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Removal of lead, cadmium, zinc, and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot stone

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Abstract

In this work, adsorption of copper (Cu), zinc (Zn), lead (Pb), and cadmium (Cd) that exist in industrial wastewater onto the carbon produced from nutshells of walnut, hazelnut, pistachio, almond, and apricot stone has been investigated. All the agricultural shell or stone used were ground, sieved to a defined size range, and carbonized in an oven. Time and temperature of heating were optimized at 15 min and 800 °C, respectively, to reach maximum removal efficiency. Removal efficiency was optimized regarding to the initial pH, flow rate, and dose of adsorbent. The maximum removal occurred at pH 6–10, flow rate of 3 mL/min, and 0.1 g of the adsorbent. Capacity of carbon sources for removing cations will be considerably decreased in the following times of passing through them. Results showed that the cations studied significantly can be removed by the carbon sources. Efficiency of carbon to remove the cations from real wastewater produced by copper industries was also studied. Finding showed that not only these cations can be removed considerably by the carbon sources noted above, but also removing efficiency are much more in the real samples. These results were in adoption to those obtained by standard mixture synthetic wastewater.

Keywords: Walnut; Hazelnut; Pistachio; Almond; Apricot stone; Wastewater; Zinc; Copper; Lead; Cadmium

1. Introduction

At least 20 metals are classified as toxic and half of these are emitted into the environment in quantities that pose risks to human health [1]. Heavy metal ions such as cobalt, copper, nickel, chromium and zinc are detected in the waste streams from mining operations, tanneries, electronics, electroplating and petrochemical industries, as well as in textile mill products [2]. Heavy metals are major pollutants in marine, ground, industrial and even treated wastewaters [3]. Industrial waste constitutes the major source of various kinds of metal pollution in natural waters. The important toxic metals i.e. lead (Pb), cadmium (Cd), zinc (Zn), and copper (Cu) find its way to the water bodies through wastewaters [4]. The release of large quantities of heavy metals into the natural environment e.g. irrigation of agricultural fields by using sewage has resulted in a number of environmental problems [5] and due to their non-biodegradability and persistence, can accumulate in the environment elements such as food chain, and thus may pose a significant danger to human health [6]. Metals of interest were Zn, Cd, Cu, and Pb. They were chosen based on their industrial applications and potential pollution impact on the environment. The increasing demand for alkaline Zn manganese batteries, instead of mercury based ones, brings serious problems when those batteries are not disposed off properly [7]. Cd is a non-essential and non-beneficial, highly toxic element to plants and animals [8]. The toxic effects of Cu are well documented [9]. Pb heads the list of environmental threats because, even at extremely low concentrations, lead has been shown to cause brain damage in children [10]. Many physicochemical methods have been proposed for their removal from industrial effluents [11], such as electro-chemical precipitation, ultrafiltra-

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tion, ion exchange and reverse osmosis [12]. A major drawback with precipitation is sludge production. Ion exchange is considered a better alternative technique for such a purpose. However, it is not economically appealing because of high operational cost [1]. Adsorption using commercial activated carbon (CAC) is an effective purification and separation technique used in industry especially in water and wastewater treatments that can remove heavy metals from wastewater [13]. Activated carbon surfaces have a pore size that determine its adsorption capacity, a chemical structure that influences its interaction with polar and non-polar adsorbates, and active sites which determine the type of chemical reactions with other molecules [10]. However, CAC remains an expensive material for heavy metal removal. Natural biopolymers are industrially attractive because of their capability of lowering transition metal-ion concentration to parts per billion concentrations. Natural materials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmentally friendly [14]. There are many studies in the literature relating to the preparation of activated carbons from agricultural wastes [15–17]. However, there is only limited research on the preparation of activated carbons using walnut, hazelnut, almond, and apricot stone for removing heavy metals from wastewaters [18–21]. Normally, these shells are used as boiler fuel or in landfills. It is proposed to utilize these abundant solid wastes as starting materials for the preparation of activated carbons because of their high carbon and low ash contents [22]. The objectives of this study were to prepare activated carbons from walnut (*Juglans regia* L.), hazelnut (*Corylus avellana*), pistachio (*Pistaca*), almond (*Amygdolus*) shells and apricot (*Armeniaca bulgar*) stone and their ability to remove zinc, copper, lead, and cadmium from industrial wastewater. Different preparation variables on the characteristics of activated products were studied to find the optimum conditions for making activated carbons with well-developed porosity. The influence of several operating parameters, such as pH, adsorbent dosage, contact time, and initial concentrations on the adsorption capacity, were investigated.

2. Materials and methods

2.1. Raw materials

Almond, walnut, hazelnut, pistachio shells and apricot stones were used as starting materials. These raw materials were broken and grinded with a Moulinex commercial blender and sieved to a particle size of 0.18 mm (US mesh size 80) in diameter. These natural raw materials appear to be very suitable starting materials for activated carbons because of their low ash content (0.31–0.78%). The elemental analysis data showed that the raw materials have a variation of compositions. Hazelnut shells have the highest C content. Walnut shells, on the other hand, have the lowest C and H contents. Apricot stone and almond shells have rather similar elemental composition. Copper sulphate, zinc chloride, lead nitrate and cadmium chloride from Merck (Darmstadt, Germany) was used as received without further purification. Furnace (Lenton, UK). All heavy metals were analyzed by an atomic absorption spectrometer (Buck Scientific Co., USA). Real wastewater was provided by Sarcheshmeh Copper Lateral Industries (SCLI), Kerman, Iran.

2.2. Process

The raw materials (almond, walnut, hazelnut, pistachio shells and apricot stones) were preheated in an oven at 100 °C for about 48 h to reduce the moisture content. They were then crushed with a high speed mill and sieved on a sieve mechanical shaker, and the size fraction of lower than 180 μm that has been passed through US standard sieve number 80, was used in this study. Pyrolysis of the starting materials and activation of the resulting chars were both carried out in a vertical stainless-steel reactor (length 550 mm, internal diameter 38 mm) which was placed in an electrical heating furnace (818P, Lenton, UK). The heating rate, temperature and dwell time could be programmed. The furnace temperature was increased at a certain rate from room temperature to a selected temperature and then held at this temperature for a predetermined time. After pyrolysis, the furnace was cooled down to room temperature. In the pyrolysis process, the effect of temperature, the hold time or heating rate on the char characteristics was studied individually by varying this particular parameter while keeping all other parameters.

Fourier transform infrared (FTIR) spectra were obtained using a spectroscope (Tensor 29, Brucker) at resolution 1 cm^{-1}. Pressed potassium bromide (KBr) pellets at a sample/KBr weight ratio of 1:100 were scanned and recorded between 4000 and 400 cm^{-1}. The pellets were placed in an oven at 120 °C for 5 h to remove any water present. Physical properties of carbons including percent yield, bulk density and surface area were determined according to procedures described by Ahmedna et al. [23].

2.3. Flow uptake experiments

Flow experiments were carried out using carbon produced by raw materials as well as activated charcoal as adsorbents. Copper sulphate, lead nitrate, zinc chloride and cadmium chloride were used as the source of Cu, Pb, Zn and Cd in the synthetic wastewater. The stock solutions of Cu, Pb, Zn and Cd (100 mg/L) were prepared by dissolving proper amount of each of noticed material in deionised water. Solutions containing 30 mg/L of each of the cations were prepared from the stock solution. Adjustment of pH was carried out using 0.1 N NaOH and/or 0.1 N HCl. All batch experiments were carried out by using columns filled by predetermined amount of the adsorbent passing through them cation solutions with flow rate of 3 mL/min. All the experiment conditions were optimized to achieve maximum removal efficiency (RE) for Cu by carbon prepared from walnut and then the optimized conditions were applied for removing other cations and/or by other carbon sources. To maximize metal removal by the adsorbent, batch experiments were conducted at ambient temperature using the optimum conditions of all pertinent factors such as temperature and time of carbonization, dose and pH. Subsequent adsorption experiments were carried out with only optimized parameters. The change in cation concentrations due to adsorption was determined by atomic absorption spectrophotometer according to standard methods. The removal efficiency percent (RE%) of adsorbent on each cation was defined as:

$$\mathrm{RE}(\%) = \left[\frac{(C_o - C_1)}{C_o}\right] \times 100$$

where C_o and C_1 is the initial and final concentration (after passing through the adsorbing material) of cation solution (mg/L), respectively. To ensure the accuracy, reliability, and reproducibility of the collected data, all the batch experiments were carried out in triplicate and the mean values of three data sets are presented.

3. Results and discussion

Removal of heavy metals from wastewater by agricultural wastes is a green chemistry method for managing our environment cleanliness. To reach optimum condition for maximum removal of heavy metals from wastewater by carbon produced from nutshells, the influence of several operational parameters such as initial pH, temperature of carbonization, time of carbonization, dose of adsorbent, flow rate of wastewater on RE for Cu as a model was investigated.

The IR spectra (Fig. 1) indicate that the carbons possess different surface structures, e.g., aliphatic, aromatic, cyclic as one can observe the bands at 1460 cm^{-1} and over the 1320–1100 cm^{-1} range. All the analyzed spectra possess bands at 3300–3500 cm^{-1} showing the presence of alcoholic, phenolic or acidic OH with hydrogen bonding. The peaks at 2000–2100 cm^{-1} can be connected to C≡C group and at 2200–2300 cm^{-1} can be caused by C≡N group. The bands at 2000–2300 cm^{-1} also can be corresponds to C=N=S or C=N=C. The peaks at 2800–2900 cm^{-1} suggest the existence of aldehyde groups. Altogether it can be seen that the carbons possess similar structures with each other and also very similar to activated charcoal of Merck, of course with more capacity to remove heavy metals.

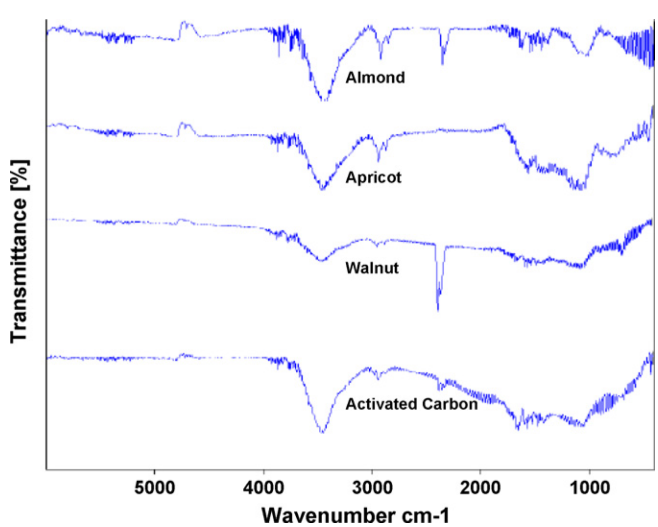

Fig. 1. FTIR spectra of different nutshell chars and standard activated charcoal.

Table 1
Physical, chemical, and surface properties of nutshell (stone)-based activated carbons

Nutshells, stone	Yield (%)	Bulk density (g/mL)	Surface area (m^2/g)
Pistachio	20	0.54	635
Almond	38	0.23	1208
Hazelnut	52	0.37	786
Walnut	57	0.39	941
Apricot	63	0.41	861

Physical properties of the carbons have been summarised in Table 1. Data shows that the highest and the lowest surface areas are related to almond and pistachio nutshell based carbon, respectively. This is in accordance to the findings of RE% for metal ions as a whole. Percent yield and bulk density may not directly relate to the carbon's effectiveness for removing heavy metals but they are important to their commercial utilization.

3.1. *Effect of pH*

Aqueous phase pH governs the speciation of metals and also the dissociation of active functional sites on the sorbent. Hence, metal sorption is critically linked with pH. To examine the effect of pH on the Cu RE%, the pH of initial solutions that should pass through the adsorbing bed were varied from 4.0 to 10.0 by adding acid or base into them.

Fig. 2 shows the uptake of free ionic Cu depends on pH. It can be observed from the figure that the uptake of Cu (II) increases with increase in pH from 33 to 98% over pH range from 4.0 to 7.0. This increase may be due to the presence of negative charge on the surface of the adsorbent that may be responsible for metal binding. However, as the pH is lowered, the hydrogen ions compete with the metal ions for the sorption sites in the sorbent; the overall surface charge on the particles becomes positive, and hinds the binding of positively charged metal ions. On the other hand, decrease in adsorption under pH 6 may be due to occupation of the adsorption sites by anionic species which retards the approach of such ions further toward the sorbent surface. In general, the Cu (II) adsorption by different adsorbent in this study has shown similar trend and the optimum pH 6–10 has been achieved.

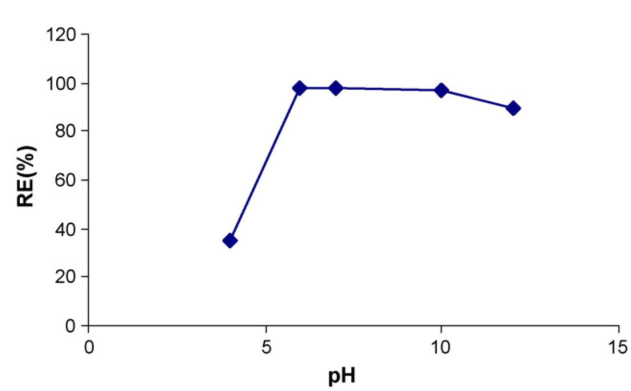

Fig. 2. Influence of pH on copper removal efficiency (RE%) using walnut carbon.

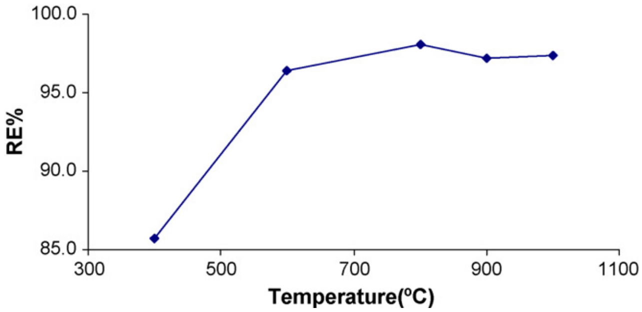

Fig. 3. Effect of carbonization temperature on copper RE% using walnut.

3.2. Effect of carbonization temperature of walnut

The effect of carbonization temperature on RE% is shown in Fig. 3. RE% was increased by increasing temperature up to 800 °C and after that its changes was not significant. Plateau in the figure may be explained that in 800 °C, maximum carbonization will be occurred in walnut shell, so that increased temperature cannot produce more activity. In all the following steps temperature of 750–800 °C was chosen to produce carbon from the shells.

3.3. Effect of carbonization time

The effect of carbonization time on RE% is shown in Fig. 4. It can be seen that carbonization time does not have much effect on the RE%. Carbonization time of 10–15 min was selected to achieve maximum efficiency.

3.4. Influence of dose

Copper ion concentration in some wastewater of copper mines (SCLI) is estimated to be at most of 30 ug/mL; therefore synthetic wastewater containing this amount of copper ions was prepared and passed through columns containing 0.1–1 g of walnut carbon. The RE% are corrected for the mass of adsorbent in the column and are given as the amount of metal ion removed per unit weight (g) of adsorbent. As depicted in Fig. 5, removal efficiency per gram of adsorbent was drawn versus amount of adsorbent while keeping other parameters constant. From Fig. 5, it can be observed that for such copper concentrations, removal efficiency per gram of the adsorbent generally improved with decreasing dose. This finding shows that 0.1 g adsorbent has enough exchangeable sites to remove the ions, so that RE% of

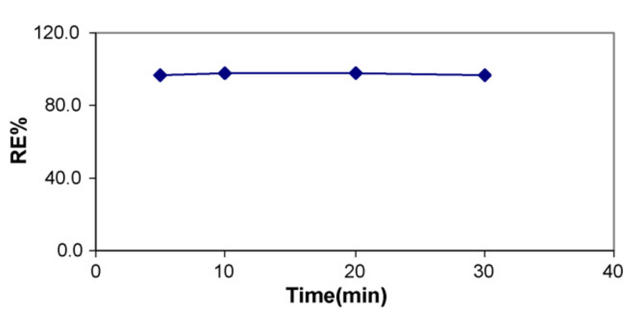

Fig. 4. Effect of carbonization time at 800 °C on copper RE% using walnut.

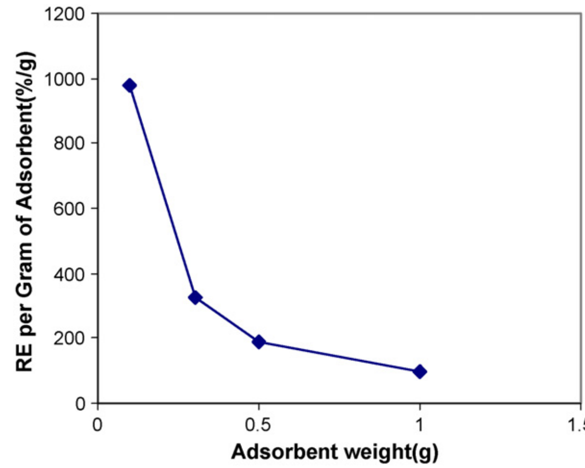

Fig. 5. Influence of amount of adsorbent on copper RE% using walnut carbon.

the ions was not changed after 0.1 g of adsorbent was applied. To obtain saturation capacity of this amount of walnut carbon, three portions, each 80 mL of 30 mg/L copper ion solution were passed through the column and after each step, RE% was calculated. Results have been shown in Fig. 6.

This figure shows that after passing 80 mL of 30 mg/L copper solution for three times through the same column containing 0.1 g adsorbent, RE% was decreased considerably from 98.1 to 11.8%.

Removal of Cu, Zn, Cd, and Pb from synthetic wastewater using walnut, hazelnut, pistachio, almond shell and apricot stone carbon. Optimized conditions obtained for removing Cu by walnut carbon was applied to take away Cu, Zn, Cd, and Pb using other nutshells and stone for one pass only. Fig. 7 shows RE% for each cation and carbon source. As depicted in figure, Cu has been removed by all the carbon sources except pistachio by more than 90%, however pistachio can remove more than 80% of Cu from wastewater. Pb is highly removed by hazelnut and walnut, thereafter apricot and almond have RE of more than 80%, and pistachio as for Cu has the lowest effect. Cd was removed by hazelnut, almond and apricot in large extent, however Zn mostly removed by walnut, almond, and pistachio.

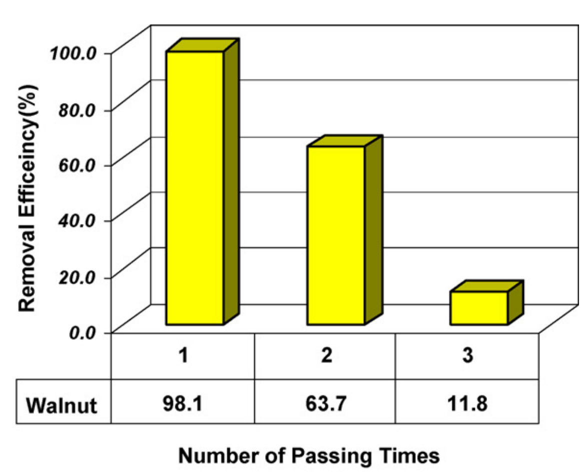

Fig. 6. Effect of times of passing of wastewater through adsorbent bed on copper RE% using walnut carbon.

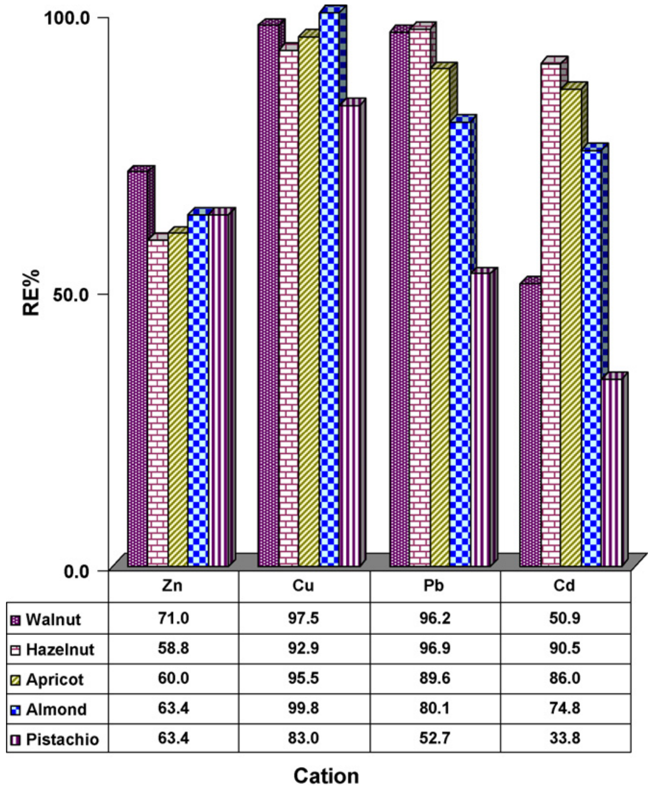

Fig. 7. Effect of walnut, hazelnut, apricot, almond and pistachio carbon on RE% of zinc, copper, lead, and cadmium.

Hazelnut and pistachio have lowest effects on Zn and Cd, respectively. In conclusion all the carbon sources can remove more than 50% of the metals from wastewater in one pass, of course except only for Cd by pistachio. Altogether, considering metals studied, Cu can be removed by all the carbon sources with high RE, and in carbon sources investigated, apricot has the highest RE.

3.5. Real sample analysis

Conditions used for various metal ions and carbon sources in synthetic samples were applied for real samples (wastewater) provided by SCLI. Results have been shown in Table 2.

These results indicate that more than 90% of the copper ions were removed from the wastewater by various carbon sources. This finding is conforming to those obtained by synthetic wastewater solutions; of course order of importance of carbon sources for removing copper ions somewhat has been changed. This may be related to the presence of other ions that may not be exist in the synthetic wastewater and also lower concentration of the copper ions in real samples. On the other hand, however RE% of zinc for real samples is greatly promising, but it is not in accordance to results for synthetic wastewater. This may be related to the presence of components that are present in real sample and also its concentration. Results showed that there is not cadmium and lead in measurable amounts in real samples so these ions could not be detected.

Table 2
RE% of pistachio, apricot, hazelnut, walnut and almond carbon for removing copper, zinc, cadmium and lead from real sample prepared from SCLI

	Pistachio	Apricot	Hazelnut	Walnut	Almond
Cu	95.6	91.6	94.1	94.1	90.3
Zn	87.9	63.2	74.4	85.7	58.2
Cd	ND	ND	ND	ND	ND
Pb	ND	ND	ND	ND	ND

4. Conclusion

The walnut (*Juglans regia L.*), hazelnut (*Corylus avellana*), pistachio (*Pistaca*), almond (*Amygdolus*) shells and apricot (*Armeniaca bulgar*) stone precursor are found to be a good raw material for developing activated carbons. The activated carbons produced from shells and stone have high surface areas. Time and temperature of carbonization had an influence on Cu adsorption. The aqueous adsorption tests indicate that the activated carbon has a notable adsorption capacity for Cu, Zn, Cd and Pb. The uptake of the Cu was greatly affected by the solution pH. The data thus obtained may be helpful for designing and establishing a continuous treatment plant for water and wastewaters enriched in Cu. The cost of removal is expected to be quite low, as the adsorbents are cheap and easily available in large quantities as compared and reported in the literature.

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