell Wastes

	Factors					Zn^{2+} Adsorbed Amount (mg g^{-1})	
experiment	A: carbon type [a]	B: acid treatment [b]	C: concentration of calcium solution (vol %)	D: temperature of thermal treatment (°C)	label	replicate 1	replicate 2
1	CC	none	25	200	CC-1	0.48	0.41
2	CC	HCl	50	400	CC-2	6.04	5.90
3	CC	H$_3$PO$_4$	100	600	CC-3	10.70	10.70
4	BC	none	50	600	BC-1	0.89	1.03
5	BC	HCl	100	200	BC-2	1.17	1.23
6	BC	H$_3$PO$_4$	25	400	BC-3	5.93	5.88
7	LC	none	100	400	LC-1	2.40	2.40
8	LC	HCl	25	600	LC-2	1.23	1.23
9	LC	H$_3$PO$_4$	50	200	LC-3	3.84	3.64

[a] CC, coconut shell carbon; BC, bituminous carbon; and LC, lignite carbon. [b] In this stage, we used an acid concentration of 1 M.

2.2. Modification of Surface Chemistry of Commercial Carbons by Using Egg Shell Wastes.

Commercial carbons were modified using a calcium solution extracted from HES. Specifically, HES wastes were washed with deionized water and dried at 35 °C. HES particles were milled and sieved to retain the 35−40 mesh fractions. The calcium solution was obtained after soaking these particles with acetic acid (25 vol %). This mixture (i.e., HES and acetic acid) was shaken using a temperature-controlled shaker operated at 150 rpm for 5 h. A ratio of 0.05 g of HES per 1 mL of acetic acid (25 vol %) was used in this stage. This solution was filtered to separate the membrane of HES, because it is insoluble in acetic acid. Finally, this calcium solution was used for the impregnation of the commercial adsorbents.

The chemical modification of commercial carbons was performed using a three-step procedure: (1) pretreatment of adsorbents using an acid solution, (2) calcium impregnation of carbons using the solution extracted from HES, and (3) thermal treatment of calcium-impregnated carbons. Figure 1 provides a schematic diagram for the different stages of this modification process. For the acid pretreatment of the commercial adsorbents, a ratio of 0.2 g of carbon per mL of acid solution was used. This pretreatment was performed at 30 °C for 2 h and under constant stirring (150 rpm). Later, the acid solution was evaporated at 55 °C and, finally, carbon samples were dried at 100 °C for 15 h. With respect to the carbon impregnation, a ratio of 0.02 g of adsorbent per mL of calcium solution was used. The contact time of adsorbent-impregnation solution was 4 h, and all experiments were performed at 30 °C using a temperature-controller stirrer operated at 150 rpm. The solution was evaporated at 55 °C and the calcium-impregnated carbons were dried at 110 °C for 15 h. Finally, the impregnated carbons were heated at desired temperature for 3 h. The modified adsorbents were washed with deionized water at 50 °C until pH was constant and finally dried at 100 °C for 24 h. These modified carbons were used in the adsorption experiments.

The application of experimental designs is a robust approach to optimize the experimental conditions for the preparation and modification of activated carbons.[5,6,31] In this study, the Taguchi method was used to optimize the carbon surface modification process.[32,33] A L$_9$ orthogonal array was applied in our experiments (see Table 2). The selected factors were as follows: carbon type (Factor A), acid treatment (Factor B), calcium concentration

of the activation agent (Factor C), and temperature of thermal treatment (Factor D). For all factors, we have considered three levels in the experimental design (see Table 2). Note that the different concentrations of activation agent (expressed as a volume percentage) were obtained by dilution of the original calcium solution extracted from HES. The response variable of this experimental design was the adsorbed amount of Zn^{2+} ions at 30 °C and batch conditions employing an adsorbent dosage of 4 g L^{-1}. It is convenient to remark that Zn^{2+} has been selected as the case study, because the literature indicates that the removal of this metal is usually difficult and traditional commercial carbons may show a low Zn^{2+} adsorption capacity.[34,35] Herein, we assume that optimization of the operating conditions of the carbon modification process, using Zn^{2+} removal as the response variable, will also imply an improvement of adsorption properties for other metallic species not considered in our experimental design. Finally, we have selected the adsorption capacity (expressed in units of mg g^{-1}) instead of the adsorption capacity normalized by the adsorbent surface area (expressed in units of mg g^{-1} m^{-2}) as the response variable of the experimental design, because the adsorbent surface chemistry plays a major role in the removal of heavy metals. In the following sections, we will provide results to support this fact.

The statistical analysis of experimental design included a discussion of the statistical weight of each factor in the modification process of commercial adsorbents and a variance analysis. Calculations were performed according with the basic concepts of the Taguchi method.[32,33] In particular, Taguchi methodology analyzes both the mean response for each run in the inner array and the variance using a proper function for the signal-to-noise ratio (S/N):

$$S/N = -10 \log \left[\frac{\sum_i (1/Y_i^2)}{n} \right] \quad (1)$$

where Y_i are the values of the response variable obtained in each of the different replicates n performed under given experimental conditions. An analysis of variance (ANOVA) was used to perform a systematic analysis of the relative importance of each factor, with respect to the adsorption capacity of modified carbons using HES wastes. This analysis is based on the following
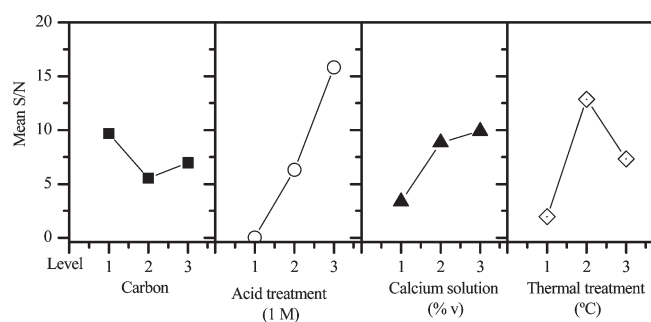
Figure 2. Graphs of S/N response for the chemical modification of commercial carbons using egg shell wastes.

equations:

$$SS_T = \left[\sum_{i=1}^{N} Y_i^2\right] - \frac{T^2}{N} \tag{2}$$

$$SS_F = \left[\sum_{i=1}^{k_F} \left(\frac{F_i^2}{n_{F_i}}\right)\right] - \frac{T^2}{N} \tag{3}$$

$$\sigma_F = \frac{SS_F}{v_F} \tag{4}$$

where T is the sum of all observations, N the total number of observations, F_i the sum of observations under the level i, n_{F_i} the number of observations under the level i, k_F the number of levels of factor F, SS_T the total sum of squares, SS_F the sum of squares for factor F, v_T the total degrees of freedom (i.e., $N - 1$), v_F the degrees of freedom of factor F (i.e., $k_F - 1$), and σ_F is the variance for factor F, respectively.

2.3. Adsorption Experiments. *2.3.1. Taguchi Design.* For the Taguchi experimental design, batch sorption experiments were performed using Zn^{2+} solutions with an initial concentration of 100 mg L^{-1}. These solutions were prepared from nitrate salt and deionized water. Standard procedures were used to determine the adsorption capacity of modified carbons under static conditions. Adsorption experiments were conducted in duplicate at 30 °C and pH 5.

2.3.2. Adsorption Isotherms of Zn^{2+}, Cd^{2+}, and Ni^{2+} Ions. Adsorption isotherms of Zn^{2+}, Cd^{2+}, and Ni^{2+} ions were obtained at pH 5 and 30 °C. Note that preliminary results indicate that these operating conditions (i.e., pH and temperature) have been identified as optimal for obtaining the maximum removal of these heavy metals. Therefore, adsorption isotherms at tested conditions are used to determine the maximum adsorption capacities of both raw and modified carbons. Metal solutions were prepared from nitrate salts and deionized water. All the adsorption experiments were conducted in duplicate at batch conditions and the average results are reported. All chemicals were of analytical grade.

2.3.3. Adsorption Experiments in Binary Solutions of Zn^{2+}, Cd^{2+}, and Ni^{2+} Ions. Binary solutions of $Zn^{2+}-Cd^{2+}$, $Zn^{2+}-Ni^{2+}$, and $Ni^{2+}-Cd^{2+}$ were used in multicomponent adsorption experiments. As stated, these solutions were also prepared from nitrate salts and deionized water. Batch experiments were performed using initial metal concentrations in the range of $0.3-2 \text{ mmol L}^{-1}$. In particular, a full factorial experimental design was applied to identify the competitive effects of these metal ions

Table 3. Results of the Taguchi Experimental Design and Analysis of Variance for Zn^{2+} Removal Using Modified Commercial Carbons

factor	sum of squares, SS	variance, σ_F
A: carbon type	26.56	13.28
B: acid treatment	379.04	189.52
C: concentration of calcium solution (vol %)	73.70	36.85
D: temperature of thermal treatment (°C)	177.33	88.66

onto the adsorption capacities of the adsorbents tested. Note that this experimental design includes different binary solutions with the same concentration of co-ions. Therefore, we consider that this experimental design is proper to obtain a general overview of the adsorbent performance for the removal of heavy metals under competitive conditions. Standard procedures were also applied to perform these adsorption experiments using an adsorbent dosage of 2 g L^{-1} at 30 °C and pH 5.

2.3.4. Metal Quantification. For metal quantification, a Perkin–Elmer AAnalyst 100 atomic absorption spectrophotometer equipped with an air–acetylene burner was used. The reproducibility of the experiments was generally within 5% of the average results. The adsorption capacities of carbons (q) were calculated by a mass balance

$$q = \frac{(C_0 - C_f)V}{W} \tag{5}$$

where C_0 and C_f is the initial and final metal concentration (mg L^{-1}), V is the volume of metal solution used for adsorption experiments (in liters), and W is the amount of carbon mass (in grams).

3. RESULTS

3.1. Taguchi Experimental Design and Statistical Analysis of the Carbon Modification. Overall, nine carbons were obtained from the orthogonal experimental design. Table 2 shows the results of Zn^{2+} adsorption experiments using these carbon samples. In particular, Taguchi orthogonal design indicates that the optimal conditions needed to obtain a modified carbon with improved adsorption capacity for Zn^{2+} removal are those employed in experiment 3: a coconut shell carbon treated with H_3PO_4, impregnated with a calcium solution (concentration of 100 vol %) and heated at 400 °C for 3 h. Interesting trends were also identified in our results. Specifically, the Zn^{2+} adsorption capacity was higher in the carbon samples treated with H_3PO_4 (i.e., samples CC-3, BC-3, and LC-3), most likely because of the formation of calcium phosphate on the carbon surface (see characterization results given below).

Figure 2 shows the S/N response graphs for the modification of commercial carbons using HES wastes, and Table 3 provides the ANOVA. Statistical analysis shows that the most important experimental design factors are the acid treatment and the calcium concentration employed during the activation step. Finally, based on these results, and considering both the adsorbent cost and its availability, it was possible to select the ideal carbon sample for additional experiments. Thus, the modified carbon obtained in experiment 6 (i.e., sample BC-3) was selected as the case study for performing removal experiments in both single and binary metal solutions.

Table 4. Elemental Composition and Chemical and Physical Properties of Bituminous Carbon Modified with a Phosphoric Acid and Calcium Solution Extracted from Egg Shell Wastes (Sample BC-3; see Table 2)

Elemental Composition	
element	content (%)
carbon	75.56
hydrogen	1.53
nitrogen	1.75
sulfur	0.20
oxygen	18.60

Textural Parameters	
property	value
S_{BET}	931 $m^2 g^{-1}$
V_{total}	0.522 $cm^3 g^{-1}$
V_{mic}	0.355 $cm^3 g^{-1}$
D_p	2.243 nm

Figure 3. N_2 adsorption isotherms at -196 °C of raw (clear squares) and modified (black squares) bituminous carbons.

Figure 4. X-ray diffraction (XRD) patterns of (a) raw and (b) modified bituminous carbons.

Results of the ultimate analysis and the chemical and physical properties of the selected modified-carbon (BC-3) and raw commercial carbon (BC) are shown in Tables 4 and 1, respectively. Figure 3 shows the nitrogen adsorption isotherms of BC and BC-3 and, according to the International Union of Pure and Applied Chemistry (IUPAC) clasification, they are a combination between Type I (characteristic of microporous materials) and Type IV (mesoporous materials). In general, all the chemical and physical properties of raw BC were not significantly affected when it was treated with the calcium solution and phosphoric acid. These results suggest that only the surface chemistry of BC was affected after the treatment. On the other hand, two interesting aspects can be analyzed from the results of ultimate analysis. First, the differences in carbon percentage may be related to the incorporation of inorganic elements on the surface of BC, thus increasing the quantity of ashes in BC-3 (8.3%), in comparison with BC (6.1%). Second, the oxygen content is also higher in the modified carbon, because of the treatment with H_3PO_4. According to the literature,[36] some phosphorus—oxygen compounds may be formed onto carbon surfaces using this acid treatment. Figure 4 shows the diffraction patterns of BC and BC-3, and it is possible to observe a significant difference between these samples. In addition to common reflections observed in the diffraction patterns of the two carbon samples corresponding to quartz and mullite crystalline phases, peaks assigned to calcium phosphate were identified in the diffraction pattern of sample BC-3 (see Figure 4b). Therefore, our results indicate that the carbon modification using HES and H_3PO_4 caused the formation of surface moieties containing phosphorus and calcium. These moieties are expected to increase the adsorption properties of modified carbons via surface complexation reactions. It is important to note that similar findings have been reported for other commercial carbons impregnated with metal ions.[37] For example, Yang et al.[37] reported the improvement of Cu^{2+} adsorption properties of activated carbon by loading of Fe^{3+} on carbon surface. These authors suggested that the improvement of adsorbent properties could be explained by complexation reactions between heavy-metal ions and metal-modified carbon surface.
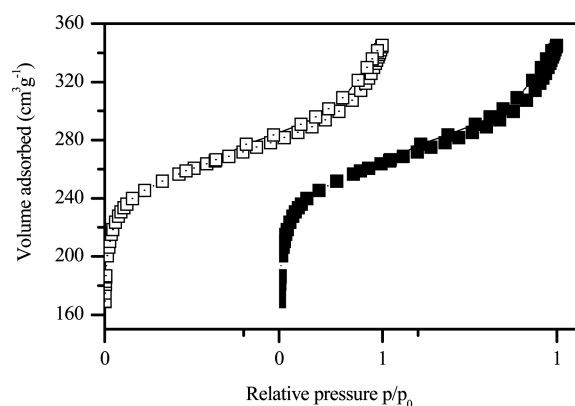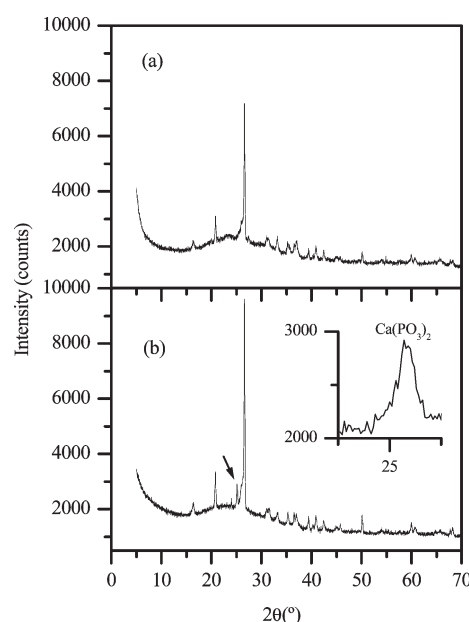
3.2. Adsorption Isotherms of Zn^{2+}, Cd^{2+}, and Ni^{2+} Ions.

Figure 5 shows the adsorption isotherms of Zn^{2+}, Cd^{2+}, and Ni^{2+} ions from aqueous solution at pH 5 and 30 °C, using both BC and BC-3. These isotherms indicate that the maximum adsorption capacities for Zn^{2+}, Cd^{2+}, and Ni^{2+} can be significantly enhanced after chemical modification of BC carbon using H_3PO_4 and calcium solution extracted from HES waste. Specifically, the maximum adsorption capacities for Zn^{2+}, Cd^{2+}, and Ni^{2+} ions are, respectively, 0.63, 0.61, and 1.0 mg g^{-1} for BC, and 10.48, 5.7, and 9.96 mg g^{-1} for BC-3; i.e., BC-3 loading capacities are an order of magnitude higher than those values observed for BC. It is interesting to remark that, although the adsorbent performance for the removal of Cd^{2+} and Ni^{2+} was not considered in the Taguchi experimental design, the optimal conditions identified for the modification of BC also improved the adsorption properties for these metallic ions.

For illustrative purposes, the adsorption capacities of BC-3 were compared with those reported in the literature for powdered egg shell (PES).[38] In particular, Otun et al.[38] reported a
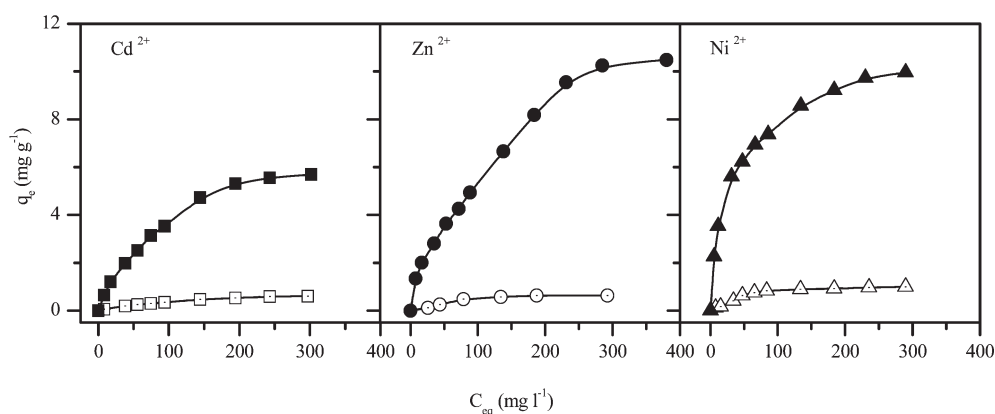
Figure 5. Adsorption isotherms of Zn^{2+}, Ni^{2+}, and Cd^{2+} ions on raw and modified bituminous carbons at 30 °C and pH 5.
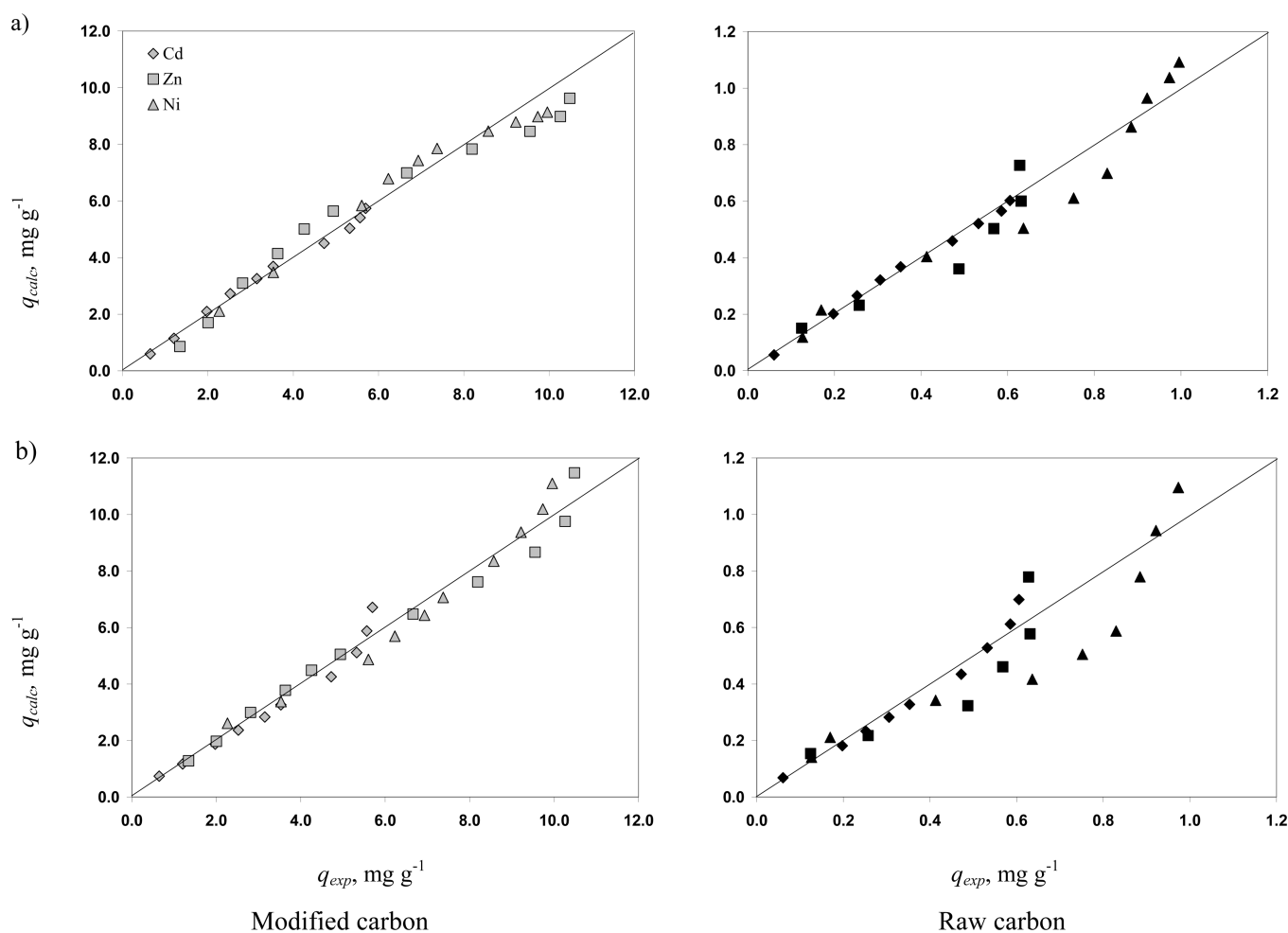

Figure 6. Comparison of experimental and calculated adsorption capacities by raw and modified bituminous carbons using (a) the Langmuir model and (b) the Freundlich model.

maximum adsorption capacity of 7 and 4 mg g^{-1} for Ni^{2+} and Cd^{2+} ions, respectively, using PES. It is clear that the adsorption capacities of BC-3 are higher than those reported for raw PES and BC. Therefore, the procedure proposed in this study for the modification of adsorption properties of commercial carbons is an alternative strategy for developing new and effective adsorbents for the removal of heavy metals from water. Moreover, the

reuse of egg shell wastes is attractive from the viewpoint of the waste recycle and minimization of pollutants.

On the other hand, we have considered both the Langmuir and Freundlich models for correlating the adsorption isotherms reported in Figure 5. Specifically, the Langmuir isotherm assumes that adsorption occurs in a monolayer, where the actives sites are identical and energetically equivalent.[39,40] This isotherm

Table 5. Parameters of Langmuir and Freundlich Isotherm Models for Adsorption of Heavy Metals from Aqueous Solution

carbon sample	metal ion	Freundlich Model				
		K_f	n_F	R^2	F_{obj}	E (%)
BC	Zn^{2+}	0.0171	1.4877	0.7004	0.2941	20.72 ± 8.55
	Cd^{2+}	0.0165	1.5211	0.9549	0.0712	7.99 ± 4.16
	Ni^{2+}	0.0406	1.6574	0.7248	0.5055	20.08 ± 10.67
BC-3	Zn^{2+}	0.4034	1.7742	0.9779	0.0370	5.24 ± 2.62
	Cd^{2+}	0.1956	1.6148	0.9476	0.0895	8.37 ± 4.64
	Ni^{2+}	1.3597	1.7742	0.9519	0.0730	7.32 ± 4.64

carbon sample	metal ion	Langmuir Model				
		q_{max}	K	R^2	F_{obj}	E (%)
BC	Zn^{2+}	1.1649	0.0057	0.8537	0.1620	14.86 ± 7.67
	Cd^{2+}	0.8535	0.0081	0.9950	0.0170	3.73 ± 2.23
	Ni^{2+}	1.4161	0.0116	0.9237	0.1950	11.42 ± 8.47
BC-3	Zn^{2+}	12.2449	0.0097	0.9511	0.2768	13.55 ± 8.66
	Cd^{2+}	7.6649	0.0099	0.9917	0.0279	4.83 ± 2.27
	Ni^{2+}	9.8083	0.0470	0.9621	0.0394	5.76 ± 2.70

is given by

$$q_e = \frac{q_m K C_e}{1 + K C_e} \quad (6)$$

where q_e is the metal adsorption capacity (expressed in units of mg g^{-1}) at equilibrium, C_e the concentration (expressed in units of mg L^{-1}) at equilibrium, q_m the theoretical maximum adsorption capacity (expressed in units of mg g^{-1}), and K represents the Langmuir equilibrium constant (expressed in units of L mg^{-1}).

The Freundlich model is an empirical expression used to describe a heterogeneous system[39,40] and is defined as

$$q_e = K_f C_e^{1/n_F} \quad (7)$$

where K_f (expressed in units of mg$^{1-(1/n)}$ L$^{1/n}$ g^{-1}) and n_F are parameters characteristic of the adsorbent-sorbate system. Data correlation of our experimental results was performed using a nonlinear regression approach,[40−42] based on the minimization of the following objective function:

$$F_{obj} = \sum_{i=1}^{n_{dat}} \left(\frac{q_e^{exp} - q_e^{calc}}{q_e^{exp}} \right)_i^2 \quad (8)$$

where q_e^{exp} and q_e^{exp} are the experimental and predicted adsorption capacity and n_{dat} is the overall number of experimental data, respectively. In this study, the stochastic optimization method Simulated Annealing[41] was used for minimization of eq 10. The criterions used in this study to measure the fitting goodness of the adsorption isotherm models were the correlation coefficient (R^2), the behavior of the relative residuals, the objective function value (F_{obj}), and the mean absolute percentage deviation (E) between calculated and experimental metal adsorption capacities, where

$$E = \frac{100}{n_{dat}} \sum_{i=1}^{n_{dat}} \left| \frac{q_e^{exp} - q_e^{calc}}{q_e^{exp}} \right|_i \quad (9)$$

Results of data fitting for both isotherms are given in Figure 6 and Table 5. Overall, it is clear that our adsorption data are best described by the Langmuir model. Specifically, this isotherm model showed a mean absolute percentage deviation (E) of 3.7%−14.9% and correlation coefficients (R^2) of 0.85−0.99. Based on these results, we have calculated the dimensionless separation factor (R_L) for the Langmuir isotherm. This separation factor is given by

$$R_L = \frac{1}{1 + K C_0} \quad (10)$$

This separation factor indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). We have calculated the values of R_L for the modified carbon BC-3 using different initial metal concentrations. Our results indicate that $R_L < 1$ for all tested conditions, confirming thereby the favorable adsorption of heavy-metal ions onto the modified bituminous carbon BC-3.

3.3. Adsorption Experiments in Binary Solutions of Zn^{2+}, Cd^{2+}, and Ni^{2+} Using the Modified Bituminous Carbon BC-3. The sorption studies of metal ions from solutions containing two or more metallic species are useful to assess the degree of interference between metal ions during the removal process. When two or more metal ions are present in solution, they may increase, decrease, or have no effect on the metal-ion adsorption capacity of the adsorbent.[43,44] Thus, adsorption data from multicomponent solutions play an important role to design treatment processes for wastewater. Experimental data for competitive adsorption in binary mixtures of Zn^{2+}, Cd^{2+}, and Ni^{2+} ions onto BC-3 are shown in Figure 7. In this figure, the metal adsorption capacity of each co-ion is plotted as a function of the initial concentration of the binary solution. For comparison purposes, the monocomponent adsorption capacity of each metal is also reported. Note that the performance of raw BC in binary metal solutions is not reported, because its adsorption capacities under competitive conditions are practically negligible.

To perform the experimental data analysis, the effect of co-ions in multicomponent adsorption using BC-3 is determined by the ratio of adsorption capacities (R_q), which is defined as

$$R_{q,i} = \frac{q_{i,\,mix}}{q_{i,0}} \quad (11)$$

where $q_{i,mix}$ is the adsorption capacity for metal ion i in the presence of the other metal ion and $q_{i,0}$ is the adsorption capacity for the same metal when it is alone in the solution at the same initial concentration of that set in the binary solution. According to the literature,[45] if $R_{q,i} > 1$, the adsorption of metal i is promoted by the presence of other metal ions; if $R_{q,i} = 1$, there is no effect on the adsorption capacity of metal i; and if $R_{q,i} < 1$, the adsorption of metal i is suppressed by other metal ions. Therefore, this analysis has been used to study the performance of BC-3 in the removal of Zn^{2+}, Cd^{2+}, and Ni^{2+} ions under competitive conditions. It is convenient to remark that the adsorption capacities from Figure 7 have been standardized and are reported on a molar basis for a direct comparison, because the analysis of adsorption behavior may be misinterpreted when they are reported on a weight basis.

In general, our results indicate that there is an antagonistic effect of all co-ions in the adsorption process of all binary systems. For all metallic ions, $R_{q,i}$ is less than unity, indicating that the simultaneous presence of other ions reduced the metal removal, because of competition effects during the adsorption
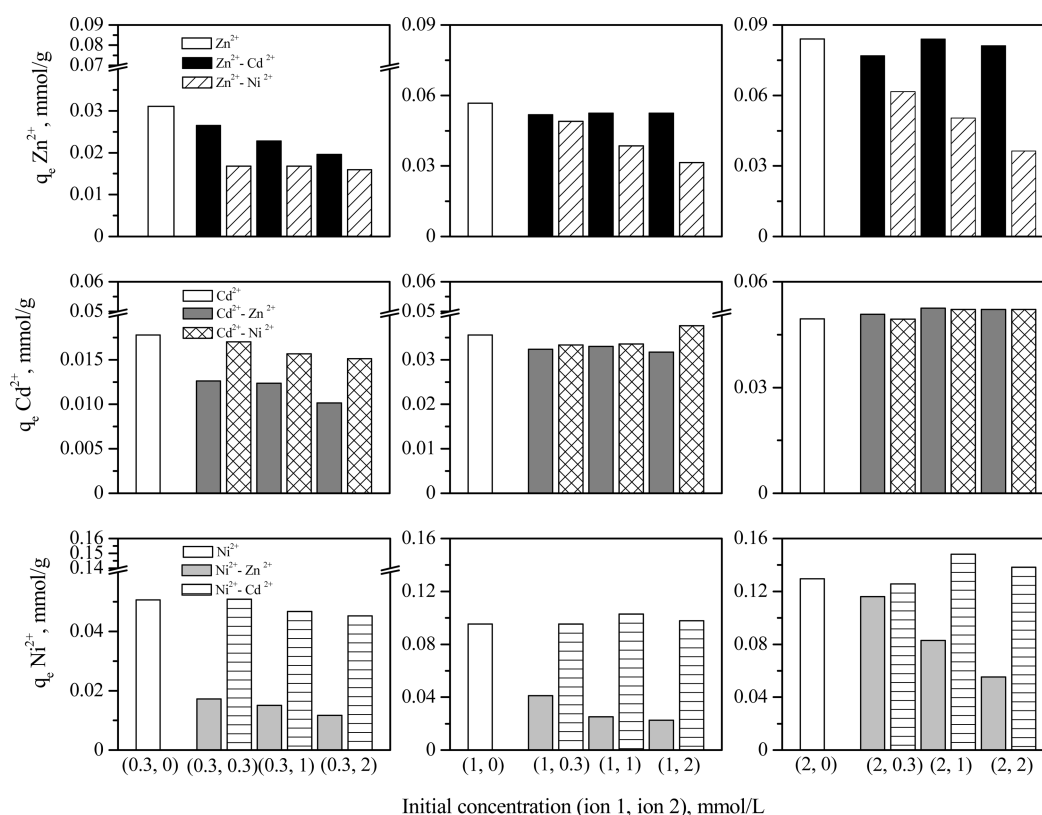
Figure 7. Results for competitive adsorption in binary mixtures of Zn^{2+}, Cd^{2+}, and Ni^{2+} ions onto modified bituminous carbon BC-3 at 30 °C and pH 5.

process. The increase of co-ion concentration may enhance the interaction between the metal ions in the aqueous phase and the adsorbent and, as a consequence, the competitive adsorption effect is dependent on the co-ion concentration; its magnitude is also different for the different heavy metals (see Figure 7). In particular, the adsorption of Cd^{2+} ions is not affected significantly by co-ion competition of Zn^{2+} and Ni^{2+} ions, especially at high Cd^{2+} initial concentrations. It is interesting to observe that Ni^{2+} adsorption using BC-3 decreases with Zn^{2+} concentration, while Zn^{2+} uptake decreased significantly when Ni^{2+} ions are present. Overall, the metal uptake reduction ranged from 0.1% to 77% for the Ni^{2+} ion, from 3% to 57% for the Zn^{2+} ion, and from 0.1% to 43% for the Cd^{2+} ion in all experiments performed.

4. CONCLUSIONS

Our study shows that the adsorption properties of commercial carbons can be significantly improved for the removal of heavy metals, using, as an activation agent, a calcium solution extracted from egg shell in combination with an acid treatment using H_3PO_4. It appears that the improvement of adsorption properties of these modified carbons relies on the formation of calcium phosphate on the adsorbent surface, which may favor the presence of complexation reactions that increase the removal of heavy-metal ions. Generally, the adsorption capacities of modified carbons can be an order of magnitude higher than those obtained using raw commercial adsorbents. On the other hand, the effect of co-ions in multicomponent adsorption of heavy metals using a bituminous carbon modified with egg shell wastes has been studied. Results indicate that the adsorption of Cd^{2+}, Zn^{2+}, and Ni^{2+} ions is affected by the co-ion competition,

especially at high metal concentrations. Overall, the metal uptake reduction may range from 0.1% to 77%, depending on the binary system under study.

In summary, this study provides new insights to develop alternative adsorbents with selective properties for the removal of metallic ions from wastewaters using low-cost reagents such as egg shell wastes. Further studies will be focused on the application of these calcium-modified adsorbents using packed-bed columns for the treatment of wastewater polluted by heavy-metal ions.

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