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Efficient removal of Co(II) metal ion from aqueous solution using cost-effective oxidized activated carbon: kinetic and isotherm studies

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ABSTRACT

Oxidized activated carbon (OAC) was prepared from a waste mixture containing palm stem, paper, and plastic and used for the removal of Co(II) from aqueous medium. Adsorption was studied as a function of OAC dose (0.03–0.1 g), time (10–180 min), pH (2–6) and initial Co(II) concentration (50 mg L^{-1}). The maximum adsorption capacity was found 83.6 mg g^{-1} at pH 4. The adsorption process followed the Freundlich isotherm model and pseudo-second-order kinetics. The OAC showed better efficiency comparable with other reported adsorbents. The results suggested that the prepared OAC could be used as a cost-effective adsorbent for the Co(II) removal from aqueous solutions.

Keywords: Oxidized activated carbon; Adsorption; Co(II); Kinetic studies; Isotherm

1. Introduction

The discharge of wastewaters coming from various industries has led to an increase in metal ion pollution throughout the world [1–3]. Cobalt compounds are crucial in several industries, including paints, electronics, metallurgy, mining, nuclear power and pigments [4,5]. Cobalt is vital for human health because it is a part of vitamin B12 [6]; however, high concentrations of Co(II) have been shown to cause diarrhea, lung irritations, bone defects, paralysis, neurotoxicological disorders, carcinogenicity, genotoxicity and bronchial asthma [7–10]. To avoid the ecological and health problems, the removal of Co(II) from industrial wastewaters and natural streams has received growing attention in recent years [11]. There are some advanced methods that have been utilized for wastewater treatment, such as electrolysis [12], membrane technology [13–15], ion exchange [16,17,18], precipitation [19], solvent extraction [20,21] and adsorption/biosorption [22–28]. However, the widespread use of these methods has been limited because of the costs associated with these methods. The adsorption method has recently gained considerable attention because of its low cost and the feasibility of its use in various applications [29,30]. The idea of using agriculture by-products in the production of activated carbon (AC) to lower the process costs has emerged. Plenty of research has been conducted on the production of AC from by-products such as: date stones, peanuts, jute fibers, sawdust, used tires, almond husk and coconut shell [31–37] for the use in sewage treatment. The adsorption capacity of these by-products can be improved by an activation process, functionalization or surface impregnation [38,39]. Though, few studies have been already

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carried out in the area of Co(II) removal from aqueous solutions [40–42]. The WHO guidelines have stated a value of 0.05 mg L^{-1} as the maximum concentration of Co(II) allowed in wastewater reuse for irrigation [43]. Additionally, USEPA stated 0.05 mg L^{-1} as the suggested maximum level of Co(II) in the domestic water for irrigation [44]. Canadian Water Quality Guidelines and the Environmental Bureau of Investigation reported that the allowed level of Co(II) in irrigation water was 0.05 mg L^{-1} [45]. Therefore, the aim of the current study was to examine the possibility of using locally prepared oxidized activated carbon (OAC) as a low-cost adsorbent for the removal of Co(II) ions from aqueous solutions. The modification of AC was done by using nitric acid treatment. The effects of several parameters on the removal efficacy of Co(II) such as pH, OAC dose and time were investigated.

2. Experimental

2.1. Chemicals and raw materials

Co(II) nitrate hexahydrate ≥98% and nitric acid 70% were purchased from Sigma-Aldrich (St. Louis, MO, USA). AC was prepared by the co-pyrolysis of local wastes as described by Naushad et al. [46]. Water was purified with a Milli-Q water purification system (Bedford, MA, USA) with a specific conductivity of 18.2 mΩ cm. A stock solution of Co(II) nitrate was prepared, and it was further diluted using Milli-Q water. Samples were filtered through a 0.22-μm PVDF syringe filter (Membrane Solutions, Texas, USA).

2.2. Preparation of AC

The mixed wastes (palm stem, paper and plastic) were simultaneously co-pyrolyzed. In this process, the precursors are carbonized, impregnated and then activated for a fixed time. The pulverized palm stem, paper and plastic wastes were mixed with a ratio of 1:1:1 by weight and initially carbonized at 400°C for 2 h. The char that was produced was chemically activated with $Ca(OH)_2$ solution. The 40 g char was mixed with 200 mL of a 2 mol L^{-1} $Ca(OH)_2$ solution. The slurry was kept in an ultrasonic bath at 40°C for 1 h to achieve maximum penetration of the solute molecules into the texture of the waste materials. The resulting homogenous slurry was dried at 110°C for 20 h, and the resulting impregnated char was activated at 500°C for 45 min. The obtained mixed-waste AC was cooled and then washed with a 0.2 mol L^{-1} HCl solution for 30 min to remove the surface ash. Subsequently, the sample was washed with distilled water numerous times to ensure the complete removal of the remaining acid (to reach a final pH of 6–7). After washing, the samples were dried, cooled and sieved through a 100-mesh filter (US Standard), and stored in airtight bottles for further study.

2.3. Modification of AC to oxidized activated carbon (OAC)

The prepared AC was oxidized using concentrated nitric acid as described in Carrasco et al. [47]. Briefly, 100 mL of concentrated nitric acid was added to 5 g of AC, and the mixture was shacked for 10 h, and then the OAC was filtered and washed several times with distilled water.

2.4. Characterization

For the scanning electron microscopy (SEM) investigations, samples were mounted on an aluminum stub, covered with a thin gold film, and examined through a JEOL microscope (JSM-6380 LA, Japan). The Fourier transform infrared spectroscopy (FTIR) spectra of the samples were obtained from a Nicolet 6700 FT-IR spectrometer (Thermo Scientific, USA).

2.5. Adsorption batch experiments

To assess the efficiency of OAC to remove the Co(II) from aqueous solutions, batch adsorption experiments were accomplished [48]. The concentrations of the metal ions in the solution were analyzed using flame atomic absorption spectrometer (PinAAcle 900 AA, PerkinElmer, USA) with oxidizing flame stoichiometry (air/acetylene) and slit width of 0.2 nm. The amounts of metal removed by OAC were calculated using Eq. (1):

$$q_e = \left[\frac{C_0 - C_e}{M}\right] \times V \tag{1}$$

3. Results and discussion

3.1. Characterization

Herein, the OAC prepared from local waste was treated with HNO_3 to increase the functionalization of the OAC surface with carboxylic groups to act as active sites for the removal of Co(II) from aqueous medium. The surface morphology of the AC and the OAC were examined by SEM. The results revealed porous surfaces with tube-like structures in the AC (Figs. 1(A) and (B), while after oxidation, the morphology changed to rough surfaces with multiple layers due to the reaction with HNO_3 (Figs. 1(C) and (D)).

To further identify the surface functional groups, FTIR spectra were obtained for the AC and the OAC. The results showed that AC possessed limited peaks related to –OH groups at 3,436 cm^{-1} and carbonyl groups at 1,704 and 1,604 cm^{-1} (Fig. 2(a)). However, for the OAC, some additional peaks were detected at 1,531 and 1,340 cm^{-1}, which might be due the nitro groups. The peak at 1,240 cm^{-1} was due to C–O stretching of the carboxylic groups (Fig. 2(b)). These results established that the surface of OAC was richer with functional groups that are expected to improve the adsorption capacity.

Gemini VII 2390 V1.03 (Micromeritics Instrument Corp., USA) was used to find the Brunauer–Emmett–Teller (BET) surface area and pores of AC and OAC via nitrogen adsorption–desorption isotherms as shown in Table 1. The surface area was found 234 m^2 g^{-1} for the OAC while it was 638 m^2 g^{-1} for AC. The loss of surface area after oxidization may be attributed to the effect of nitric acid oxidation, which breaks some of AC cavities during functionalization process. However, the surface area was less in case of OAC, but the presence of –COOH groups allow the strong interaction with the metal ions and facilitate their separation. Hence, the adsorption capacity of OAC for the adsorption of Co(II) was higher than that of AC.

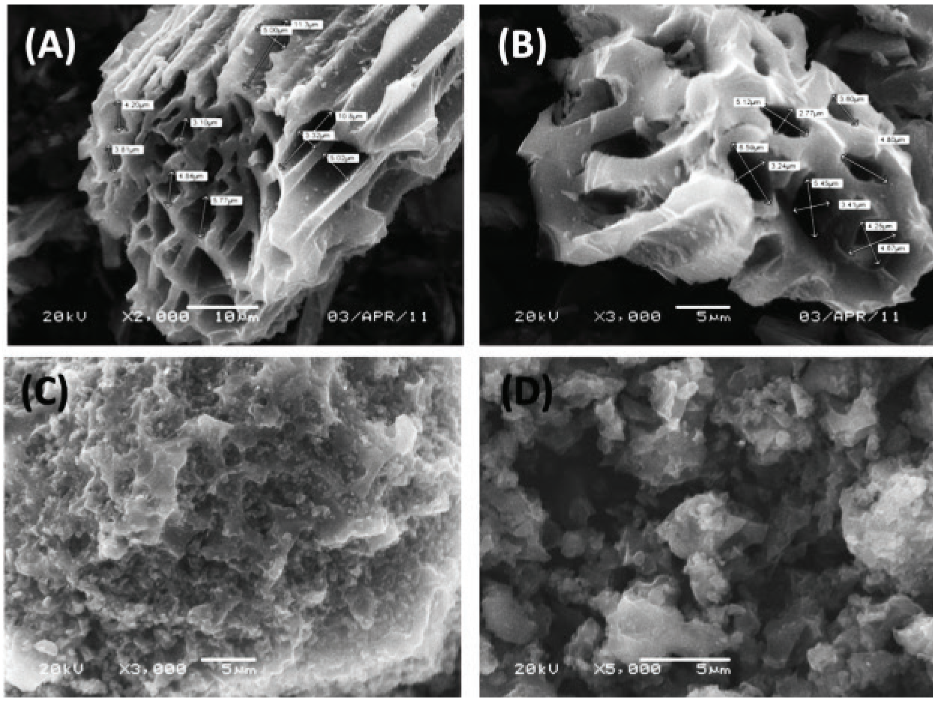

Fig. 1. SEM images of: (A) and (B) AC, and (C) and (D) OAC at different magnifications.

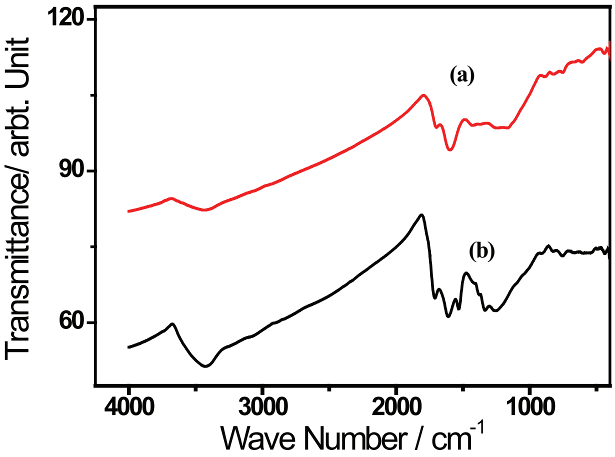

Fig. 2. FTIR spectra of: (a) AC and (b) OAC.

3.2. Adsorption studies

The initial pH of the solution is a main factor to be considered during the adsorption studies [41,49–51]. The effect of the solution pH values between 2 and 6 at room temperature on the uptake of Co(II) ion with fixed initial concentration of 50 mg L^{-1} onto OAC was examined. The adsorption capacity was 78.3 mg g^{-1} at pH 2.0, which was increased with increasing pH and reached a constant value 84.0 mg g^{-1} at pH 4 and then it became constant (Fig. 3(a)). The low adsorption capacity in the acidic medium was due to the large amounts of hydrogen ions adsorbed at the surface of OAC at low pH, which might electrostatically repel the positively charged metal ions and prevent their approach to the OAC surface [1]. When the pH was increased, the concentration of hydronium ions decreased, and the positively charged metal ions adsorbed onto the free binding sites. The maximum uptake of Co(II) was found at pH 4.0, which was considered to be the optimum value and was used in all further experiments.

Table 1
Physical properties of oxidized (OAC) and unoxidized activated carbon (AC) samples

Parameter	AC	OAC
S_{BET} (m^2/g)	638.42	234.15
TPV (cm^3/g)	0.35	0.15
APD (Å)	21.65	23.13

Note: TPV – total pore volume; APD – average pore diameter.

Fig. 3(b) shows the removal percentage of Co(II) by OAC at different time intervals. As given, the adsorption of Co(II) was rapid in the starting, and equilibrium was reached at 120 min where the adsorption was 74.11 mg g^{-1}. The fast adsorption of Co(II) at beginning was possibly due to the high availability of active sites at the surface on OAC. Since these sites were mostly occupied by the Co(II) as well as the repulsion between the adsorbed Co(II) on the OAC surface and Co(II) in the solution phase, the adsorption rate was decreased.

The influence of OAC dose on the adsorption capacity of Co(II) was verified for doses between 0.03 and 0.1 g (Fig. 3(c)). Initially, the adsorption capacity was decreased sharply with increasing the OAC dose. The adsorption capacity of Co(II) was decreased from 27 to 9 mg g^{-1} with increasing the adsorbent dose from 0.03 to 0.1 g for an initial Co(II) concentration of 200 mg L^{-1}. The decrease in adsorption capacity with increase in the adsorbent dose is mainly due to the increase of free adsorption sites in the adsorption reaction. These results

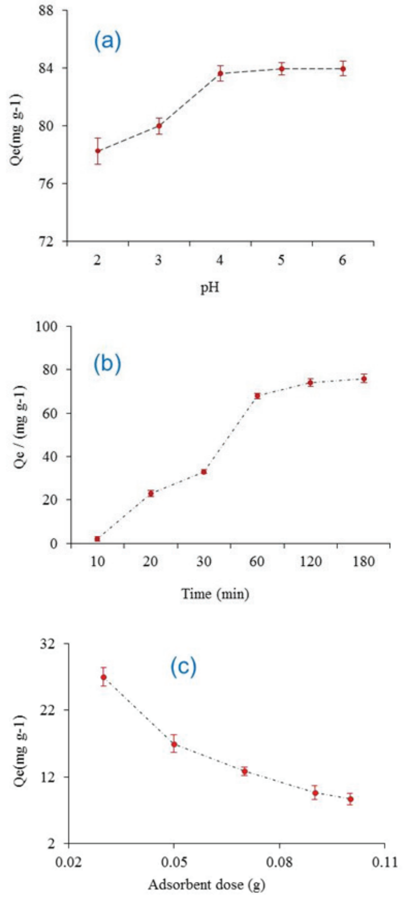

Fig. 3. Removal of Co(II) metal ions using OAC at different (a) pH, (b) time and (c) OAC dose at temperature 25°C and initial concentration of 42 mg L^{-1}.

corresponded with results obtained by other investigators for the adsorption of Co(II) onto ion-exchange resins [1].

3.3. Kinetic modeling in a batch system

Information about the kinetics of the analyte uptake is necessary to choose the optimum operating batch processing conditions. A contact time of 120 min was adequate to reach equilibrium, and there was no significant change in the adsorption capacity with longer contact times. Therefore, the values of the adsorbed and unadsorbed Co(II) levels after 120 min were specified as the equilibrium values.

Pseudo-first-order and pseudo-second-order models were applied to the data to analyze the adsorption kinetics of Co(II) ions. The first-order Lagergren equation is commonly applied for the adsorption of Co(II) from an aqueous solution [52], and the linear form of the equation is represented as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{2}$$

The value of k_1 was calculated from the slope of the graph of $\log(q_e - q_t)$ vs. time t (Fig. 4(a)).

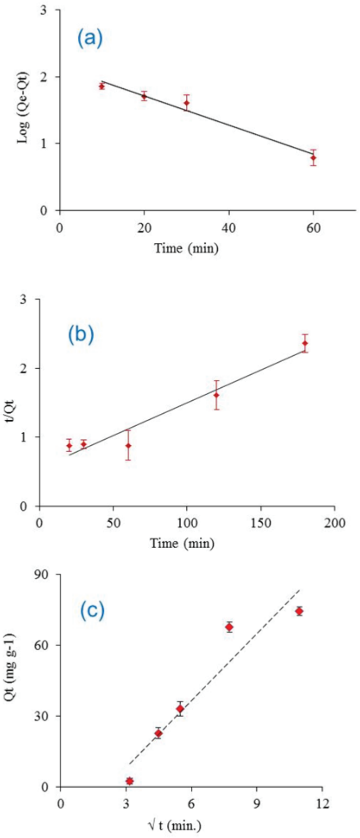

Fig. 4. Kinetic models for Co(II): (a) pseudo-first-order, (b) pseudo-second-order and (c) intraparticle diffusion.

Pseudo-second-order equation [53] can be given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

The values of k_2 and q_e were calculated from the intercept and slope of the plot t/q_t vs. time t, respectively (Fig. 4(b)).

The intraparticle diffusion model is given as [54]:

$$q_t = k_{id} t^{1/2} + C \tag{4}$$

The values of k_{id} and C were evaluated from the slopes and intercepts of the plot q_t vs. $t^{1/2}$ (Fig. 4(c)). The parameters for these three models are shown in Table 2. The high correlation coefficient (R^2) values for pseudo-first-order model demonstrated that the data conformed well to the pseudo-first-order rate model. The values of k_{id} (9.4) and the negative value of C (–20) showed that the adsorption process is affected by more than one mechanism including diffusion and surface interaction adsorption due to presence of OH and COOH groups.

3.4. Modeling of the isotherms

The adsorption isotherm was obtained by varying the initial concentration of Co(II) ions from 10 to 600 mg L^{-1}. Two different adsorption isotherm models, the Langmuir and Freundlich models, were applied for estimation of the results [55].

The Langmuir isotherm model states that the adsorbate forms a monolayer over a homogenous surface of the adsorbent with a fixed number of equal sites and no contact between the adsorbate molecules [56]. The Langmuir equation (Eq. (5)) can be given as [57]:

$$\frac{C_e}{q_e} = \frac{1}{(q_{\max} \times b)} + \frac{C_e}{q_{\max}} \tag{5}$$

The correlation coefficient, R^2, for Co(II) ions adsorption onto OAC was 0.302, and this value showed that the adsorption was not fit by the Langmuir isotherm (Fig. 5(a)).

The Freundlich isotherm is commonly used to define the adsorption characteristics for heterogeneous surfaces [58] as it considers heterogeneous energies on the surface. The Freundlich isotherm equation is given as:

$$\log q_e = \log K_F + \frac{1}{n} C_e \tag{6}$$

Fig. 5(b) shows the graph of logq_e vs. logC_e, and it should be linear with the intercept and slope corresponding to logK_F and $1/n$, respectively.

Table 2
The adsorption kinetic model rate constants (initial concentration of 600 mg L^{-1}, 25°C and pH 4)

Reaction order	Rate constant (k)	q_e (mg g^{-1})	R^2
Pseudo-first order	4.99×10^{-2}	139	0.988
Pseudo-second order	1.6×10^{-2}	105	0.995
Intraparticle diffusion	9.4	–	0.900

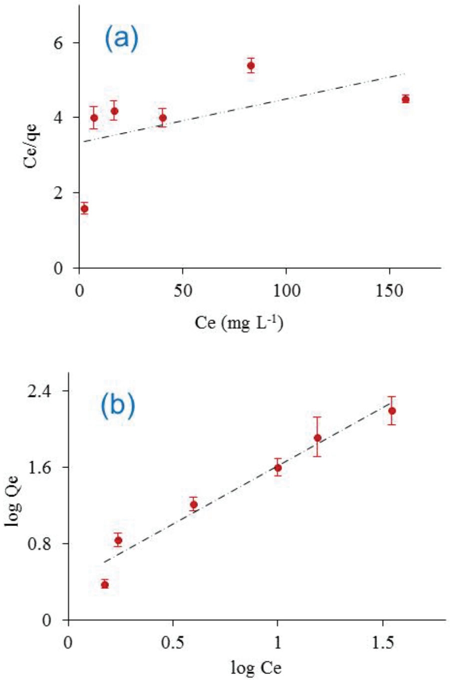

Fig. 5. Isotherms models for Co(II): (a) Langmuir and (b) Freundlich (OAC with mass 0.03 g, initial concentration of Co(II) ions from 10 to 600 mg L^{-1}, temperature 25°C, pH 4).

From these experimental results, the correlation coefficient (R^2) obtained from the linear regression was better fit for the Freundlich model (R^2 = 0.957) compared with the Langmuir model (R^2 = 0.302) over the complete range of concentrations. Additionally, the value of n was more than unity (Table 3), which proved that the adsorbate was favorably adsorbed onto the adsorbent [59].

A comparisons of the adsorption capacities $q_{\max}$ (mg g^{-1}) for the different types of adsorbents [6,60–70] previously used for the removal of Co(II) from aqueous medium is given in Table 4. It should be noted that the Co(II) adsorption capacity on OAC was better than that of other reported adsorbents. These data proved that OAC is a good adsorbent for the removal of Co(II) from aqueous medium.

Table 3
Isotherm model constants (initial concentration of 600 mg L^{-1}, 25°C and pH 4)

Model	Constant	OAC
Langmuir	K_L	30.2×10^{-2}
	b	0.35×10^{-2}
	$q_{\max}$	86.2
	R^2	0.302
Freundlich	K_F	53.3×10^{-2}
	n	1.278
	R^2	0.957

Table 4
Comparisons of maximum monolayer adsorption capacities of Co(II) using various adsorbents

Adsorbent	$q_{\max}$ (mg g^{-1})	Reference
Synthetic hydroxyapatite	20.2	[6]
Marine green algae	46.1	[60]
Almond green hull	45.5	[61]
Ceralite IRC-50	58.8	[62]
AC	13.9	[40]
Esterified coir pith	34.1	[63]
Crab shell	20.5	[64]
Chitosan	76.3	[65]
Natural zeolites	14.4	[66]
Kaolinite	0.9	[67]
Natural vermiculite	49.5	[68]
Cation-exchange resins IRN77	86.2	[41]
Synthetic hydroxyapatite	17.7	[69]
Anaerobic granular sludge	12.3	[70]
OAC	83.6	This study

4. Conclusions

From the aforementioned investigations, it is clear that the scavenging of Co(II) by OAC can be applied successfully for the wastewater treatment. The maximum adsorption capacity was 83.6 mg g^{-1} for the adsorbent dose of 0.03 g and an initial Co(II) concentration of 42 mg L^{-1} at pH 4. The adsorption kinetics of Co(II) ions onto OAC were in good agreement with pseudo-first-order model. The kinetic data were well defined by the pseudo-first-order kinetic model. Adsorption isotherm studies revealed that the adsorption of Co(II) was better fit by Freundlich isotherm model rather than Langmuir model assuming the multilayer adsorption of metal ions onto the OAC surface. The adsorption intensity value (n = 1.27) of the Freundlich model indicated promising adsorption of Co(II) onto the OAC. Overall, this study demonstrated that OAC derived from local waste was a potential candidate for the removal of Co(II) from water samples, thus indicating a commendable substitute for the commercially accessible AC.

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