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Adsorption of Iron(II) and Cadmium(II) Ions Separately using Carbon Materials from Hazelnuts and Walnuts Waste Shells

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An inexpensive and efficient carbon materials as adsorbents were obtained from hazelnuts and walnuts waste shells. Their adsorption capacity with respect to iron(II) and cadmium(II) ions was studied. The results show that the carbonaceous material obtained from hazelnut shells has the best adsorption capacity with respect to Fe^{2+} & Cd^{2+}, which is not inferior to commercial activated carbon. Studies of iron (II) and cadmium(II) of various concentrations showed that within 20-30 min, the best extraction rate and adsorption for both metal ions were achieved with a solution of 0.0025 M. For Fe^{2+} ions, the adsorption value and extraction rate have achieved good results at pH = 3-5, and for Cd^{2+} ions at pH = 5-6. Furthermore, the prepared adsorbent exhibited the excellent adsorption abilities even in the presence of various metal ions and successfully used as sorbents for drinking and wastewater treatment without modification and activation.

Keywords: Adsorbent, Hazelnuts shell, Walnuts shell, Heavy metals, Water pollution.

INTRODUCTION

Water pollution by heavy metals is one of the most acute environmental problems. Their presence of these metal ions in water causes various damages to health, so improving water quality is an important task in connection with the safety of public health [1-3]. Heavy metals are characterized by high toxicity; in terms of toxicity to the human body, they are second toxicants after pesticides.

Existence of great amount of heavy metals in waste waters may be caused by accumulation of various waste as a result of human activities, industrial accidents, *etc.* [4,5]. Based on the existing complex environmental background, control of concentration of heavy metals in water is very important.

Water purification is associated with high financial costs. Among modern methods of water purification, the sorption method has an advantage [6-8]. The efficiency of extracting heavy metal ions from water is determined by the quality of the sorbent. In this regard, carbonaceous materials and their modified forms are of great interest, although these materials have a high cost [9-11].

Cellulose is a natural polymer and agroindustrial waste is a good source of cellulose. By using household waste containing cellulose fibres, a renewable and inexpensive adsorbents can be obtain for the wastewater treatment [12,13]. Tatishvili *et al*. [14] developed a method for obtaining high-quality carbon material (soot) from used tyres. Further, they used this method to develop another method [15] for preparing sorbents with developed surfaces using cellulose fibre-containing secondary household wastes, such as hazelnut and walnut shells, apple and peach pods and wood sawdust. This technology can be used to process plastic and cellulose containing wastes and obtain cheap carbonaceous materials. The obtained carbon sorbents were used for removing Co^{2+}, Cu^{2+} and Pb^{2+} heavy metal ions from wastewater [16-19]. Among these sorbents, the carbon materials obtained from hazelnut and walnut shells exhibited the best adsorption capacities; since then, several studies have focused on these materials.

In this research, the sorption characteristics of carbon materials obtained from the hazelnut and walnut waste shells were applied for removing iron(II) and cadmium(II) ions separately. The prepared adsorbent was found to be effective adsorbents for the removal of both heavy metals.

EXPERIMENTAL

The carbon materials were obtained from the hazelnut and walnut waste shells as per reported method [15]. Briefly, the walnut and hazelnut shells were loaded into a stainless steel reactor, which was made up of stainless steel and served as a catalyst. Under carbon dioxide atmosphere, the shells were heated at a consistently increasing temperature, 12-15 ºC/min, until a final temperature of 750-850 ºC was attained, obtaining the walnut and hazelnut shells as carbon materials (Yield: 19-30%). The leftover reagent and the gases formed during the heating process were both recovered, pumped back into the reactor and employed as energy sources.

Characterization: The physico-chemical properties of carbon materials obtained from the hazelnut and walnut shells, *viz*. BET surface areas (ASAP 2020 Plus porometer (Nitrogen) and volumes of micropores (physisorption analyzer (BASIS MODEL) were also determined. The standard method (D1506-15USA) and scanning electron microscopy (SEM, TESCAN VEGA 3) were used to determine the ash content and the chemical composition of the carbon materials, respectively.

Procedure: The applications of as-obtained carbon materials were explored under the static conditions (t = 25 ºC), adsorbates were 100-100 mL of 0.01 M solutions of Fe^{2+}/Cd^{2+}; and the sorbent mass (fraction size = 40 µm) was 1 g. An AAS (ANALYST 200-1004 TAM; Perkin-Elmer) was used to measure the metal ions concentration. For model solutions with different concentrations, pH values and mixed solutions [*viz*. (i) Pb^{2+}, Cd^{2+} and Co^{2+}; (ii) Fe^{2+}, Cu^{2+} and Cd^{2+}; and (iii) Fe^{2+} and Cd^{2+}] were applied in the system.

For investigating the adsorption capacity of Fe^{2+} and Cd^{2+} ions on the as-obtained carbon materials, the time delay of the adsorbents in the solutions was used as an evaluation index. The static adsorption capacity was evaluated according to the following equation:

$$A = \frac{V(C_o - C_t)}{m} \tag{1}$$

where, A = value of adsorption (mg/g); V = volume of solution (L); C_o, C_t, = initial and final concentration of the solution (mg/L); m = mass of adsorbent (g).

The degree of extraction (∝) was calculated according to the following equation:

$$\text{Degree of extraction } (\propto) = \frac{(C_o - C)}{C_o} \times 100\% \tag{2}$$

The as-prepared carbon materials exhibited high BET surface areas and purity, indicated that the proposed method is suitable for developing inexpensive sorbents for the adsorption/treatmentpurposes. For the obtained sorbent, the specific surface area, area of micropores and volume of micropores were found to be 492.95-637.3 m^2/g, -217.00 and 427.85 m^2/g and -0.10 and 0.20 cm^2/g, respectively.

RESULTS AND DISCUSSION

The physico-chemical characteristics and morphologies of the as-obtained carbon materials are presented in Table-1 and Fig. 1, respectively. The obtained carbon materials from hazelnut shell have the largest BET surface area, which is comparable to the surface area of commercial activated carbon, whereas the walnut shell's carbonaceous material had a relatively small BET surface area. Similar trends were observed for the values of micropore areas and volumes. For both carbon materials, the ash and moisture contents were ≤ 3.5% and ≤ 4.3%, respectively. The carbon contents of the as-obtained materials was in the range 85.0-89.5%, while other inorganic impurities were found individually or in the form of oxides. Furthermore, the carbonaceous materials obtained from the hazelnut and walnut shells showed the morphological differences due to the different sizes and shapes of grains.

Adsorption parameters

Effect of time: Fig. 2 shows the influence of time in solutions on the degree of extraction. Both sorbents exhibited the similar sorption characteristics for the studied cations. However, the kinetic curves of Fe^{2+} and Cd^{2+} adsorption were slightly different. For Fe^{2+} and Cd^{2+}, the equilibrium concentrations were reached after 30-40 min and 5-10 min, respectively. Thus, for Cd^{2+} ions, the degree of extraction was relatively high during the first 5-10 min (Fig. 2b).

Effect of initial concentration: Among the three studied samples, carbon material derived from the hazelnut shell performed the best (Fig. 3). The best adsorption and degree of extraction of both (Fe^{2+} & Cd^{2+}) ions were achieved in a 0.0025 M solution within 30 min at different concentrations.

The maximum extraction efficiency (80-100%) was achieved at low concentration of iron(II) ions (0.005-0.0025 M) and 40-70% of cadmium ions. In case of high concentration, the amount of adsorbent should be increased in proportion to the degree of contamination.

Effect of pH: As shown in Fig. 4, the highest value of adsorption and degree of extraction for Fe^{2+} ions were obtained at pH 3-5. At pH > 5, $Fe(OH)_2$ precipitated in the solution,

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS OF CARBONACEOUS MATERIALS OBTAINED FROM HAZELNUT SHELLS AND WALNUT SHELLS

Carbonaceous material	BET surface area (m^2/g)	Micropore area (m^2/g)	Micropore volume (cm^3/g)	Ash content (%)	Humidity (%)
Hazelnut shell	637.3	427.65	0.20	2.9	1.4
Walnut shell	506.0	380.26	0.15	3.5	4.3
Commercial activated carbon	708.7	473.78	0.21	4.2	1.3

Carbonaceous material	Chemical composition of samples % (averaged)											
	C	O	Ca	K	Si	S	Fe	Ni	Cu	Zn	Al	F
Hazelnut shells	85.0	11.0	2.0	0.6	0.10	0.1	0.40	0.30	0.2	0.20	–	–
Walnut shells	89.5	7.4	0.8	1.4	0.00	0.4	0.15	0.04	0.2	0.10	–	–
Commercial activated carbon	89.5	8.6	0.7	0.4	0.01	–	0.09	–	0.4	0.01	0.0	0.2

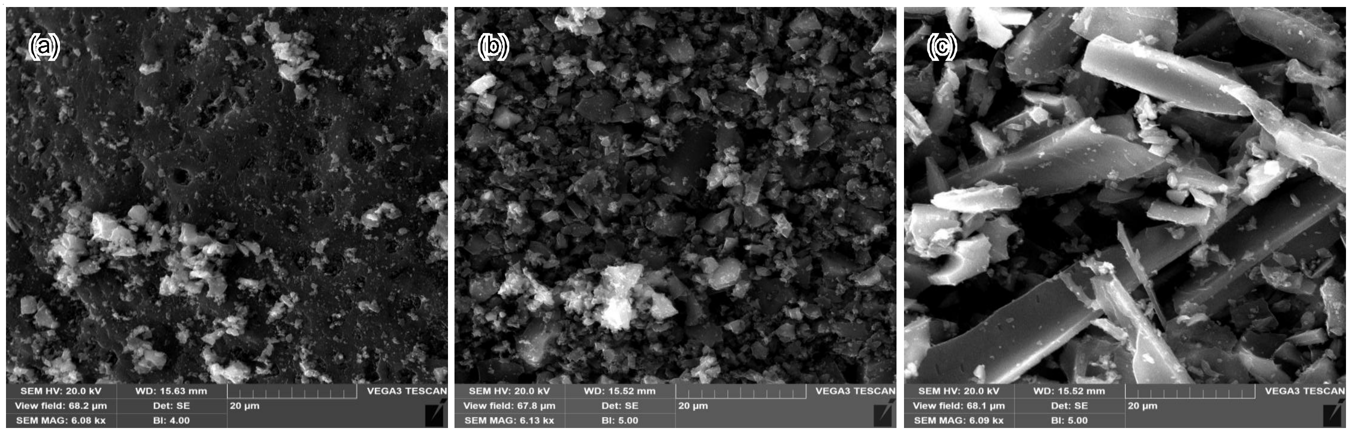

Fig. 1. SEM images of (a) SEM hazelnut shells carbon material, (b) walnut shells carbon material, and (c) commercial activated carbon

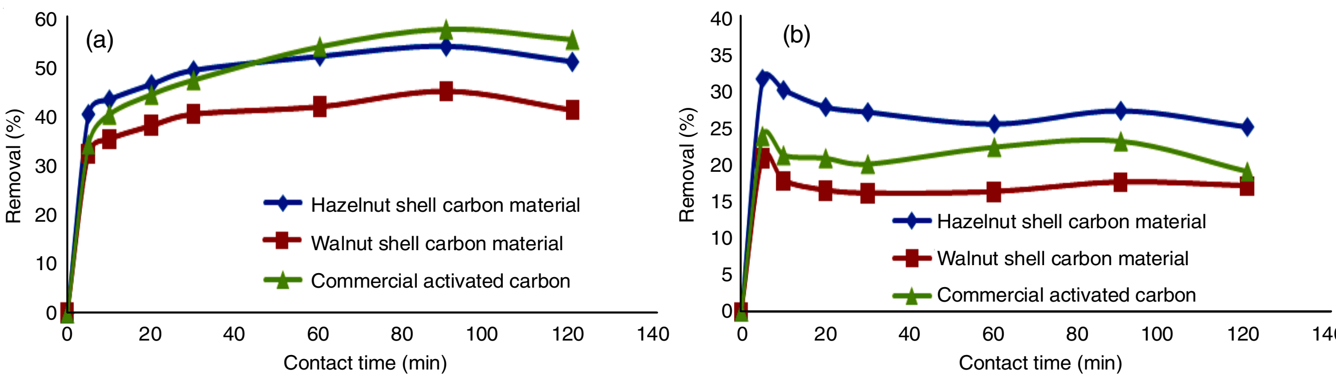

Fig. 2. Effect of time on the extraction degree of Fe^{2+} ions (a) and Cd^{2+} ions (b) (Conditions: $m_{ad.}$ = 1 g, $V_{sol.}$ = 100 mL, t = 25 °C , $C_{Fe(II)}$ = 0.56 g/L; $C_{Cd(II)}$ = 1.12 g/L)

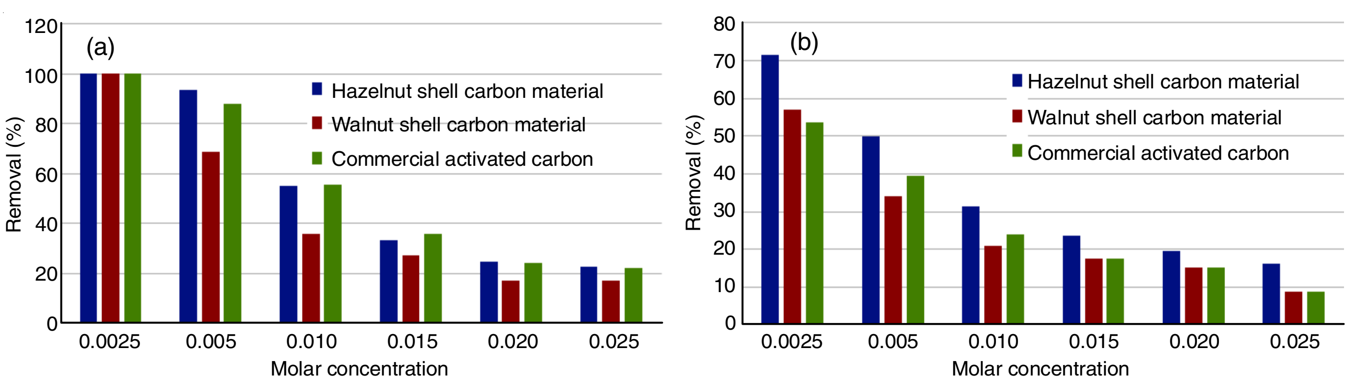

Fig. 3. Effect of intial concentration on the extraction degree of Fe^{2+} ions (a) and Cd^{2+} ions (b)

and at pH < 2, a complex was formed which could not adhere to the active centres of the adsorbents, thus decreasing the adsorption of metal ions. Both of these led to the decreased degree of extraction at these pH ranges. The effect of pH was also influenced by the charge of the adsorbent surface. At low pH, H_3O^+ ions were present in large quantities in the solution, which neutralized the negatively charged adsorbent surface, and thereby decreasing the diffusion effect by increasing the adsorption rate [20-23]. This may be attributed to the fact that diffusion restrictions in the adsorption layer were removed because the concentration was neutralized when the solution was mixed. Thus, the degree of extraction can be improved and the removal efficiency can be increased by slightly acidifying the aqueous solutions of iron(II) ions (pH should be between 5 and 3).

In case of Cd^{2+} ions, the maximum adsorption and degree of extraction were obtained at pH = 5. At pH = 6, the hydrolysis of cadmium salt resulted in the formation of the insoluble $Cd(OH)_2$ in water, which may precipitated in the solution. With further increasing pH, the amount of H_3O^+ ions and their associated positive charge decrease, while the electrostatic attraction of the adsorbent for metal cations increases [24,25]. At low pH, due to the high availability of H_3O^+ ions, decreases the number of active centres and thus affected the adsorption of metal ions onto the carbon materials. Moreover, at higher pH values, the adsorption capacity increased, which may be

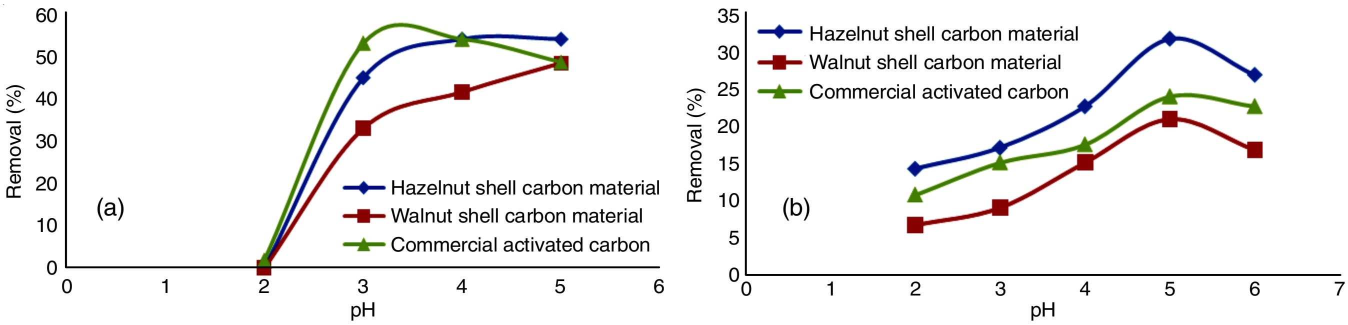

Fig. 4. Effect of pH on the extraction degree of iron(II) ions (a) and cadmium(II) ions (b) ($m_{ad.}$ = 1 g, $V_{sol.}$ = 100 mL, t = 25 °C, $C_{Fe(II)}$ = 0.56 g/L; $C_{Cd(II)}$ = 1.12 g/L)

attributed to the weak inhibitory effect of H_3O^+ ions. The influence of pH on the adsorption of metal cations was mainly attributed to the changes in proton charge.

Applications: Natural and wastewater usually contains ions of several heavy metals. Therefore, the applicability of the prepared adsorbents were examined in three polymetallic systems, namely (i) Pb^{2+}, Cd^{2+} and Co^{2+}; (ii) Fe^{2+}, Cu^{2+} and Cd^{2+}; and (iii) Fe^{2+} and Cd^{2+}. In each case, the same experimental conditions were taken into consideration using adsorbent size of 40 µm.

The sorption capacities of hazelnut and walnut shell carbon materials and commercial activated carbon for lead(II), cadmium(II), cobalt(II), iron(II) and copper(II) ions were in the ranges 83.5-94.0 mg/g, 22.5-22.3 mg/g, 12.2-13.2 (Fig. 5a), 9.8-10.5 mg/g (Fig. 5b) and 15.08-15.79 mg/g, respectively; for Fe(II)-Cd(II) pair, with respect to Fe(II) and Cd(II) ions, the sorption capa-cities fluctuated in the ranges 18.5-19.5 mg/g and 30-31 mg/g, respectively (Fig. 5c). This affinity occurred because the solute molecules dissolved in water and decomposed to form hydrated ions.

In case of the individual cations, the sorption capacity was the highest for Pb(II) ions, and it was the lowest for Co(II) ions (Fig. 5a). The ionic radii (r) considerably influenced the adsorption of metal ions on the sorbents. For an ion with the same charge, a larger crystal radius implied better adsorption [24]. This is because with increase in radius, the polarizability increases, which increases the ability to be attracted to the negatively charged surface of the sorbent and thus, the adsorption capacity. Simultaneously, with increase in the ionic radius, ion hydration decreased, which also increased the adsorption value. A similar explanation applies to the rest of the cases.

The lyotropic or Hofmeister series of the heavy metal ions considered as adsorbates in present study were arranged in decreasing order of adsorption capacity: A(Pb(II) > A(Cd(II) > A(Cu(II) > A(Fe(II) > A(Co(II), where A is adsorption value.

Metal ions' radii arranged in the decreasing order were as follows: $r_{Pb}2+$ = 1.21 Å > $r_{Cd}2+$ = 0.99 Å > $r_{Cu}2+$ = 0.87 > $r_{Fe}2+$ = 0.8 Å > $r_{Co}{}^{2+}$ = 0.78 Å [24], where r is the ionic radius. The high adsorption capacities of the sorbents for lead(II) ions may be attributed to the electronegativity of the ions and the ionic radii. The ionic electronegativity (2.33) and ionic radius (1.21 Å) of lead(II) ions are the highest among all metals considered herein; these characteristics increased the force of attraction between the metal ions and the active centres of sorbents. For metal ions with higher electronegativity, strong ionic bonds are formed with the oxygen atoms on the surface of the adsorbent [25].

Conclusion

The carbon materials obtained from the hazelnuts and walnuts waste shells exhibited high BET surfaces, porosities, good adsorption capacities without activation and modification, and were successfully used as sorbents. Among the materials considered herein, the walnut shell carbon materials showed the best adsorption capacity for Fe^{2+} and Cd^{2+} ions separately as well as in polymetallic systems. This performance is compa-

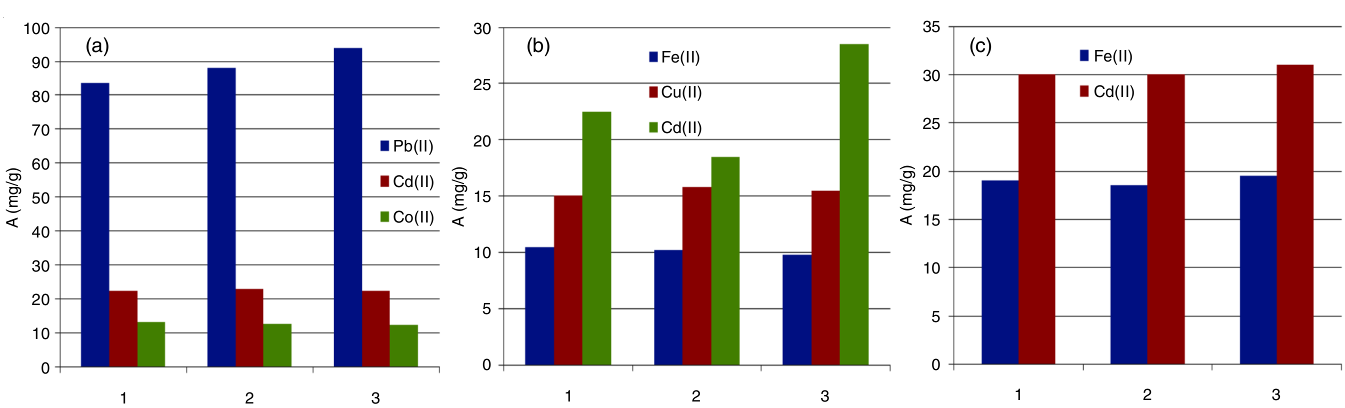

Fig. 5. Adsorption uptake of Pb(II), Cd(II), Co(II) (a); Fe(II), Cu(II), Cd(II) (b) and; Fe(II) and Cd(II) (c). (Conditions: Metals concentration 0.01 M, T = 30 min, $m_{sorb.}$ = 1 g, $V_{sol.}$ = 100 ml, t = 25 °C) [1. Hazelnut shell carbon material; 2. Walnut shell carbon material; 3. commercial activated carbon]

rable to that of commercially available activated carbon. The walnut shell carbon material had low adsorption capacity for Fe^{2+} ions. However, adsorption can be improved by increasing the sorbent amount. These adsorbents are advantageous because of their low cost and high adsorption capacities towards the heavy metals.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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