Mesopotamia Environmental Journal
ISSN 2410-2598
Journal homepage http//:www.bumej.com

DOI: http://dx.doi.org/10.31759/mej.2018.4.3.0072

Description of Cu^{+2} removals from aqueous solution using egg shell as low cost adsorbent

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To cite this article:

Chyad T.F., Description of Cu^{+2} Removals from Aqueous Solution Using Egg Shell As Low Cost Adsorbent *Mesop. environ. j*., 2018, Vol. 4, No.3, pp. 72-80.

Received date: 30/5/2017 accepted date: 12/1/2018 published date:15/6/2018

Abstract:

The removal of heavy metal ions from wastewater by as egg shell was investigated in the present study. The adsorbent behavior of metal ions on the resin was investigated depending on contact time, pH, resin dosage, and initial metal concentration. The adsorption process depending on pH shows maximum removal of metal ions at a pH of 6 for egg shell for initial metal ion concentrations of 1.33 mg/l, with resin dose of 20 g and the equilibrium time was reached in 105 minute. The results indicate that egg shell can be used as an efficient adsorption material for removal of heavy metal ions from waste water. Application of this model was described by the equations of Langmuir, Frendlich and Elvich isotherm, Frendlich isotherm model provided best correlation compared with other isotherm models.

Key words: *copper; egg shell; adsorbent; Wastewater*.

Introduction

The removal of toxic metals from wastewater is a matter of great interest in the field, which is a serious cause for pollution of environment. Numerous metals such as chromium, mercury, lead, copper, cadmium, manganese, etc., are known to be significantly toxic. Copper is a metal that is used widely in the many industries. So that it is expected to discharge large quantities to environment which leads to serious pollution of the environment. These facts have motivated many physicochemical methods for heavy metal removal from aqueous solution, including adsorption, chemical precipitation, solvent extraction, reverse osmosis, ion exchange, chemical oxidation and reduction, filtration, and electrochemical treatment. Among the various water-treatment techniques described, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness [1]. The presence of inorganic pollutants such as heavy metals in aquatic systems is of considerable concern because of their non-biodegradability, mobility and toxicity. Heavy metals can accumulate in the human body over time, causing serious health effects [2]. Accordingly, removal of heavy metals from wastewaters has received a great attention in recent years [3]. Waste eggshells contain high contents of calcium carbonate (85–95%); therefore, their recycling or reuse has the potential to reduce environmental pollution while acting as a cost effective material for the immobilization of heavy metals in wastewater and soil [4]. More recently, Ok et al. [5, 6, and 7] reported that lime based waste materials such as eggshells can be used as an alternative to $CaCO_3$ for the immobilization of heavy metals in contaminated soils. However, little is known about the use of eggshells remove heavy metals from aqueous systems [8]. Therefore, this study was conducted to evaluate the effectiveness of waste eggshells and coral on removal of Cu^{+2} from aqueous solutions. The metal sorption was based on the Langmuir and Freundlich adsorption isotherm models [9]. The objective from this study is to investigate removal of Cu^{+2} by adsorption on egg shell waste.

Materials and Methods

Materials

Waste egg shell

Natural and boiled egg shell was collected and washed with tap water several times then air-dried and incubated in hot air oven at 40 ºC for 30 minutes (because protein component in egg shell can denature at high temperature; > 40ºC). Consequently, egg shell were ground to a powder in a grinder, and sieved in 60-100 mesh (0.25-0.104 mm). Material was then crushed mechanically and passed through a 1-mm sieve to obtain a homogeneous particle size. The prepared sorbent was then stored in a desiccator until further experimentation.

Batch experiments

Batch equilibrium tests are carried out to specify the best conditions of contact time, pH, initial concentration, resin dosage and shaking velocity. This means that these tests are suited to identify activity of the reactive material and the sorption isotherm. Series of 250 ml flasks are employed. Each flask is filled with 100 ml of copper solution which has initial concentration of 50 mg/l. About 0.25 gm. of adsorbent was added into different flasks. The solution in the each flask was kept stirred in the high-speed orbital shaker at 270 rpm for 2 hours. The measurements were carried out using atomic absorption spectrophotometer.

Results and Discussions

Equilibrium Time

The contact time should be fixed at a certain value that ensures reaching equilibrium concentrations. Figure 1 shows the effect of contact time for Cu^{+2} removal using 20 gm. of eggshell added to 100 ml of contaminated solution for batch tests at

25ºC and 250 rpm. The figure demonstrates that the removal percentage of the contaminant is significantly increases with the increasing of the contact time. The kinetic data show that 50% $Cu^{+2}$is removed mainly at 90, 105, 120 and 135 minutes. It is important to note that there is no significant change in the residual concentrations after the time of 135 minutes. The initial adsorption rate was very fast and this may be due to the existence of greater number of resin sites available for the adsorption of metal ions. As the remaining vacant surface sites decreasing, the adsorption rate slowed down due to formation of repulsive forces between the metals on the solid surface and in the liquid phase [10].

The increase in uptake of metal ions with contact time can be due to the decrease mass transfer coefficient of the diffusion controlled reaction between resins and metal ions. This is a crucial parameter for an optimal removal of metal ions in the waste water [11]. Therefore, the sorption experiments in other batches were considered to be conducted at these contact times.

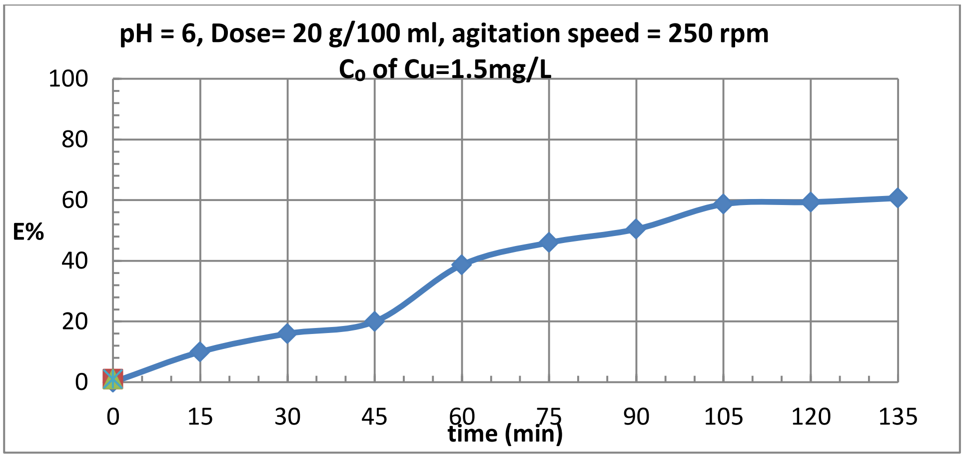

Fig.1.removal efficiency of Cu+2 on egg shell as a function of contact time

Initial pH of the Solution

The sorption of Cu+2on eggshell was examined at different pH values ranged from 2 to 10 with initial concentrations of 1.5 mg/L and different values of contact time Figure 2. The pH of the solutions was adjusted to the required value with 0.1 M H2SO4 and NaOH solutions. It is clear that the best initial pH of the sorption is about 6. The retention of metals on the resin was studied as a function of hydronium ions. Hydronium ion concentration (pH effect) is an important parameter affecting the ion exchange process. NaOH and HCl were used for pH adjustment. pH affects both the surface charge of adsorbent and the degree of ionization of heavy metals in solution [12].The maximum removal for strong electric field are present and electrostatic effects may become the dominant factor, such that small ions, which have a higher charge density are bound more strongly [13, 14].This may be attributed the competition the hydrogen, sodium, and metal ions on the sorption sites, at low PH values. A pH values higher than 7 insoluble copper ions hydroxides starts precipitate from the solutions making true sorption studies impossible [15, 16].Any increasing or decreasing of the pH from this optimal value can be lead to reduce the sorption of these contaminants.

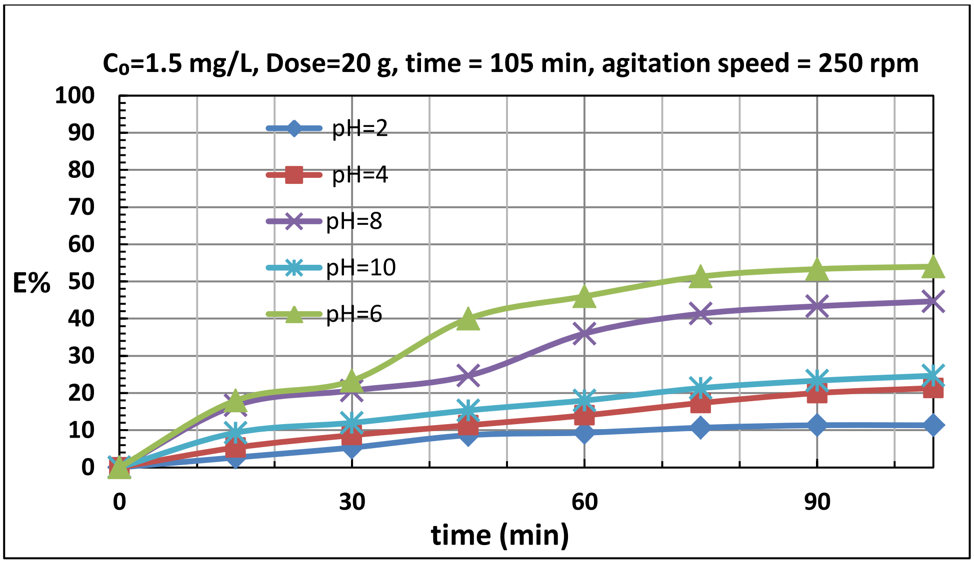

Fig. 2 removal efficiency of Cu^{+2} with egg shell at different pH solution.

Egg shell Dosage

The dependence of Cu^{2+}sorption on sorbent dosage was studied by varying the amount of eggshell from 5 to 30 gm. added to 100 ml of contaminated solution at 25ºC and keeping other parameters as follows; Co= 1.33mg/L, pH = 6 and contact time 135 minute. As illustrated in Figure 3 the removal efficiencies of the heavy metal improve with the increasing sorbent dosage from 5 gm. to 20 gm. While it is approximately constant afterwards of 20 g. This is due to the fact that the higher dose of sorbent in the solution produces a greater availability of sorption sites. Also, after a certain dose of sorbent, the maximum sorption sets in. So, the amount of $Cu^{+2}$is bounded to the sorbent. It is apparent that by increasing the resin amount, the sorption density, and the amount of adsorbed metal ion per unit mass increases [17].Sorption of metal ion was increased as the resin amount rises. The results were expected because for a fixed initial metal concentration, increasing adsorption amount provides greater surface area or ion exchange sites or adsorption site [18]. The decrease in ion exchange density can be attributed to the fact that some of ion exchange remains unsaturated during the sorption process; whereas the number of ion exchange sites increases by an increase in sorbent and this results in an increase in removal efficiency [19]. Therefore the amount of the contaminant remains constant even with further addition of the sorbent dosage.

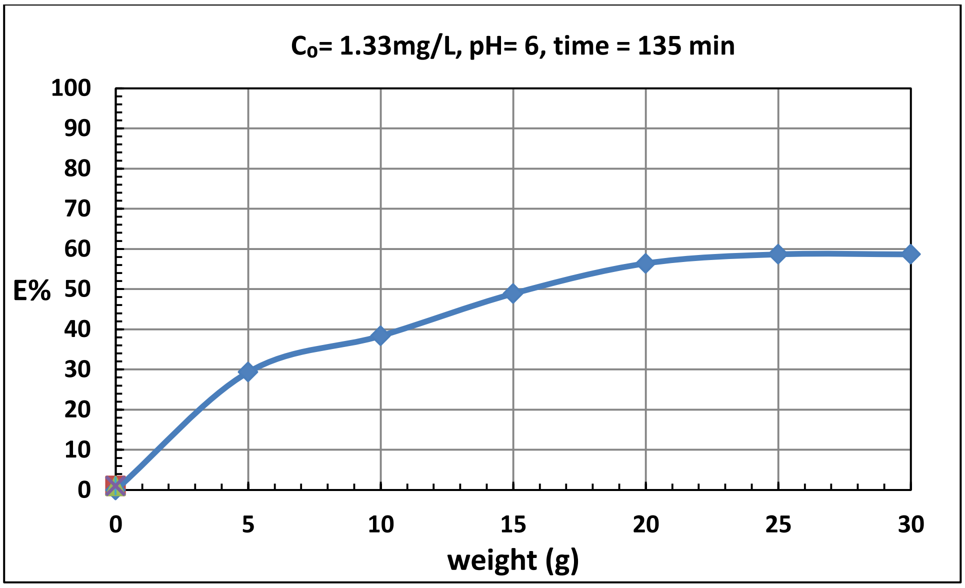

Fig. 3Effect of egg shell dosage on removal efficiencies of Cu^{+2}.

Initial Concentration of Cu^{+2}

Figures 4 show the effect of the initial concentration of Cu^{+2} on the sorption due to the eggshell. The figures indicate that the amount of these contaminants sorbed per unit mass of sorbent increase with the increasing in initial concentration as indicated in Table 1.

Table 1: Initial concentration of copper ions.

Initial concentration(mg/l)	1	1.33	1.5	1.8
Efficiency(%)	47	56.39	62.667	68.333

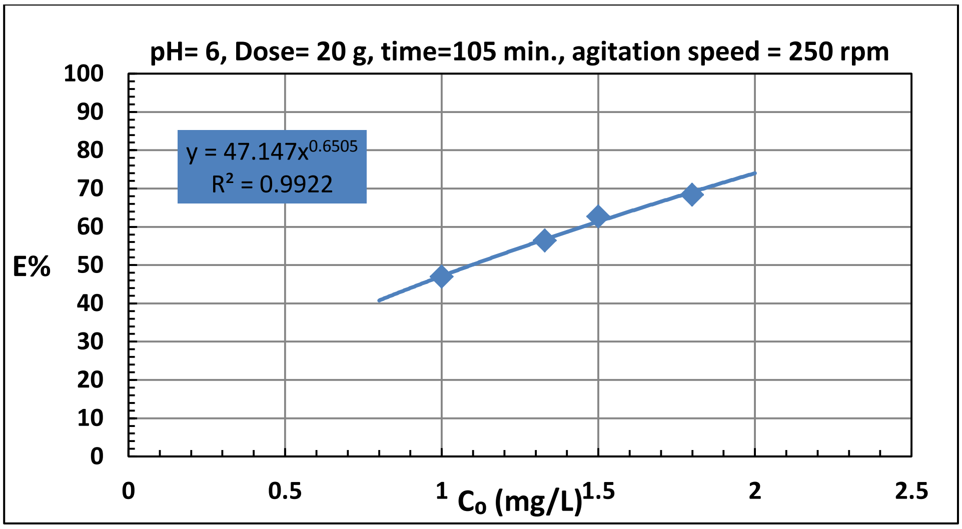

Fig 4. Effect of initial concentration on the removal efficiency of Cu+2 on egg shell

Sorption Isotherms

Sorption isotherms are mathematical models describe the distribution of the sorbate species among liquid and sorbent, based on a set of assumptions that are mainly related to the heterogeneity / homogeneity of sorbents, the type of coverage and possibility of interaction between the sorbate species. These isotherms relate contaminant uptake per unit mass of sorbent, q_e, to the equilibrium sorbate concentration in the bulk solution phase, C_e. Accordingly, the estimated coefficients of the each model were estimated depending on the slope and intercept of the best fit line of Figures 5. using liner regression analysis technique as shown in Table 2.

Fig.5 Linear isotherm models for sorption of Cu^{+2} onto eggshell (Co=1.33 mg/l, pH=6, agitation speed=250 rpm, contact time=105 minute).

Model	Parameters	Cu^{+2}
Langmuir	q_m (mg/mg)	**7.037**
	b (L/mg)	**3.8314**
	R^2	**0.5936**
Freundlich	K_F (mg/mg)(l/mg)$^{1/n}$	**8.026**
	n	**0.6069**
	R^2	**0.9173**
Elovich	q_m (mg/mg)	**-11.07**
	(l/mg)K_E	**0.3749**
	R^2	**0.837**

Depending on the results of Table 2. it is clear that the Frendlich isotherm model provides the best correlation in comparing with other isotherm models for Cu+2sorption.

Figure6. shows the validity of the Frendlich model using the equilibrium concentration values and the estimated parameters of Table2.

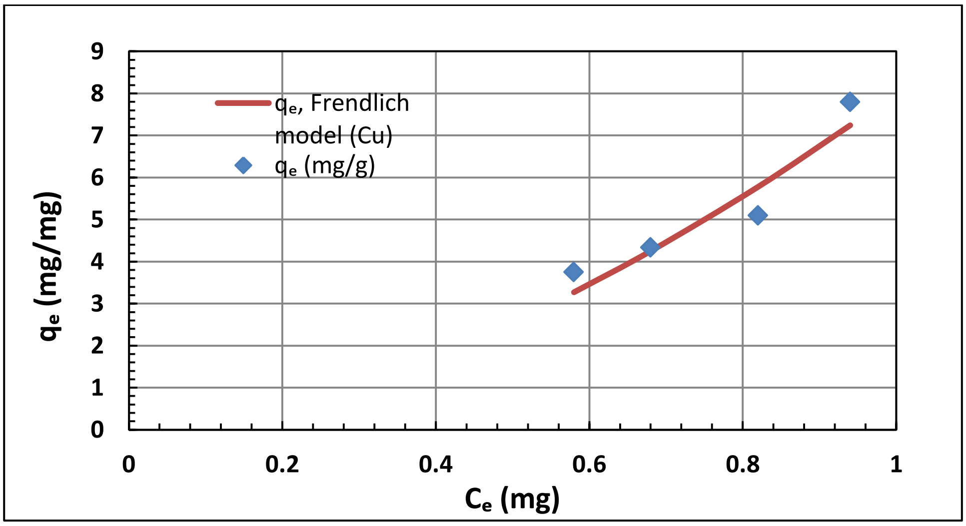

Fig. 6: Comparison of the experimental results with the q_e values obtained by Frendlich isotherm model for Cu^{+2} sorbed by egg shell.

Conclusions

This study successfully proved that Cu^{+2} could be adsorbed from an aqueous solution in significant amounts by eggshell waste.

In batch model, adsorption studies:

- The equilibrium time of Cu^{+2} was found at 105 minutes.
- The best initial pH of the sorption was found to be 6 and an increasing or decreasing of the pH from this optimal pH causes reduction in the sorption of the contaminants.
- Removal efficiencies of these heavy metals improved when the increasing sorbent dosage increased to value of 20 g. and remained approximately constant after this amount.
- Application of this model is described by the equations of Langmuir, Frendlich and Elvich isotherm. However, Frendlich isotherm model provided a best correlation compared with the other isotherm models.

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