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Alkaline Pre-extracted Chestnut Shell As A Natural Adsorbent: Optimization Of Phenol Removal

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Adsorption of phenol from aqueous solutions on chestnut (*Castanea sativa*) shell, pre-extracted with alkali and pretreated with formaldehyde in acid medium was studied. An incomplete 3^3 factorial design was applied to investigate the influence of the phenol concentration (0.01-0.255-0.5 g L^{-1}), temperature (10-35-60ºC) and pH (2.5-6.0-9.5) on the amount of phenol adsorbed and on the adsorption percentage. Statistical analysis of the results showed the significance of the individual factors, their interactions and quadratic effects on the adsorption process. The best conditions for phenol removal were the pH 2.5 and a temperature of 50ºC for all the initial concentrations essayed.

1. Introduction

Phenolics belong to the group of priority pollutants to be removed from water and wastewaters. The presence of phenolic compounds in waters is undesirable because of their toxicity to human health.

The use of low-cost adsorbents obtained from natural wastes as a replacement for conventional methods of removing contaminants has attracted the attention of researchers. However, the use of unmodified wastes, in general, has several problems such as low adsorption capacity and high chemical and biological oxygen demands and high total organic carbon due to the release of soluble organic compounds contained in the residues (Ngah and Hanafiah, 2008). Therefore, these materials need to be modified or treated before being applied. Several chemicals such as base solutions, concentrated sulphuric acid, organic acid solutions, oxidizing agents, mineral salts and formaldehyde have been used to increase the adsorption capacity (Vázquez et al., 1994, 2007; Taty-Costodes et al., 2003; Batzias, 2004; Ngah and Hanafiah, 2008).

Chestnut shell from the *Castanea sativa* species is generated as a waste during the peeling of chestnut to produce food derivatives. In a previous work (Vázquez et al., 2009), cadmium ions and phenol adsorption on acid-formaldehyde pre-treated chestnut shell was optimized; however, the adsorption capacities were quite low, especially in the case of cadmium adsorption.

Phenolic compounds extracted from chestnut shell with alkaline compounds under different conditions were analyzed in a previous work, in order to establish their properties for different potential applications including: their use as phenol substitutes

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in the formulation of adhesives for wood derivatives, as chrome substitutes in leather tanning, and as a source of antioxidants compounds (Vázquez et al., 2008). Extraction process generated a solid waste, which could be recycled and re-used. Thus, in this work, alkali pre-extracted chestnut shell was used as a low-cost adsorbent for the removal of phenol from aqueous solutions. In order to optimize the adsorption process, an incomplete 3^3 factorial design was applied to investigate the individual and interactive effects of the initial concentration, temperature and pH on the shell capacity for removing phenol and on the adsorption percentage.

2. Materials And Methods

2.1 Adsorbent preparation

Chestnut shell supplied by a food factory (Marrón Glacé, S.L., Ourense, NW of Spain) was air-dried till equilibrium moisture content (approximately, 18% w/w), ground in a hammer mill and after classified, the fraction with particle sizes between 0.1 and 2 mm was selected.

The extraction experiment was carried out in a 2-l Pyrex glass reactor with mechanical stirring and temperature control. Chestnut shell and water at a solid/liquid ratio of 1/10 (w/w) were mixed at room temperature, heated and, once the selected temperature was attained (90ºC), the alkali was added (Na_2SO_3 1.5% and NaOH 3%, % o.d. shell) and contact time begun to run. After one hour, the suspension was vacuum filtered and the solid residue was washed with water and dried at room temperature.

In order to polymerise and immobilise the water-soluble phenolic compounds, the pre-extracted shell was treated with formaldehyde in acid medium according to Vázquez et al. (1994).

The natural pH of the alkali pre-extracted chestnut shell (around 7.0) was determined by stirring 1 g of shell in 100 mL of distilled water for 24 h.

2.2 Statistical design of experiments

An incomplete 3^3 factorial design (Box-Behnken model) was employed (Table 1) to study the influence of initial adsorbate concentration (X_1, 0.01-0.255-0.5 g L^{-1}), temperature (X_2, 10-35-60ºC) and pH (X_3, 2.5-6.0-9.5) on the amount of adsorbed contaminant (Y_1, mg adsorbed/g of chestnut shell) and on the adsorption percentage (Y_2, %). Twelve experiments were required and all of them were done in duplicate. The following variables were kept constant: solid/liquid ratio, 1/50 (g mL^{-1}); contact time, 8 days (the optimum contact time for attaining adsorption equilibrium determined in previous experiments), and particle size between 0.1 and 2 mm.

Multiple regression analysis using SPSS 13.0 software was employed to fit the experimental data with polynomials of the form of Equation 1:

$$Y_j = a_{0j} + a_{1j} X_1^* + a_{2j} X_2^* + a_{3j} X_3^* + a_{12j} X_1^* X_2^* + a_{13j} X_1^* X_3^* + a_{23j} X_2^* X_3^* + a_{11j} X_1^{*2} + a_{22j} X_2^{*2} + a_{33j} X_3^{*2} \quad (1)$$

where Y_j is the predicted response, X_i^* is the coded value of the independent variable: -1 (low level), 0 (central point) and 1 (high level), a_{0j} is a constant, a_{ij} is the ith linear coefficient, $a_{ikj}(i \neq k)$ is the linear-by-linear interaction between the input variables and a_{iij} is the quadratic coefficient.

All main factors and interactions that presented a probability value lower than 0.1 were considered statistically significant. The validity of the equations obtained was verified

by application of the F test, analysing the correlation coefficients (R^2 and adjusted R^2) and by comparison between the calculated and experimental values of the Y_j.

2.3 Adsorption experiments

Phenol solutions were prepared with reagent grade phenol (Scharlau Chemie, Barcelona, Spain).

Batch adsorption experiments were conducted in a series of Erlenmeyer flasks covered with Parafilm® to prevent contamination. Fifty milliliters of solution of known concentration and pH were put in contact with 1 g of pre-treated chestnut shell, and placed in a water bath shaker maintained at 90 rpm at the desired temperature. Once the adsorption process was completed (8 days), the solution was filtered using glass microfibre filter paper and analyzed for remaining phenol concentrations by gas chromatography (HP 5890 Series II Gas cromatograph, USA) (Vázquez et al., 2007). All measurements were done in triplicate and the results averaged.

A kinetic experiment was performed at an initial phenol concentration of 0.01 g L^{-1}, natural pH and a temperature of 25ºC to determine the contact time to reach the adsorption equilibrium. The pH adjustments of the solutions were made with 0.1 M H_2SO_4 or 0.1 M NaOH using a MP230 pHmeter (Mettler-Toledo, Switzerland).

3. Results And Discussion

Phenol uptake capacity of the alkali extracted chestnut shell pre-treated with formaldehyde was determined as a function of time to determine the optimum contact time for the adsorption of phenol on the shell. Figure 1 shows the time course of the adsorption process together the previous results obtained for the natural chestnut shell pre-treated with formaldehyde for an initial phenol concentration of approximately 10 mg L^{-1} at 25ºC and natural pH.

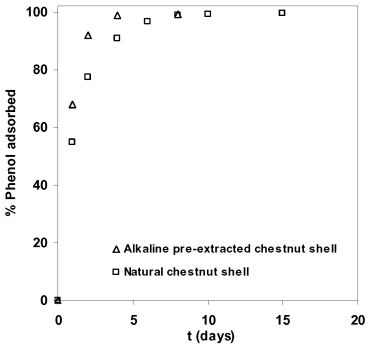

Figure 1. Effect of contact time on the adsorbed phenol percentage by alkali pre-extracted and natural chestnut shell (10 mg L^{-1}; 25ºC; natural pH)

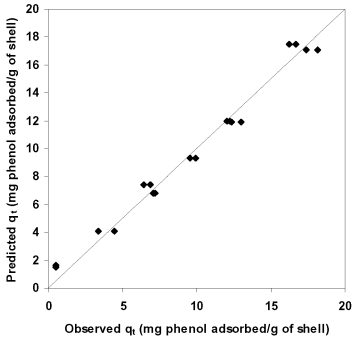

Figure 2. Predicted vs. experimental values for adsorption capacity of alkali pre-extracted chestnut shell for the removal of phenol

Both materials exhibited a similar maximum value of the adsorbed phenol percentage, nearly 100%. However, the phenol adsorption process on alkali extracted chestnut shell was faster than that on natural chestnut shell. As an example, a 68.3% of the maximum value was reached in one day for the alkaline shell whilst only a 55.4% was obtained for the natural shell. In order to compare the results for both materials, the contact time selected for the equilibrium experiments was extended to 8 days, the time in which more than 99% of the removal was reached.

Table 1 shows the experimental results obtained for the adsorption capacity of alkali pre-extracted shell and the adsorption percentage of phenol. It was observed that in all the conditions essayed, the amount of phenol adsorbed by the alkali pre-extracted shell was similar to the value obtained for the natural chestnut shell (Vázquez et al., 2009), although the highest value of the adsorption capacity was slightly lower (18.1 mg g^{-1} versus 21.9 mg g^{-1}).

The coefficients of the models (Equation 1) were determined and those found to be significant together with the different statistical parameters employed (i.e. the coefficient standard deviation (SD) and significance and the model correlating parameters (R^2 and adjusted R^2), standard deviation and significance) are presented in Table 2. Relatively high correlation coefficients were obtained for both dependent variables and Figure 2 shows, a good fit between the calculated and the experimental results for the sorption capacity of the alkali pre-extracted chestnut shell.

Table 1. Factorial design and experimental results for the dependent variables

	Independent variables			Dependent variables	
Exp.	X_1^*	X_2^*	X_3^*	Y_1 (mg g^{-1})	Y_2 (%)
1.1	-1	-1	0	0.38	77.85
1.2	-1	-1	0	0.38	76.89
2.1	1	-1	0	6.44	26.79
2.2	1	-1	0	6.86	28.56
3.1	-1	1	0	0.49	98.87
3.2	-1	1	0	0.49	99.46
4.1	1	1	0	16.25	67.64
4.2	1	1	0	16.71	69,55
5.1	-1	0	-1	0.51	99.46
5.2	-1	0	-1	0.51	99.66
6.1	1	0	-1	18.14	70.56
6.2	1	0	-1	17.37	67.58
7.1	-1	0	1	0.51	99.15
7.2	-1	0	1	0.51	99.35
8.1	1	0	1	12.38	48.16
8.2	1	0	1	12.98	50.50
9.1	0	-1	-1	7.06	56.64
9.2	0	-1	-1	7.18	57.69
10.1	0	1	-1	12.02	96.53
10.2	0	1	-1	12.24	98.32
11.1	0	-1	1	3.38	27.14
11.2	0	-1	1	4.43	35.54
12.1	0	1	1	9.96	79.98
12.2	0	1	1	9.58	76.89

Table 2. Coefficients of the models (Eq. 1) and the statistical parameters establishing their validity

	Y_1			Y_2		
	Coefficient	SD	Sig.	Coefficient	SD	Sig.
a_0	6.000	0.336	0.000	79.303	1.714	0.000
a_{1j}	6.461	0.237	0.000	-20.084	1.212	0.000
a_{2j}	2.602	0.237	0.000	18.759	1.212	0.000
a_{3j}	-1.332	0.237	0.000	-8.108	1.212	0.000
a_{12j}	2.432	0.336	0.000	4.781	1.714	0.013
a_{13j}	-1.269	0.336	0.001	-4.858	1.714	0.011
a_{23j}	-	-	-	-	-	-
a_{11j}	-	-	-	-	-	-
a_{22j}	-	-	-	-12.156	2.100	0.000
a_{33j}	2.046	0.411	0.000	-	-	-
R^2		0.983			0.973	
Adj. R^2		0.977			0.963	
SD		0.949			4.849	
Sig		0.000			0.000	

By analyzing the results in Table 2, it could be observed that, at a 90% confidence level, the three variables studied are equally significant both on phenol uptake (Y_1) and on adsorption percentage (Y_2). The interactions C_0·T and C_0·pH were also significant, together with the quadratic factors pH·pH for the amount of phenol adsorbed and T·T for the adsorption percentage.

The response surfaces for phenol adsorption capacity as a function of initial concentration and temperature at the lowest pH, and for the adsorption percentage as a function of temperature and pH at the lowest initial concentration are presented in Figures 3 and 4, respectively. As found in previous work (Vázquez et al., 2009), at all the pHs essayed, the increase in both initial phenol concentration and temperature led to an increase of the sorption capacity of the shell (Figure 3), although the higher values were found at low pH (from 1.5 to 22.1 mg g^{-1} for pH = 2.5 and from 1.4 to 16.9 mg g^{-1} for pH = 9.5). Additionally, the influence of temperature was low operating at low phenol initial concentration. With respect to the % of phenol adsorbed (Figure 4), low pH and high temperature increased the percentage of phenol adsorbed and, as it could be expected, the highest values were obtained at the lowest initial concentration. Above a certain temperature (which decreased with decreasing initial concentration), an initial increasing in adsorption % with increasing temperature was followed by a decrease.

The analysis of the results obtained has revealed that the best conditions for phenol adsorption by alkali pre-extracted chestnut shell were pH = 2.5 and 50ºC. Values of the adsorption capacity from 1.8 to 20.7 mg g^{-1} were obtained in the range of phenol initial concentration studied.

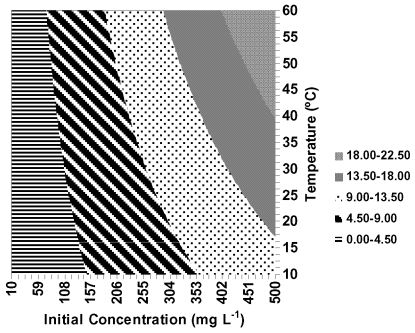

Figure 3. Dependence of phenol adsorption capacity (Y_1) of alkali pre-extracted chestnut shell on initial concentration (X_1) and temperature (X_2) at a pH = 2.5

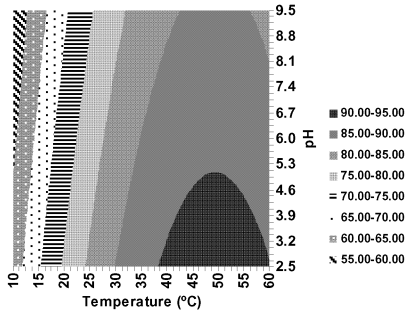

Figure 4. Dependence of adsorbed phenol percentage (Y_2) by alkali pre-extracted chestnut shell on temperature (X_2) and pH (X_3) at an initial concentration of 10 mg L^{-1}

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