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International Conference on Environment 2010

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13-15th December 2010
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UNIVERSITI SAINS MALAYSIA

1969-2009

SECTION 2: SUSTAINABLE MANAGEMENT OF ENVIRONMENT, WASTEWATER, SOLIDS, HAZARDOUS WASTE

RAPID REMOVAL OF HEAVY METAL IONS FROM AQUEOUS SOLUTIONS BY LOW COST ADSORBENTS

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ABSTRACT

Heavy metals are frequently present in the aquaticstreams by different industrial wastewaters. The presence of these metals in the environment isof importance concern due to their toxicity and health effects on the human and living creatures. In the present investigation, different agricultural solid wastes namely: eggplant hull, almond green hull, and walnut shell were introduced as low cost adsorbents and used for the removal of heavy metals such as cobalt, strontium and mercury ions from aqueous solutions. Activation process and/or chemical treatments using H_2O_2 and NH_3 were performed on these raw materials to increase their adsorption performances. The effectiveness of these adsorbents was studied in batch adsorption mode under a variety of experimental conditions such as: different chemical treatments, various amounts of adsorbents, initial metal-ion concentrations, pH of solutions, contact times, and solution temperatures. To the best of our knowledge, most of these adsorbents have not been previously used for the removal of mentioned ions from water. High metal adsorption efficiencies were achieved for all cases only in the first 2-3 minutes of adsorbents' contact times. The optimum doses of almond green hull adsorbent for the maximum Sr(II) adsorption were found to be 0.2 and 0.3 g for 45 and 102 mg/L solutions, respectively. Optimum dose of this sorbent for maximum cobalt-ion adsorption were 0.25 g for 515 mg/L concentration and 0.4 g for 110 mg/L concentrated solutions. The maximum adsorption capacity of this sorbent for cobalt was found to be 45.5 mg/g. Maximum adsorption capacity of eggplant hull for mercury was 147.06 mg/gwhich is higher than most conventional adsorbents. The monolayer adsorption capacity of mercury for walnut shell was obtained as 151.5 and 100.9 mg/g for two different treated sorbents. The adsorption behaviors of metal ions on optimum adsorbents were also examined. It was observed that adsorption of all metal ions followsboth Langmuir and Freundlich isotherms.
The present study revealed that such low cost materials could be used as efficient adsorbents for the removal of heavy metal ions from wastewater streams.

Keywords: Almond green hull; Eggplant hull; Walnut shell; Solid waste; Adsorption.

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The present study revealed that such low cost materials could be used as efficient adsorbents for the removal of heavy metal ions from wastewater streams.

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INTRODUCTION

Heavy ions are considered hazardous contaminants due to their toxicity, even at low concentration, and non biodegradability. Heavy metal ions such as cobalt, mercury and strontium, are detected in the waste streams from mining operations, coal combustion and petrochemical factories. There are various methods for removing heavy metals from aqueous streams such as chemical precipitation [1], reverse osmosis [2], ion exchange [3], coagulation [4], and adsorption [5–8]. Mentioned ions are the priority pollutants listed by USEPA as they can easily pass the blood-brain barrier and affect the fetal brain. These heavy ions can be removed successfully from aqueous solutions by reverse osmosis, coagulation, and ion exchange, etc. However, these methods are much less efficient for low concentrations, for

which they can be expensive and can even fail to reach legal limits. For low concentration of these ions, it is appropriate to use adsorption methods.

In the present investigation, different agricultural solid wastes namely: eggplant hull, almond green hull, walnut shell and moss are used which are the most common agricultural products with large quantity in Iran. The object of the present work was to investigate the possibility of mentioned ions removal from water by low cost adsorbent prepared from the local agricultural solid wastes. Several prominent factors such as temperature, initial concentration, pH and also isotherm models were investigated in this study.

MATERIALS AND METHODS

Materials. All mentioned agricultural solid wastes were collected from local sources. Walnut shell which was used for preparing activated carbon, was dried in an oven for about one day at 120°C. Dried sample was powdered, sieved (below mesh No. 170), and impregnated with $ZnCl_2$ concentrated solution (136.28 g/mol, 98%) in a weight ratio of 1:0.5 (shell:ZnCl2). The resulting black product was then dried in an oven at 120°C for about 5 h. Impregnated sample was placed on a ceramic boat, inserted in a tubular furnace, and then heated to the carbonization temperature under N_2 flow at the rate of 5°C/min. After carbonization, the sample was cooled down in N_2 atmosphere. The carbonized sample was washed several times sequentially with hot and finally cold distilled water to remove any residual chemicals. Activated carbon product was then dried in the oven at 130°C. The adsorbent particle size distribution was obtained and the mean diameter was about 0.088mm.

Three other adsorbents i.e. almond green hull and eggplant hull, as agricultural residue, and moss were washed with distilled water several times to remove water soluble impurities followed by drying in an oven at 180°C. Dried samples were ground and then the following two different chemical treatments were carried out to extract soluble organic compounds of the adsorbent and also to enhance chelating efficiency:

- Mixing with the solution of hydrogen peroxide (2%vol) + ammonia (2%vol), and
- Mixing with the solution of nitric acid (20%).

All the chemical and reagents used were of analytical reagent grade obtained from Merck company.

Methods. All adsorption experiments were carried out using adsorbents with the particle sizes less than 88µm. Adsorbate containing solutions were prepared by dissolving necessary amount of heavy metal salt in the distilled water. Each solution was then diluted to obtain standard solutions. Batch adsorption studies were carried out with identified amount of sorbents and 50 ml of heavy metal solutions with a desired concentration in two conical flasks, simultaneously. The flasks containing adsorbent and adsorbate were agitated for predetermined time intervals on a mechanical shaker with 720 rpm. At the end of agitation, the suspensions were filtered by the aid of microporous filter paper. The amount of heavy metal ions in the final 25 ml volume was determined by atomic absorption spectrophotometer (Varian, spectra-110-220/880 Australia Pty. Ltd.) equipped with a Zeeman atomizer. The obtained results for two similar solutions were averaged and then reported as the experimental data.

RESULTS AND DISCUSSION

Effect of pH. In order to determine the effect of pH on Hg(II) removal by activated carbon, some experiments were conducted using two different initial concentrations of 9.7 and 44.6 mg/L. The effect of pH can be seen in Fig. 1.The pH of each solution was adjusted by

addition of HCl and/or NaOH. It is seen that the removal efficiency of Hg(II) decreases with increasing pH. Some authors indicated that surface charge is an important factor for the adsorption of metal ions [9] and it is very much dependent on the pH of the solution [10]. By increasing OH^- functional group, competing between mercury ions and this group starts and OH^- occupies active sites of the adsorbent. Therefore, accessed surface area and subsequently adsorption of mercury ions will be decreased.

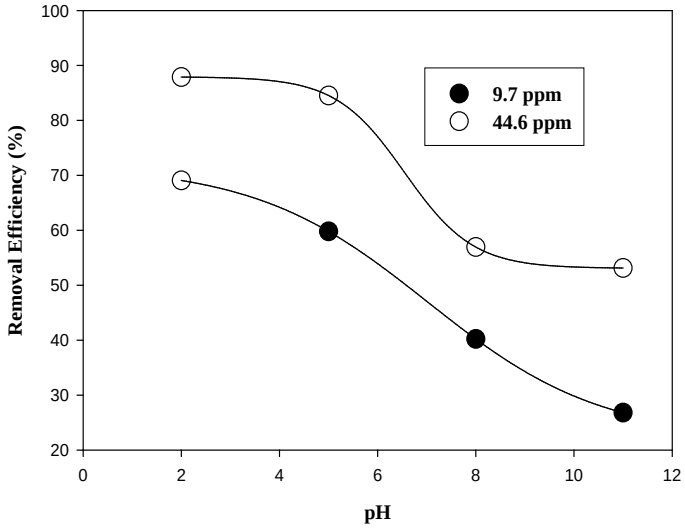

Figure 1: Effect of pH on the adsorption of Hg (II) (time=15 min, temperature=29^{o}C)

As shown in Fig. 1, the maximum adsorption is observed at pH 2. It is seen that, for the dilute solution (9.7 ppm or mg/L) the removal efficiency was decreased with a mild slope, but for the concentrated one (44.6 ppm) it was constant in the initial stage (pH range of 2–5) and then sharply decreased. The removal efficiency reached a plateau at the pH range of 8–11. It can be concluded that at any pH, Hg(II) removal by activated carbon is very much greater for the concentrated solution than the dilute one. This is the result of stronger adsorption driving force in the concentrated solution. In general, the results indicated that the adsorption is highly pH dependent. Similar results have been also reported in other studies [11].

On the other hand the effect of the solution pH on mercury ion adsorption for eggplant hull sorbent is illustrated in Fig. 2 for initial metal concentrations of 52.6 mg/L. The results from the adsorption capacity studies show that the hydrogen ion concentration plays a substantial role in defining the mercury adsorption process. The adsorption percentage increases in the pH range from 2 to 5 and stays almost constant for pH higher than 5. The oxygen-containing functional groups on the eggplant hull surface are responsible for this metal adsorption. It is determined that various oxygen-containing groups with acidic character and different chemical properties (carboxylic, carboxylic in lactone-like binding structures, phenolic hydroxyl and carbonylic groups) are present on the eggplant hull surface. The mercury adsorption include formation of surface complexes with the participation of these functional groups on the surface of adsorbent.

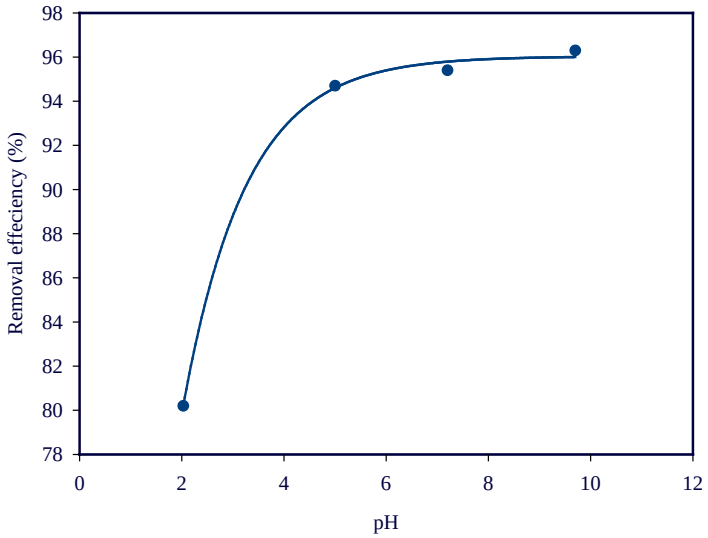

Figure 2: Effect of pH on the mercury ion removal (C_0=52.6 mg/l, T=25^{o}C, Sorbent dose=0.1g, t=5 min).

Effect of Temperature. Figs. 3 to 6 show the variation of heavy ions concentration versus time at different sorption temperatures. To remove Hg(II) ion from water by walnut shell activated carbon, parameters with constant values in the solutions were: ion concentration of 44.6 mg/L, adsorbent dose of 0.05 g, and pH= 5. The experimental data show (Fig. 3) that solution concentration of Hg(II) ions reduces with temperature increase, indicating an endothermic nature of the sorption processes, while the time required for reaching equilibrium remains practically unaffected. Also, the concentration of Hg(II) in solutions decreases with the time and attained equilibrium within 30–60 min. It is well recognized that the characteristic of the sorbent surface is a critical factor which affects sorption rate parameters and also diffusion resistance plays an important role in the overall transport of the ions. Improving the adsorption capacity with temperature suggests that active centers on the surface available for adsorption increase with the temperature. This could also be attributed to the pore size variation and enhancing rate of intraparticle diffusion of solute since diffusion is an endothermic process. Similar results are also obtained for other adsorbents at different conditions.

Fig. 4 is depicted from the experimental data and shows increase in the adsorption rate of Hg(II) ion from water at different temperatures using eggplant hull. The experimental conditions for all cases were the same with initial mercury concentration of 52.6 mg/L, Sorbent dose of 0.1g, and pH of 5. These results also confirm similar findings as above.

Fig. 5 shows the effect of temperatures (10, 25 and 45^{o}C) on the adsorption of Sr(II) at different operating times for a fixed 0.3 g dose of treated almond green hull. The initial concentration was kept constant at 45.5 mg/L. The experimental data indicate that Sr(II) ion adsorption increases rapidly during early contact times and the process achieves almost 90% of its removal efficiency. The results also indicate that there is not a significant difference among the amounts of Sr(II) adsorbed at different temperatures especially after 3 min. This is another reason for the great potential between Sr(II) and almond green hull and independency of the adsorption process to the temperature.

Fig. 6 shows the effect of temperatures (15, 25 and 35^{o}C) on the adsorption of Co(II) at different times for a fixed sorbent dose of 0.25 g and particles with mesh No. 325. The initial concentration was 51.5 mg/L for all cases. The experimental data indicate that Co(II)

ion adsorption increased by increasing time. The result of this case is also similar to the above results.

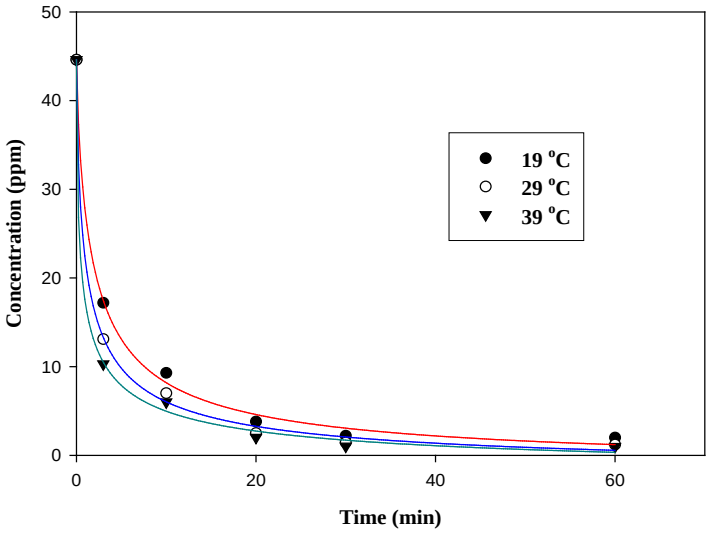

Figure 3: Effect of temperature on Hg(II) adsorption by walnut shell activated carbon.

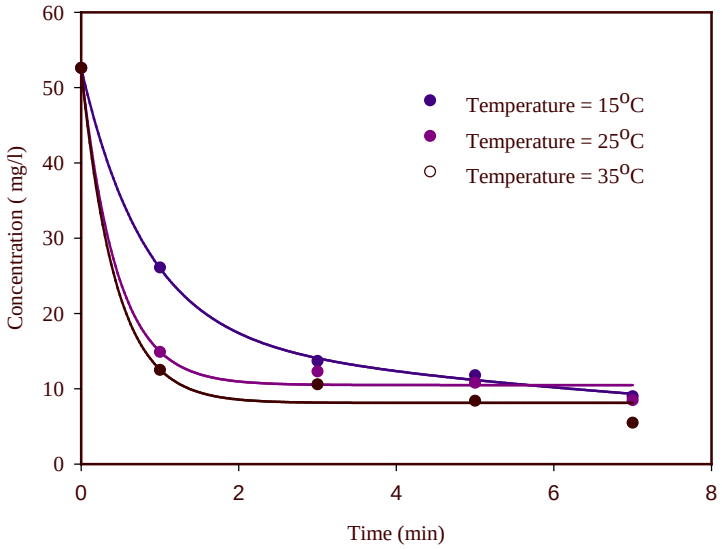

Figure 4: Effect of temperature on Hg(II) adsorption by eggplant hull.

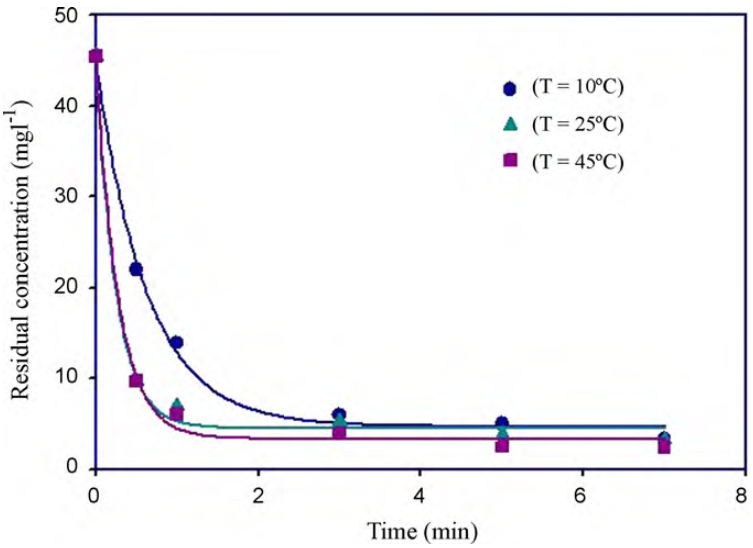

Figure 5: Effect of temperature on Sr(II) adsorption by the treated almond green hull.

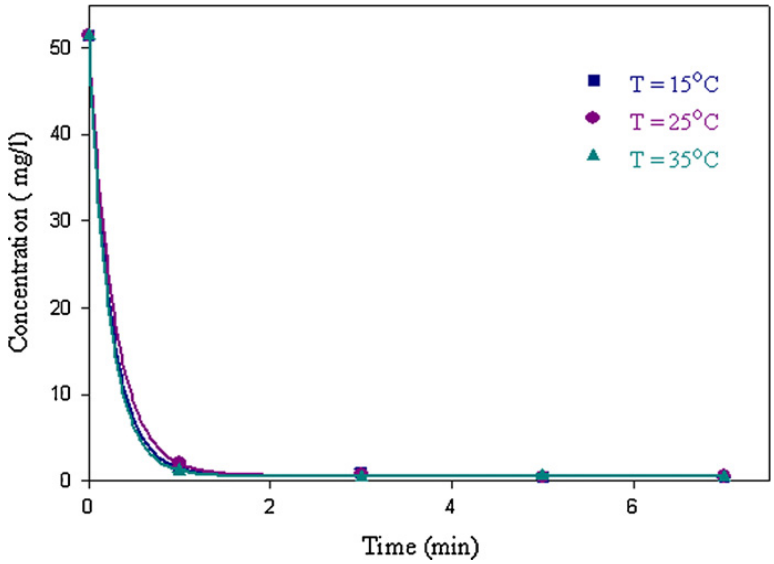

Figure 6: Effect of temperature on Co(II) adsorption by almond green hull.

Effect of initial concentration and contact time. Usually in Heavy ions adsorption studies, it is observed that the ions removal increased almost linearly with the enhancement of objective materials concentration. Many researchers have experienced similar results [12-13]. In our investigation, the effect of initial heavy ions concentration was also studied using solutions with different initial concentrations, while keeping all other parameters constant. The results in two different types are shown in Figs. 7 to 10. The first type is based on the adsorption capacity of adsorbents (mg/g) for walnut shell activated carbon and eggplant hull, and the other one is based on the residual concentration in the final solutions (mg/L) for almond green hull.

Fig. 7 shows the effect of initial Hg(II) concentration of 9.7, 20.8, 44.6 and 107mg/L on its removal efficiency using walnut shell activated carbon at 29^{o}C. The amount of Hg(II) ion adsorbed is increased in the initial stage (0–20 min range) and after that it has enhancement to reach equilibrium in approximately 60 min time.

The removal of Hg(II) ion by eggplant hull as an adsorbent are studied with various concentrations of 11.2, 24.6, 52.6 and 105.6 mg/L at 25^{o}C while all other parameters were kept constant (Fig. 8). In these experiments similar results were achieved by increasing the initial concentrations.

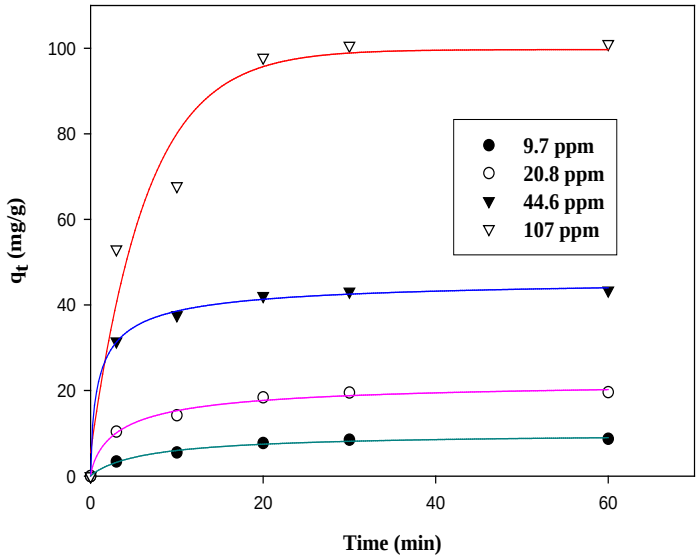

Figure 7: Effect of initial concentration on Hg(II) adsorption using walnut shell activated carbon.

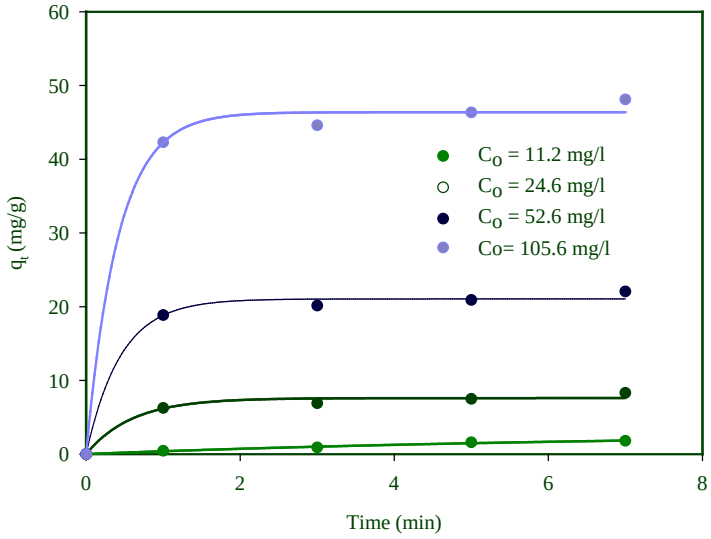

Figure 8: Effect of initial concentration on Hg(II) adsorption using eggplant hull.

The adsorption of Sr(II) has been also investigated using two different concentrations of 45 and 102 mg/L at different amounts of almond green hull (0.2, 0.3, and 0.4 g) and the results are shown in Fig. 9.

The effect of initial concentration at different levels ranging from 51.5–110mg/L and constant dose and size of almond green hull (0.25 g and mesh no. 325) can be seen in Fig. 10. It is found that the removal efficiency of Co(II) was increased especially at short time of 1 min, but the absolute amount of Co(II) adsorbed per unit weight of almond green hull was

decreased. Sorption efficiency and adsorbed amount per unit weight of Co(II) removal at 17.8, 51.5, and 110 mg/L concentrations and 1 min time are: 98.5% (3.50 mg/g), 97.22% (10.01 mg/g), and 75.5% (16.60 mg/g), respectively. The equilibrium times are found to be the same for all different concentrations studied. Similar results are also reported by researchers for a variety of adsorbate–adsorbent systems [14-16].

It is clear from all the above cases that the sorption amount of metal ions increased with increasing the initial ion concentration. The amounts of metal ions adsorbed are increased sharply with time in the initial stage and then have a gradual enhancement to reach equilibrium.

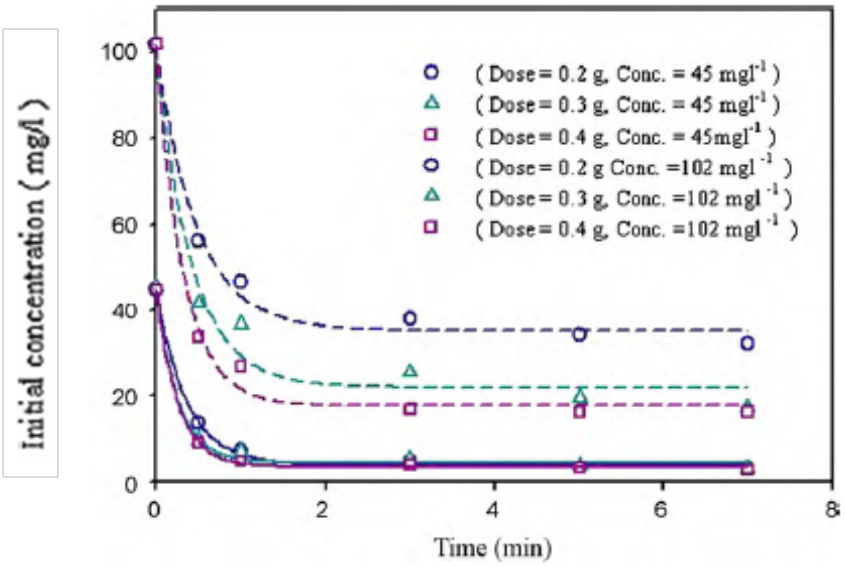

Figure 9: Effect of initial concentration on Sr(II) adsorption using the treated almond green hull.

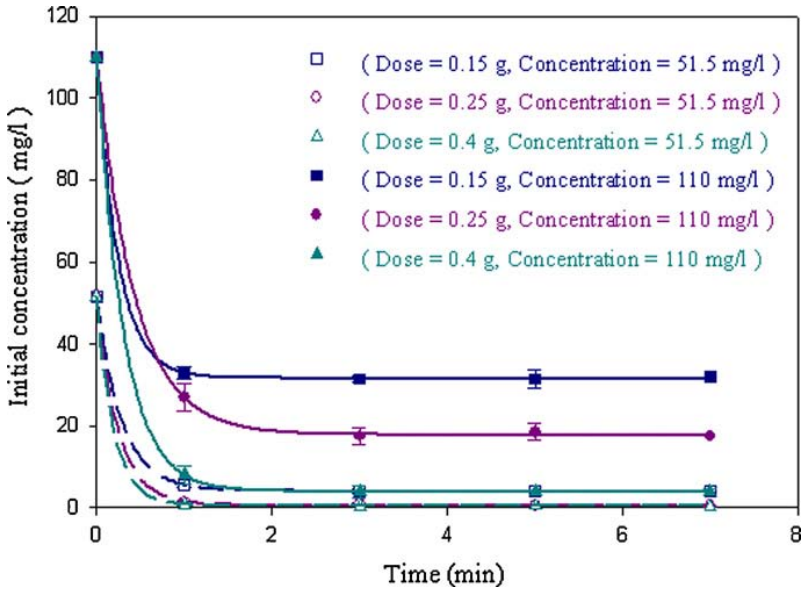

Figure 10: Effect of initial concentration on Co(II) adsorption using almond green hull.

Adsorption Isotherms. A study on the variation of initial ions concentration at a fixed amount of adsorbent per 50mL solution was carried out at room temperature. The adsorption isotherms for metal ions sorption on different adsorbents were obtained for various concentrations, while keeping all other parameters constant. The isotherm data are correlated with Freundlich and Langmuir model for further investigation. Langmuir and Freundlich equations are commonly used for describing adsorption equilibrium for water and wastewater treatment applications. Freundlich model often gives a better fit particularly for adsorption from liquids and can be expressed as:

$$q_e = K_f C_e^{\,1/n} \quad (1)$$

where q_e (mg/g) is the amount of ion adsorbed at equilibrium, and K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity. Usually, for a good adsorbent $1 < n < 10$. A smaller value of n indicates better adsorption and formation of relatively strong bond between adsorbate and adsorbent. Langmuir adsorption isotherm is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \quad (2)$$

In this model, q_m (mg/g) is the amount of adsorption corresponding to complete monolayer coverage and b (L/mg) is the Langmuir constant related to the energy or net enthalpy of adsorption. When C_e/q_e is plotted against C_e, a straight line with the slope of $1/bq_m$ is obtained. The values of Freundlich and Langmuir constants obtained from the plots are given in Table 1 for comparison. It is seen that the Langmuir model fitted the results slightly better than the Freundlich model.

Table 1: Parameters of the isotherm models for adsorption of heavy ions from water

Process	Langmuir model			Freundlich model		
	q_m (mg/g)	b (l/mg)	R^2	K_f (mg/g)	n	R^2
Hg(II), Eggplant hull	147.06	0.00648	0.989	1.160	1.136	0.999
Sr(II), Almond green hull	116.30	0.0048	0.994	3.590	1.950	0.992
Hg(II), Walnut shell activated carbon	151.51	0.0091	0.998	1.860	1.215	0.996
Co(II), Almond green hull	45.50	0.1700	0.98	14.500	4.160	0.88

CONCLUSION

The present study revealed the feasibility of using new cheap adsorbents derived from agriculture solid wastes for the removal of mercury, cobalt and strontium from aqueous solutions. The adsorption behavior is well described by the pseudo-second-order kinetic and Langmuir isotherm models. The adsorption capacity of mentioned adsorbents are obtained as 151.51, 116.30, 45.5 and 147.06 mg/g for removing heavy ions by almond activated carbon, almond green hull and eggplant hull, respectively.

ACKNOWLEDGEMENTS

The authors are gratefully acknowledged the assistance of the Water supply organization of Khorasan Razavi.

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