



Review

Kinetic and equilibrium studies of cobalt adsorption on apricot stone activated carbon

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ABSTRACT

The activated carbon from apricot stone with H_3PO_4 and its ability to remove Co^{2+} are reported. The FTIR spectroscopy brings insights on interactions between the functional groups of the carbon and Co^{2+} . Adsorption studies are carried in batch mode by varying the initial Co^{2+} concentration and pH. A comparison of two kinetic models on the overall adsorption rate shows that the system is described by the pseudo-second-order kinetic model. The Freundlich model fits the data with a monolayer adsorption capacity of 111.11 mg/g at pH 9. The enthalpy and free energy indicate an endothermic and not spontaneous process.

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1. Introduction

Effluents contaminated by heavy metals are commonly produced from many kinds of industrial processes. Heavy metal residues in contaminated habitats may accumulate in microorganisms, aquatic flora and fauna, which in turn, may enter into

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the human food chain and results in health problems [1,2]. Cobalt is an oligo element that is essential for human health since it is a part of vitamin B12. However, higher concentration of cobalt may cause low blood pressure, paralysis, diarrhoea, lung irritation and bone defects [3]. So its removal of cobalt from aqueous solution is necessary because of frequent appearance of this metal ion in wastewaters from industrial activities, including metallurgical, mining, paints, electronics and pigments [4]. Among various treatment technologies, the adsorption onto activated carbon is one of the most effective and reliable physicochemical methods [5,6]. However, commercially available activated carbons are usually derived from coal or wood, and therefore are relatively expensive [7]. Hence, there is a need to produce low cost and effective carbons that can be applied for the water pollution control. A wide variety of inexpensive materials, have been exploited for the cobalt removal from aqueous medium, including lemon peel [1], peat [4], palygorskite [8], cross linked calcium alginate beads [9], chitosan-coated perlite beads [10], crab shell [11], kaolinite [12], bentonite [13], sepiolite [14], bagasse pith [15] and activated carbon [16,17]. Agricultural by-products exist in large amounts and about 20,000 tonnes of apricot stones per year are produced in Algeria [18], which represent consequently a solid pollutant to the environment (Table 1). Many years ago these by-products were used as a fuel in rural areas but now the preparation of activated carbon is considerably encouraged. Apricot stone is a cheap precursor for activated carbon source. Therefore, it is important to evaluate its performance as adsorbent. The advantages of the adsorption reside in the simplicity operation, low cost compared to other separation methods and no sludge [19,20], the adsorption on activated carbon is an efficient and economic processes. This study deals with the adsorption ability of apricot stone activated carbon ASAC for the removal of cobalt from synthetic aqueous solutions. The influences of the operating parameters such as initial Co^{2+} concentration, pH, temperature, adsorbent dosage and particle size on ASAC is explored.

2. Experimental

2.1. Materials and methods

Analytical grade reagents are used in all experiments. $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (99%) is purchased from Merck company. Apricot stones obtained from Boumerdes region in (North Algeria), are air-dried, crushed and screened to obtain two fractions with geometrical mean sizes ranging from $63 \mu\text{m}$ to 2.5mm . 100 g of the selected fraction are impregnated with concentrated H_3PO_4 (85%) and dried by air. Then it is activated in a hot air oven at 250°C (4 h). The carbonized material is washed with distilled water to remove the free acid until the pH of the activated carbon reached 6.8 and dried at 105°C . The clean biomass is mechanically ground and sifted to get a powder of different particle sizes: <63 , $[63-80]$, $[80-100]$, $[100-200]$, $[200-315]$, $[315-800] \mu\text{m}$ and $[0.8-1]$, $[1-1.6]$, $[1.6-2] \text{mm}$.

Table 1
The state of apricot culture in 2006.

Country	Production (tonnes)	Area (ha)	Yield (%) (q/ha)
Turkey	370,000	64,000	57.813
Iran	285,000	32,000	89.063
Italy	244,048	29,287	126.54
Pakistan	215,000	29,000	74.14
Algeria	110,000	40,000	27.50

2.2. Determination of zero point charge pH(zpc)

The zero point charge pH(zpc) of ASAC, i.e. the pH for which the surface charge is zero, is determined using a procedure similar to that described previously [21]. 20 ml of 0.01 mol/L of KNO_3 solutions are placed in different closed conical flasks. The pH of each solution in each flask is adjusted to a value between 2 and 14 by adding HCl or NaOH solution. Then, 0.1 g of ASAC is added and the final pH is measured after 24 h under agitation at room temperature. The pH(zpc) is the point where the curve of final pH versus initial pH crosses the line at final pH = initial pH.

2.3. Batch mode adsorption studies

The effects of the experimental parameters such as, the initial Co^{2+} concentration (10–80 mg/L), pH (2–13.5), adsorbent dosage ($5-50 \text{g L}^{-1}$) and temperature (298–323 K) on the adsorptive removal of Co^{2+} ions is studied in a batch mode for a specific period of contact time (0–90 min). The stock solution is prepared by dissolving the accurate amount $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (99%) in distilled water, the other solutions are prepared by dilution. pH is adjusted with HCl (0.1 M) or NaOH (0.1 M). For the kinetic studies, desired quantity of ASAC is contacted with 20 ml of Co^{2+} solutions in Erlenmeyer flasks. The flasks are then placed on a rotary shaker at 250 rpm and the samples are taken at regular time intervals and centrifuged at 3000 rpm for 10 min. The Co^{2+} content in the supernatant is measured using flame atomic absorption spectrometry (FAAS, model Perkin Elmer 2380). The amount of Co^{2+} adsorbed by activated carbon q_t (mg/g) is calculated by using the following equation (A1):

$$q_t = \frac{[(C_o - C_t) \cdot V]}{m} \quad (\text{A1})$$

where C_o is the initial Co^{2+} concentration and C_t is the Co^{2+} concentrations (mg/L) at any time, V is the volume of solution (L) and m is the mass of the activated carbon (g).

The metal removal percentage can be calculated as follows Eq. (A2):

$$R(\%)_t = \left[\frac{(C_o - C_t)}{C_o} \right] \times 100 \quad (\text{A2})$$

Due to the inherent bias resulting from linearization of the isotherm model and kinetic model, the non-linear regression Root Mean Square Error (RMSE) test was employed as criterion for the quality of fitting [22]. The RMSE of a model is evaluated by (A3)

$$\text{RMSE} (\%) = \sum_1^n \left[\frac{(q_{e(\text{exp})} - q_{e(\text{cal})})^2}{n-2} \right]^{1/2} \quad (\text{A3})$$

where $q_{e(\text{exp})}$ (mg/g) is the experimental value of uptake, $q_{e(\text{cal})}$ is the calculated value of uptake using a model (mg/g), and n is the number of observations in the experiment (the number of data points).

The Sum of Error Squares (SSE, %) is one method which has been used in the literature to test the validity of each model that has been used. The SSE is given in Eq. (A4) [23]:

$$\text{SSE} (\%) = \sum_1^n \left[\frac{(q_{e(\text{exp})} - q_{e(\text{cal})})^2}{n} \right] \quad (\text{A4})$$

The smaller RMSE and SSE value indicates the better curve fitting.

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