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APPLICATION OF MODIFIED MAIZE HULL FOR REMOVAL OF Cu(II) IONS FROM AQUEOUS SOLUTIONS

Discharge of industrial waste containing heavy metals to the environment is a main concern because of their toxicity to many life forms. Adsorption process is one of the conventional methods in order to adsorb heavy metals from wastewater effluents. Therefore, the removal of Cu(II) from aquatic solutions using modified maize hull was investigated. All experiments were performed in batch conditions. The residual Cu(II) concentration was measured by AAS. Upon increasing the adsorbent dosage, pH, and contact time and decreasing Cu(II) concentration, the removal efficiency of Cu(II) ions increased. In optimum conditions, 50% of copper was removed by modified maize hull. The experimental data were best fitted by the Langmuir type 2 model and the adsorption kinetic model followed a pseudo-second order type 1 model. It seems that the use of the modified maize hull to remove Cu(II) ions is very suitable, low-cost, and efficient.

1. INTRODUCTION

Heavy metal pollution has become one of the most challenging environmental problems. Heavy metals is a general collective term applying to the group of metals and

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metalloids with the atomic density greater than 6 g/cm^3 [1]. Many industries such as electroplating, metal-processing, paint, plastics alloy, batteries, ammunition and the ceramic glass industries, mining and smelting of metalliferous, surface finishing industry, energy and fuel production, fertilizer and pesticide industry and application, metallurgy, iron and steel, electroplating, electrolysis, electro-osmosis, leatherworking, photography, electric appliance manufacturing, metal surface treating, aerospace and atomic energy installation etc. produce and discharge wastes containing heavy metals into the environment [2, 3]. Because of low or non-biodegradability, heavy metals accumulate and their amounts are increased along the food chain. Hence, their toxic effects are more pronounced in the animals at higher tropic levels [4]. Heavy metals toxic to humans as well as to other forms of life are Fe, Cr, V, Se, Co, Cu, Cd, Ni, As, Hg, Pb, Zn, etc. [5].

Copper, used in many industries, is an essential element for human health. It plays an important role in carbohydrate and lipid metabolism and in the maintenance of heart and blood vessel activity, but, its high concentrations in the blood can be dangerous [6]. The World Health Organization (WHO) recommended a maximum acceptable concentration of Cu(II) ions in drinking water of 1.5 mg/dm^3 . Therefore, its concentration should be reduced to a lower than WHO standard [7].

Various methods exist for removing heavy metals from aqueous solutions. The main techniques utilized to reduce the concentration of the heavy metals in effluents include chemical ion exchange, chemical oxidation, precipitation, electro-dialysis, reverse osmosis, and ultrafiltration. These processes may be ineffective or very expensive, especially when the concentrations of metals are in the range of $1\text{--}100 \text{ mg/dm}^3$ [8–10]. Most of these methods can have such limitations as low efficiency, sensitive operating conditions, production of sludge, and expensive disposal of the sludge [11]. Activated carbon is very suitable for the adsorption of heavy metals and has many applications in this field. However this adsorbent has some limitations such as high cost and loss during the regeneration. For these reasons, the use of low-cost materials such as agricultural waste materials as adsorbents to remove heavy metals from effluents has been selected [12, 13]. Agricultural waste materials are usually composed of lignin and cellulose as the main ingredients. Other components are extractives, hemicelluloses, proteins, lipids, starches, simple sugars, hydrocarbons, water, ash, and many more compounds that contain a variety of functional groups active in the binding process. The functional groups present in biomass molecules are carbonyl, acetamino groups, structural polysaccharides, phenolic, amino, amide, alcohols, sulphhydryl carboxyl groups, and esters. The groups have the ability to bind heavy metals by replacement hydrogen ions for metal ions in solution or by donation of an electron pair from the groups to form complexes with metal ions in solutions [14]. So far, many low-cost agricultural waste materials have been used for removal heavy metals such as banana stem, canola, sawdust, rice husk, walnut shell, maize bran, tree fern, wheat bran, cashew nut shells, tree leaves, tea factory waste wheat, nettle ash, rice straw, wheat bran, and almond husk, corncob [1, 5, 9]. Maize is one of

the most important cereal crops of Iran and it ranks fourth in cultivated area and production after wheat, barley, and rice [15]. The aim of the present study was to examine adsorption of Cu(II) ions from aqueous solutions on modified maize hull by tartaric acid as a cheap-agricultural waste material. Various variables affecting the Cu(II) adsorption such as pH, contact time, adsorbent dosage and initial metal ion concentration were investigated to optimize the process.

2. EXPERIMENTAL

Adsorbent. The maize hull used in the study was collected locally from Mazandaran province in Iran. First, maize hull was washed with tap water to ensure complete removal of dust and ash. Then, it was rinsed seven times with double-distilled water and dried at 50 °C for one day. After drying, adsorbent passing through a 1 mm sieve was crushed. For modification, 5 g of grinded maize hull was mixed with 35 cm³ of 1.2 M tartaric acid (TA). The mixture was stirred until homogeneous state and dried at 50 °C for an overnight. After stirring, treated maize hull washed with double-distilled water to remove the residual tartaric acid. After washing, the adsorbent dried an overnight at natural conditions. After drying, the adsorbent was kept in a polyethene container for next use [16].

Adsorption study. All experiments were performed in batch conditions. The effects of variables such as initial Cu(II) concentration (10–150 mg/dm³), contact time, pH (2–6), and adsorbent dosage (1–6 g/dm³) were investigated in batch conditions for contact times 5–180 min. The stock solutions of Cu(II) were prepared by dissolving CuSO₄·5H₂O in distilled water. pH was adjusted with 0.1 M HCl or 0.1 M NaOH. In each experiment, a certain amount of Cu(II) solution and a dose of adsorbent were placed in a flask and mixed with a shaker at 120 rpm for 180 min. After mixing, the used adsorbents were separated from the suspensions by filtration through 0.45 µm cellulose filter paper. The residual Cu(II) concentration was measured using an atomic absorption spectrometer (AAS). The adsorbed Cu(II) and removal efficiency R were calculated from the following equations:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$R, \% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where, q_e is the amount of adsorbed Cu(II) per unit mass of adsorbent (mg/g). C_0 and C_e are initial and equilibrium Cu(II) concentrations (mg/dm³), respectively. V is the volume of Cu(II) solution (dm³), and m is the weight of the modified maize hull (g).

Adsorption isotherms and kinetics. To describe the distribution of metal ions between the solid and liquid phases, various isotherm models such as Langmuir, Freundlich, and Temkin were used. The Langmuir model assumes that the adsorption of the target pollutant occurs on a homogeneous surface without any interactions between them. According to the Freundlich model, adsorption of the target pollutant occurs on a heterogeneous surface. The Temkin model assumes that the adsorption energy decreases linearly with the surface coverage because of adsorbent–adsorbate interactions. The kinetic studies are important for adsorption processes because these studies show the relationship between time and the uptake rate. In the present study, the obtained kinetic data from batch studies have been analyzed by using models of pseudo-first order, pseudo-second order, intraparticle diffusion, and the Elovich model. The linear equations of isotherms and kinetics models are given in Table 1 [17, 18].

Table 1

Linear equations of isotherms and kinetic ones [17, 18]

Isotherm		Kinetic equation	
Langmuir 1	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e$	pseudo-first order	$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$
Langmuir 2	$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} \times \frac{1}{C_e}$	pseudo-second order (type 1)	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$
Langmuir 3	$q_e = q_m - \frac{1}{K_L} \times \frac{q_e}{C_e}$	pseudo-second order (type 2)	$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} \times \frac{1}{t} + \frac{1}{q_e}$
Langmuir 4	$\frac{q_e}{C_e} = K_L q_m - K_L q_e$	pseudo-second order (type 3)	$q_t = q_e - \frac{1}{k_2 q_e} \times \frac{q_t}{t}$
Freundlich	$\log q_e = \frac{1}{n} \log C_e + \log K_F$	pseudo-second order (type 4)	$\frac{q}{t} = k_2 q_e^2 - k_2 q_e q_t$
Temkin	$q_e = B_1 \ln K_t + B_1 \ln C_e$	pseudo-second order (type 5)	$\frac{1}{t} = -k_2 q_e - k_2 q_e^2 \times \frac{1}{q_t}$
		intraparticle diffusion	$\log q_t = \log k_i + 0.5 \log t$
		Elovich model	$q_t = \frac{1}{\beta} \ln (a\beta) + \frac{1}{\beta} \ln t$

3. RESULTS AND DISCUSSION

To enhance adsorption capacity, there are several methods for modification of adsorbent such as oxidation, halogenations, and etherification [1]. Vaughan et al. [19]

oxidized the corncob with phosphoric acid (PA) and citric acid (CA). They reported that the exchange capacity of the oxidized corncob depends on the used acid and the metal type in solution. The modified corncob with CA had a higher capacity for Cd, Ni, and Pb adsorption while the modified corncob with PA had a higher capacity for Cu ions. In another study, Wong et al. [20] examined Cu and Pb adsorption on rice husk (RH) modified with oxalic acid, carboxylic (CA, salicylic, mandelic, tartaric, nitrilotriacetic (NTA), and malic acids). The highest adsorption capacity was achieved when modified RH with tartaric acid were used. The purpose of this study was to modify maize hull with the tartaric acid to remove Cu(II) from aquatic solution. It was shown that adsorption efficiency was improved. The introduced free carboxyl groups of TA increase the net negative charge on maize hull, thereby increasing its binding potential for cationic contaminants [21].

3.1. EFFECT OF pH ON REMOVAL EFFICIENCY OF Cu(II) IONS

pH of the solution is very effective in distributing the charge on the adsorbent surface [7]. All the experiments were performed in the pH range from 2 to 6, since Cu(II) ions started to precipitate as $\text{Cu}(\text{OH})_2$ in more alkaline solutions. The effect of pH on the Cu(II) adsorption onto modified maize hull is shown in Fig. 1.

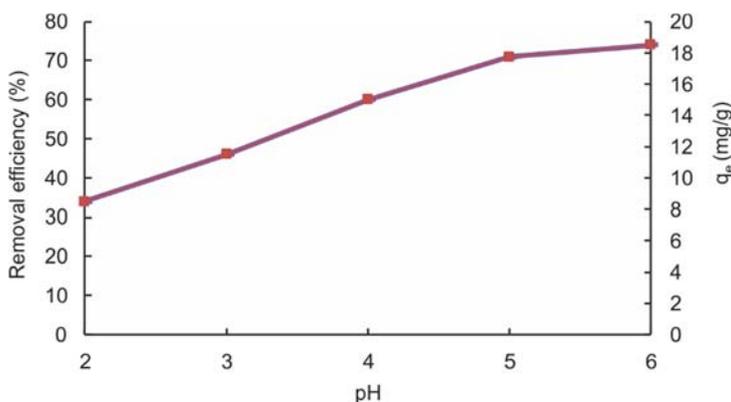


Fig. 1. Effect of pH on the removal efficiency of Cu(II); time 120 min, $[\text{Cu}(\text{II})]$ 50 mg/dm^3 , adsorbent dosage 2 g/dm^3

Adsorption of Cu(II) ions increased remarkably upon increasing pH. By increasing pH from 2 to 6 after a contact time of 120 min, the removal efficiency and amount of adsorbed Cu(II) ions increased from 34% to 74% and from 8.5 to $18.5 \text{ mg} \cdot \text{g}^{-1}$, respectively. The increase in adsorption capacity was due to dissociation of carboxylic groups at higher pH. This could be explained by the increase in density of the negative charge on the cell surface, causing proton removal on the cell binding sites, thereby increasing its adsorption capacity [22]. The results of linear regression analysis showed that there was a significant relationship between pH and Cu removal ($P = 0.003$).

3.2. EFFECT OF CONTACT TIME ON THE REMOVAL EFFICIENCY OF Cu(II) IONS

To determine the contact time necessary to achieve the equilibrium, sampling was performed for 5–180 min. After increasing the contact time from 5 to 90 min, the removal efficiency increased from 40 to 74% (Fig. 2). The removal efficiency sharply increased during the first 60 min. The equilibrium value was reached approximately after 90 min when the most active sites on the surface of the adsorbent had been saturated [23]. According to the results of the linear regression analysis, there was a significant relationship between contact time and removal efficiency of Cu(II) ions ($P = 0.01$).

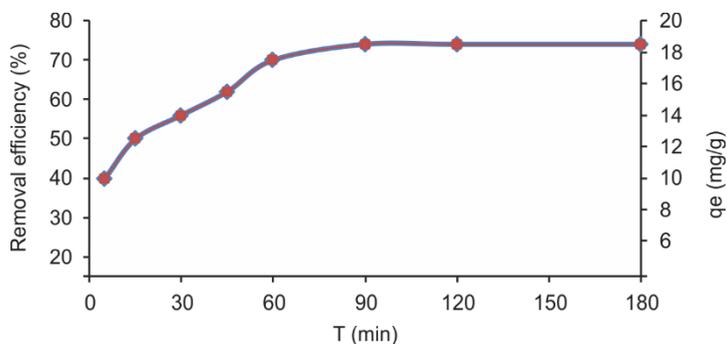


Fig. 2. Effect of contact time on the removal efficiency; pH 6, [Cu(II)] 50 mg/dm³, adsorbent dosage 2 g/dm³

3.3. EFFECT OF Cu(II) ION CONCENTRATION

The effect of initial concentration of Cu(II) ions on the removal efficiency is shown in Fig. 3.

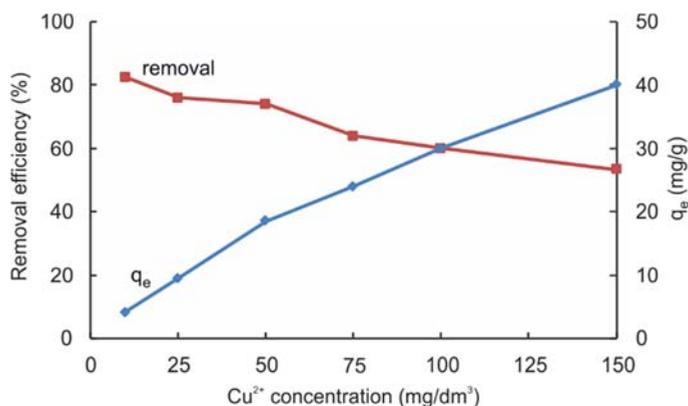


Fig. 3. Effect of Cu(II) concentration on the removal efficiency; time 90 min, pH 6, adsorbent dosage 2 g/dm³

The removal efficiency of Cu(II) ions decreased upon increasing their concentration from 10 to 150 mg/dm³ (Fig. 4). It was 82.5% for the concentration of 10 mg/dm³ and decreased to 53% for 150 mg/dm³. At higher concentrations, the lower removal rate of Cu(II) ions can be due to reduced (e.g., saturation) of active sites on the adsorbent surface [24]. Linear regression analysis showed that there was a significant relationship between initial concentration and removal efficiency ($P = 0.001$).

3.4. EFFECT OF MODIFIED MAIZE HULL DOSAGE

Figure 4 shows the effect of modified maize hull dosage on adsorption of Cu(II) ions. because of the availability of more and more binding sites for complexes of Cu(II) ions, The removal efficiency increased by increasing the adsorbent dose up to 5 g/dm³. For higher doses, however, it remained constant.

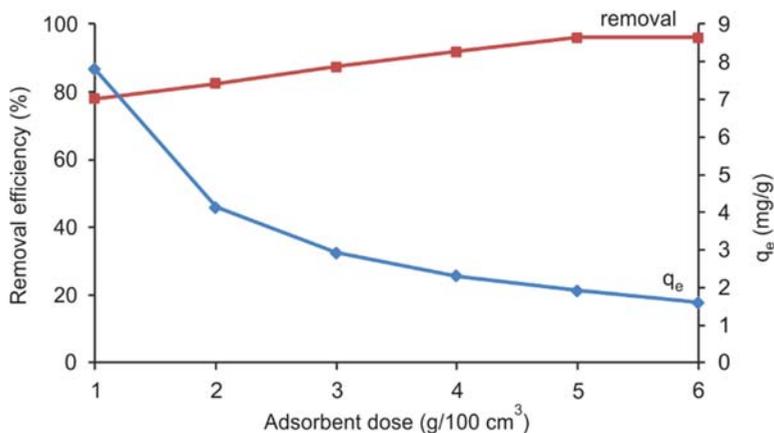


Fig. 4. Effect of adsorbent dose on the removal efficiency of Cu(II); time 90 min, pH 6, [Cu(II)] 10 mg/dm³

Despite the fact that the removal efficiency increased upon increasing the modified maize hull dosage, the amount of adsorbed Cu(II) ions per gram of modified maize hull decreased. The main reason for this decrease is the increase in the weight of the modified maize hull at constant Cu(II) concentration. However it is possible that at higher doses of modified maize hull, its aggregation or agglomeration might occur, leading to a decrease in the specific surface area, and simultaneous increase in temperature. The particle interaction at higher adsorbent dosages may also facilitate desorption of some of the loosely bound metal ions from the sorbent surface [25]. According to linear regression analysis, it can be concluded that there was a significant relationship between the adsorbent dose and removal rate of Cu(II) ions ($P = 0.001$).

3.5. ADSORPTION KINETICS AND ISOTHERMS

The isotherm models and adsorption kinetic data are shown in Fig. 5 and in Table 2, respectively. The coefficient of determination (R^2) for the Langmuir type 2 was (Fig. 5) greater than 0.99, which was slightly more than the R^2 value obtained from the other equations. So, the Langmuir 2 model better than other models fitted the equilibrium data obtained for adsorption of Cu(II) ions on modified maize hull.

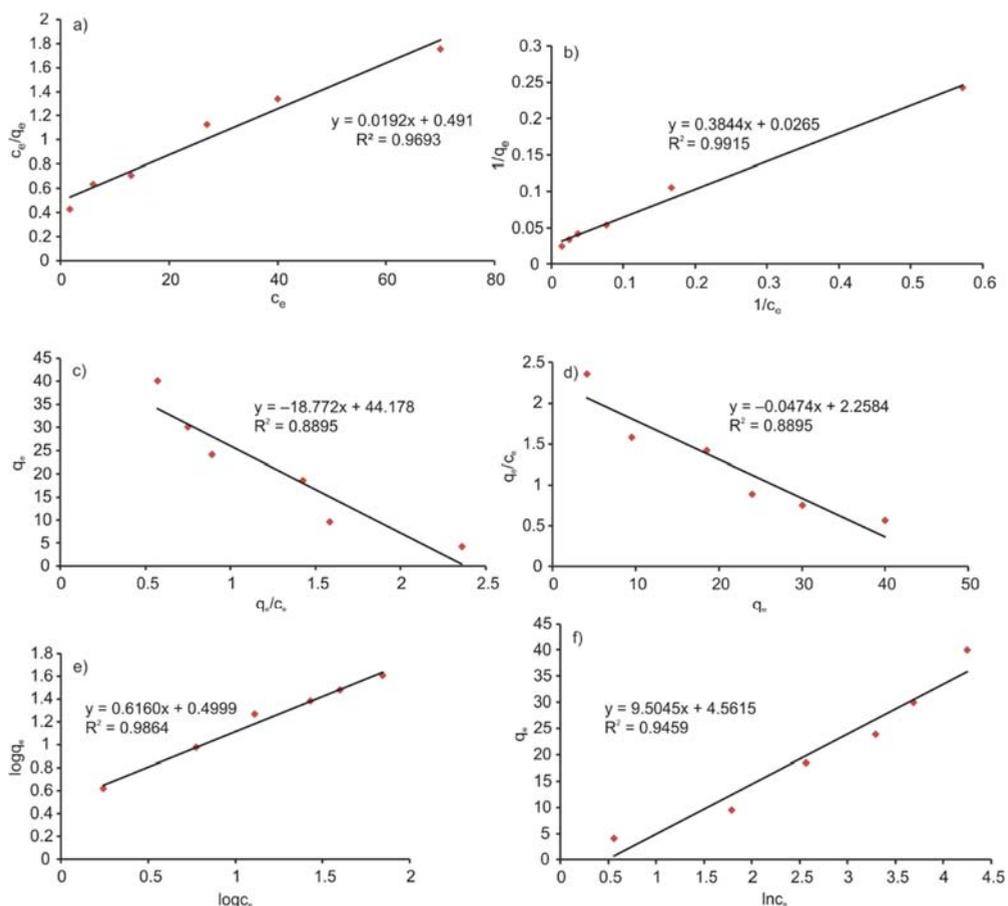


Fig. 5. Isotherm models: a) Langmuir 1, b) Langmuir 2, c) Langmuir 3, d) Langmuir 4, e) Freundlich, f) Temkin

Thus in the Langmuir model, it is assumed that the Cu(II) ions adsorption occurs on a homogeneous surface in a monolayer without any interaction among adsorbed ions. The separation factor R_L value was 0.09–0.59, which confirms the favorable adsorption

of copper on modified maize hull. The results of the kinetic investigations showed that the highest determination coefficient was related to the pseudo-second order type 1.

Table 2

Kinetic constants of the adsorption of Cu(II) ions on modified maize hull

Model	R^2	q_e [mg/g]	k_1 [1/min]	k_2 [g/(mg·min)]	K_i [mg/(g·min) ^{0.5}]	a [mg/(g·min)]	β [g/mg]
Pseudo-first order	0.92	11.17	0.03	–	–	–	–
Pseudo-second order (type 1)	0.99	19.6	–	0.006	–	–	–
Pseudo-second order (type 2)	0.89	17.8	–	0.01	–	–	–
Pseudo-second order (type 3)	0.81	18.15	–	0.01	–	–	–
Pseudo-second order (type 4)	0.81	19.5	–	0.009	–	–	–
Pseudo-second order (type 5)	0.89	20.6	–	0.01	–	–	–
Intraparticle diffusion	0.85	–	–	–	9.6	–	–
Elovich	0.95	–	–	–	–	21.4	0.37

4. CONCLUSION

Adsorption of Cu(II) ions from aqueous solution using modified maize hull and tartaric acid as low-cost adsorbent was investigated. The optimal parameters for removing copper (optimum C_0 50 mg/dm³) were pH 6, contact time 90 min, and adsorbent dose 5 g/dm. The removal efficiency of Cu(II) ions was higher than 96% at optimal conditions. The isotherm data show that the adsorption model of Langmuir type 2 and kinetic model of the pseudo-second order type 1 fit best experimental data. The findings of the current study showed that maize hull biomass modified with tartaric acid (as low-cost adsorbent) can be employed as an alternative to commercial activated carbon for the adsorption of Cu(II) ions from aqueous solutions.

SYMBOLS

- q_e – the equilibrium adsorption capacity, mg/g
 C_e – Cu(II) ion concentration at equilibrium, mg/dm³
 q_m – maximum adsorption capacity, mg/g
 K_L – adsorption equilibrium constant of the Langmuir isotherm, dm³/mg
 K_F – constant of Freundlich isotherm, (mg/g)·(mg/dm³)^{1/n}
 K_i – Temkin isotherm equilibrium binding constant, dm³/g
 q_t – adsorption capacity at time t , mg/g

- k_1 – pseudo-first order constant, 1/min
 k_2 – pseudo-second order constant, g/(mg·min)
 k_i – intraparticle diffusion constant, mg/(g·min^{0.5})
 a – initial adsorption rate of the Elovich equation, g/(mg·min)
 B_1 – constant related to heat of sorption, J/mol
 β – Elovich equation parameter related to the surface coverage, g/mg
 n – empirical constant of the Freundlich isotherm

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