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A Unique Modified Eggshell Method as a Model to Reduce and Remove Copper(II) from Aqueous Solutions for Water Treatment

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ABSTRACT

The aim of this study was to investigate the removal of Cu^{2+} using eggshells and iron-modified eggshells. Batch adsorption experiments were conducted to assess the impact of various operational parameters, including contact time, pH, isotherms, and kinetics. The samples were characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDS). XRD analysis confirmed the presence of crystalline phases, specifically trigonal and hexagonal structures, in both eggshell samples. The addition of iron resulted in a reduction in the average crystallite size from 33.157 nm to 16.086 nm. The FTIR spectra exhibited a carbonyl peak at 1804 cm^{-1}. The results indicated that Cu^{2+} adsorption on eggshells occurred rapidly, reaching equilibrium within 80 min, with an optimal pH range of 6.0 to 7.0. Furthermore, the modified eggshells demonstrated superior Cu^{2+} removal compared to unmodified eggshells due to the increased external surface area. The copper concentration on the eggshell surface increased from 0% to 94.58%, suggesting an ion exchange between iron and copper within the modified eggshell. The experimental data exhibited a better fit with the Freundlich isotherm model, indicating the presence of heterogeneous adsorption sites for Cu^{2+}. The kinetics of adsorption followed a pseudo-second-order rate equation. This study highlights the efficacy of using eggshells, particularly iron-modified eggshells, as a cost-effective and accessible method for the efficient removal of heavy metals like Cu^{2+} from drinking water or industrial wastewater.

Keywords: Egg-shell, Modified eggshell, Adsorption, Heavy metals.

INTRODUCTION

Heavy metals in aquatic systems are of considerable concern to the environment due to their difficult composition; and they can accumulate in the human body over time, causing serious health problems. Reduction and removing these heavy metals from water resources has become very important recently[1].

The most significant methods for treating water over the past few decades include screening, filtration, centrifugation, micro- and ultrafiltration, crystallization, sedimentation, and gravity separation, as well as flotation, precipitation, coagulation, oxidation, solvent extraction, evaporation, distillation, reverse osmosis, ion exchange, electro-dialysis, and adsorption[2]. However, these techniques have certain limitations, such as high energy consumption during pressure plumb operations, the use of chemicals in certain cases, the need for pre and post-treatment processes, and costs that are influenced by the volume of water[3]. Adsorption is a commonly employed technique in the treatment of drinking water due to its numerous benefits. It exhibits high effectiveness in eliminating a broad spectrum of contaminants from water, making it suitable for application in diverse water sources, such as groundwater and surface water. Adsorption processes typically yield high removal efficiencies for targeted contaminants and can be regenerated and reused, thereby enhancing their cost-effectiveness. Additionally, these processes are often relatively straightforward to operate and maintain.[4]

The presence of copper in water resources and the environment due to industrial activities such as copper and gold mining, electronic factories, and wire electric factories[5]. The concentration levels of copper in drinking water due to WHO should not exceed 0.2 ppm, while high concentration than 6 ppm can cause serious illnesses like vomiting, abdominal cramps, skin irritation, nausea and anemia, while excess Cu(II) can accumulate in the kidneys, liver, brain and other human organs it causes health problems[6,7].

Egg-shell consists of calcium carbonate, sulphate, and phosphate as a major component beside some minerals existed as the minor elements such as sodium, potassium, iron, copper….etc. The distribution of components is as follow: calcium carbonate (96%), organic deposited (2%) calcium phosphate (1%) and magnesium carbonate (1%). Eggshell powder has many attractive applications, which drew researchers to its importance, due the presence of a large amount of calcium[8]. Egg shell powder has been used in wild range in water-treatment process as alternative adsorbent agent, it showed high affinity to remove heavy metals, anions, dyes, and other elements from aqueous solutions[9,10].

Egg shell structure modified by attached some function groups such as carboxylate, hydroxyl, amide and amine groups…etc. they applied for binding to remove elements from aqueous solutions. Liu *et al.,* designed experiment to modified egg shell structure, by attacheding functional group such as polyethyleneimine (PEI) or polyaziridine to the surface of the eggshell to remove chromium (iv). The results represent that the capacity of removing chromium has been expanded by 150%[11]. Ahmad and his co-author applied egg-shell and coral waste to remove Pb^{2+}, Cd^{2+} and Cu^{2+} from aqueous solutions without any modifications. Egg-shell and coral waste showed high affinity to remove heavy metals due to the following selectivity Pb^{2+}>Cu^{2+}>Cd^{2+}[12].

There are few studies that illustrate coated, attached, or activated the surface of egg shells by inorganic functional groups like metal oxide[13]. From this point we examine the ability to remove copper ions from wastewater, by eggshell and activated eggshell by adding iron sulphate.

MATERAIL AND METHODS

Preparation of Eggshell (adsorbent)

The Eggshell sample was collected from house waste and washed with deionized water to remove impurities and interference materials. The membrane was removed by hot deionized water. The sample was dried at 90^0C using dry furnace. Aforementioned sample was grinded and sieved to obtain a homogenous size.[14]

Preparation of solutions

To test the ability of the eggshell powder to remove metals ions from aqueous solutions, Artificial solutions were prepared to examine the removal, a 1000 ppm of stock solution of copper(II) prepared as followed: (7.8590 g, 0.0315 mol) of copper(II) sulfate pentahydrate $CuSO_4.5H_2O$ was dissolved in 2 L of deionized water. From aforementioned solution a different concentration (100,200,300,400,500) ppm were prepared.

Coated eggshell powder by iron oxide

To increase the influence of the eggshell powder to remove copper(II) ions from aqueous solutions, the external surface area is raised by iron oxide as coated materials on eggshell.

Unmodified eggshell powder labeled as Eg1, while modified eggshell by iron Eg2. The fine eggshell powder was rinsed with deionized water several times before drying at 100. To precipitate the iron oxide on the surface of the eggshell powder, 20 mL of 5N NaOH solution was added dropwise while the eggshell powder was immersed in a 50 mL of (10.0000 g, 0.0360 mol) $FeSO_4.7H_2O$. For an hour, the solution with stirreding. The iron oxide-coated eggshell powder was filtered off, washed with deionized water, and dried at 100°C.

Method of removing

Batch adsorption was performed using one synthetic ion solution Cu^{2+} to regard concentration, pH, and contact time.

To adjust dynamic adsorption, a percentage 1:100 between powder and solution, about 0.5 g were added to 50 mL, and placed on a magnetic stirrer, the solution concentration in liquid phase was determined by atomic absorption AAS after the adsorption process. The mass balance equation used to identify the removal percentage.

$$qe = \frac{C^{\circ} - Ce}{m} * V \quad (1)$$

Nevertheless, C_o and C_e were the initial and final copper ions concentration, respectively, V represent solution volume, and m the mass if eggshell in gram. q_e the removing of copper in eggshell.

The Characterizations

Five techniques such as XRD, FTIR, SEM, EDX, and AAS were applied to identify crystal structure, external structure morphology, elemental percentage, and the main functional groups for egg-shell powder and the solution concentration in a liquid phase.

The adsorption process factors

Different factors governed the uptake of copper ions from an aqueous solution. Here, two main factors have been examined pH, and contact time at a specific temperature with five different concentrations from 100-500 ppm. While pH was determined between[2-10].

Two models Langmuir and Freundlich have been applied to describe the interaction between adsorbent and adsorbate. The isotherms are calculated from 100-500 mL with constant egg-shell doses. While Kinetic experiments were applied using a constant dose of eggshell and Cu(II) concentration at a different period from 0-60 minute. The amount of metal ion adsorbed, q_t, was calculated from the equation;

$$qt = \frac{C^{\circ} - Ct}{m} * V \quad (2)$$

C_O and C_t are the initial and unbaked of copper ions, respectively.

RESULTS & DISCUSSION

Characterization and analysis

The spectra result of X-ray diffraction for natural and functionalized egg shells in Fig. 1. The main peak for both samples were observed at 29.99 and 29.89 respectively at 2 theta scale, it was indicated to calcium carbonate $CaCO_3$ which demonstrated the fact of considerable hardness of the eggshell. In addition, other peaks have been detected at 23, 31, 36, 39, 43, 48, and 57° at 2 theta scales. XRD resulted in peaks on Fig. (1) identical with JCPDS file and the peaks were corroborated with the presence of calcite $(CaCO_3)$[15].

The formation of other peaks may be consideration of Magnesioferrite, and Magnetite in the structure of Eg2. The result illustrates that the average of crystallite size has been reduced approximately from 33.157 nm to 16.086 nm, due to the addition of iron.

Which calculated by Scherer equation:

$$D = \frac{0.89\lambda}{\beta \cos\theta} \quad (3)$$

Where D is egg-shell grain size, λ is XRD instrument wavelength and the width of peak is signing by β and θ is Bragg`s angle[16,17].

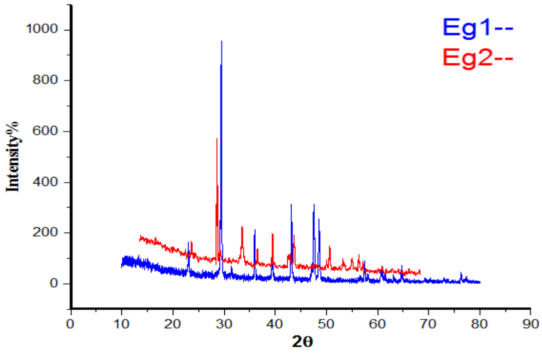

Fig. 1. XRD patterns of Eg1 and Eg2

The FTIR spectra of eggshell powders Eg1, Eg2. The peak around 1804 cm^{-1} was signed to carbonyl functional group C=O. The formation of C=C and C=O stretching vibration functional groups were detected at 1440 cm^{-1}. C-H recorded at 720 cm^{-1}. Furthermore, Fig. 2 shows the removal of Cu^{2+} ion by Eg1 and Eg2 most of functional groups were shifted to lower wavelength intensity. After loading Cu^{2+} ions the result illustrated that Cu^{2+} ions have attached to H, O and Fe atoms of OH and C=O functional groups and form Cu-O and Cu-Fe peaks which recorded below 540 cm^{-1}.[14-16, 18,19,20]

The general surface morphology and the mechanisms of adsorbents have been determined up by scanning electron microscope SEM of samples. Fig. 3 (a, b, and c) showed SEM of eggshell powder Eg-1, coated eggshell by iron Eg-2, and after adsorption copper Eg-3. It's can be seen a clear porous, irregular surface and non-adhesive structure of the eggshell surface. As shown, the crystal structure of the eggshell particle had an angular fracture pattern[18].

After adsorption the peak of iron decreased from (61.6 wt%) to 0.13 wt%). And copper peak appeared from (0 to 94.58 wt%). This results indicate that ion-exchange between iron and copper has been occur in modified eggshell.

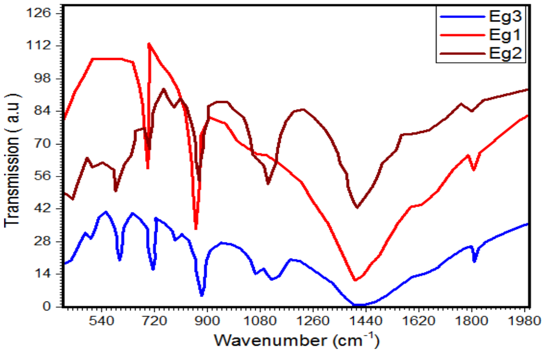

Fig. 2. FTIR result of natural Eg1, Functionalized egg-shell Eg2 and after removal copper Eg3

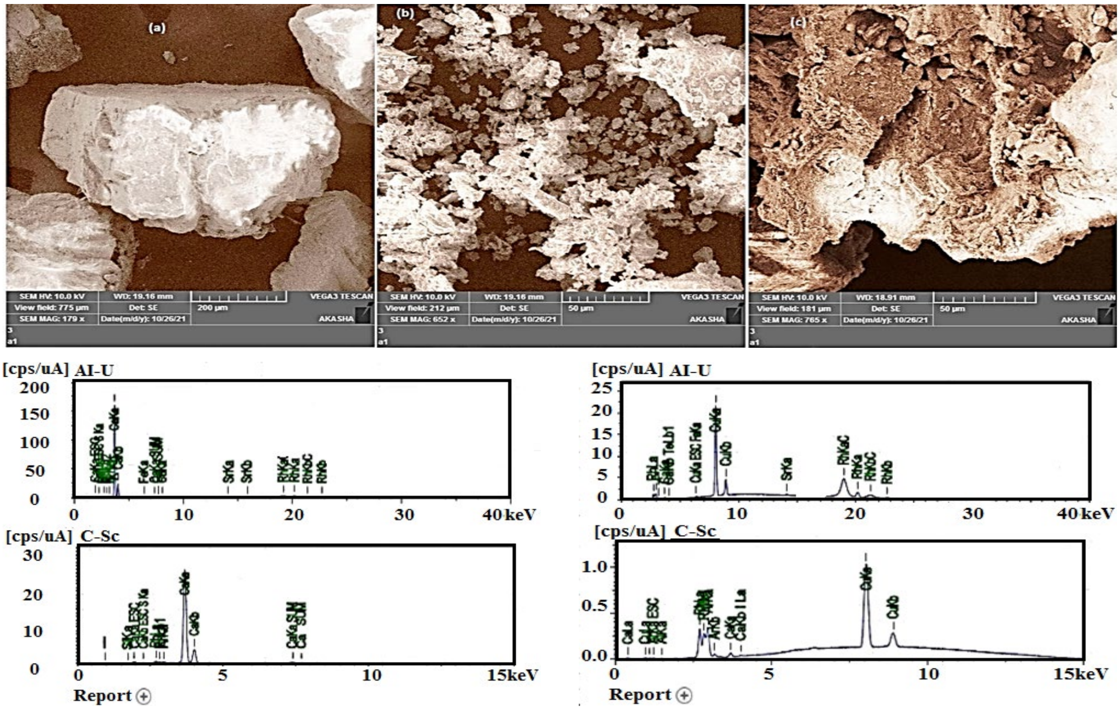

Fig. 3. SEM images with DES spectra of Eg1 (a), Eg2 (b), and Eg-3 (c)

Table 1: EDX results for Eg-1, Eg-2, and after adsorption process

Samples	Ca	Fe	Cu	K	Sr	Al
Eg1	98	0.051	0.065	0.227	0.607	-
Eg2	0.639	61.6	-	1.25	-	1.019
Eg3	1.793	0.113	94.58	-	2.26	1.24

Removal of copper ions from aqueous solution

The impact of pH and contact time

Time is a major consideration in adsorption process. From Fig. 6 the results illustrate that the adsorption of Cu^{2+} has been gradually increased with contact time at constant concentration until 80 min and optimum solution pH, then the removal percentage becomes constant (equilibrium is attained). The adsorption rate of Eg2 is higher than Eg1; it was improved by 28.6% and 15.6% respectively. To explain the Effect of contact time, copper ions attached to the active site of eggshell powders, and the percentage shifted may be unsaturated sites that took more time to cover by copper ions during the process. The results recorded that the active sites of modified eggshell higher than eggshell powder[21].

A series of pH solutions from 2 to 8 have been checked on Eg1 and Eg2. The results showed that the higher rate of removal of copper ions when pH value was 6 to 7 in this points there are low concentration of hydroxide and hydrogen[22,23]. Eg-2 illustrates high removal rate than Eg-1.

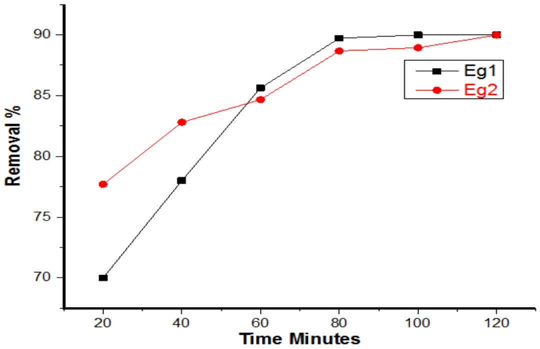

Fig. 4. The impact of contact time on Eg1 and Eg2

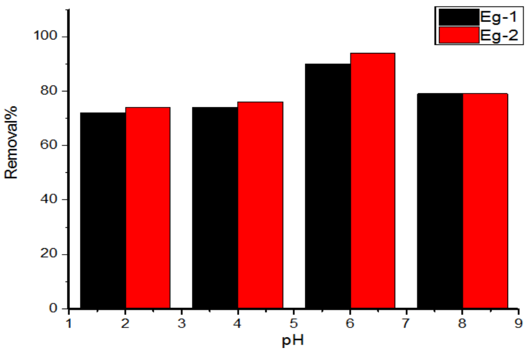

Fig. 5. the effect of pH on Eg-1 and Eg-2

Adsorption isotherms

Adsorption isotherm models such as Langmuir and Freundlich isotherms have been applied to evaluate adsorption phenomena. Langmuir model describe monolayer, while Freundlich model describe multi-layer process[24]. According to Longmuir theory, the adsorption process on a solid surface is governed by kinetic principles. It involves a continuous bombardment of molecules onto the surface, accompanied by the desorption or evaporation of corresponding molecules from the surface. This occurs without any accumulation of molecules at the surface[25]. On the other hand, The Freundlich adsorption isotherm model characterizes the reversible and non-ideal nature of the adsorption process. Unlike the Langmuir isotherm model, the Freundlich model allows for multilayer adsorption and is not limited to monolayer formation. In this model, the distribution of adsorption heat and affinities is not required to be uniformly distributed across the heterogeneous surface.[26] Table 2 exhibit the equation of the two models. Moreover, Adsorption kinetics refers to the study of the rate at which adsorption occurs, which is the process of molecules or ions binding to the surface of a solid or liquid. Two commonly used kinetic models for describing adsorption kinetics are the pseudo-first-order model and the pseudo-second-order model. The pseudo-first-order model assumes that the rate of adsorption is directly proportional to the concentration of adsorbate remaining on the surface of the adsorbent. Pseudo-second-order kinetics: The pseudo-second-order model assumes that the rate of adsorption is proportional to the square of the concentration of adsorbate remaining on the surface of the adsorbent[27]

The Langmuir and Freundlich isotherm models for removal of copper ions from aqueous solution and their correlation coefficients are also shown in Table 2. The correlation factors R^2 of Freeundlich for Eg1 and Eg2 is 0.958 and 0.668 respectively, and 0.949 and 0.405 for Langmuir. For overall data the Freundlich isotherm simulated the experimental data better, therefore, it's multilayer adsorption and it assumes that copper ions covered all sites of eggshell powder with strong binding bonds, 1/n value fallen between 1 to 10 so it represents a good adsorption[29].

Figures 6 and 7 showed Langmuir and Freundlich isotherms equilibrium and all information of plots.

Table 2: Adsorption isotherm model laws

Isotherms	General formula	Linear Form	Represent of linear form	Parameters	Ref
Freundlich	$q_e = K_f (C_e)^{\frac{1}{n}}$	$Log(q_e) = LogK_f + \frac{1}{n} Log(C_e)$	Log q_e vs Log C_e	K_F, 1/n	(28)
Langmuir	$q_e = q_{\max} \frac{K_L C_e}{1+K_L C_e}$	$\frac{1}{q_e} = \frac{1}{q_{\max} K_L C_e} + \frac{1}{q_{\max}}$	1/C_e vs 1/q_e	q_{max}, KL	(25)

Table 3: Isotherm and kinetic parameters for the removal of Cu^{2+} for Eg 1 and Eg 2

1-Isotherm paramerts	Parameters	Eg1	Eg2
Freundlich	K_F	2.2615	56.1733
	1/n	1.171	0.1977
	R^2	0.9582	0.668
Langmuir	q_{max} (mg.g^{-1})	675.67	221.23
	K_L	0.00485	0.0208
	R^2	0.949	0.405
2-Kinetics parameters			
Pseudo First order	q_e(mg/g)	6.553	7.636
	k_1(min^{-1})	-0.0014	-0.00099
	R^2	0.979	0.977
Pseudo Second order	q_e(mg/g)	112.86	148.148
	k^2(g. mg^{-1} min^{-1})	0.0016	0.000312
	R^2	0.993	0.961

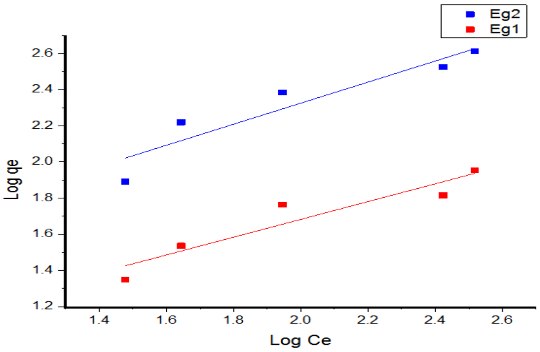

Fig. 6. Freundlich isotherm for Eg1 and Eg2

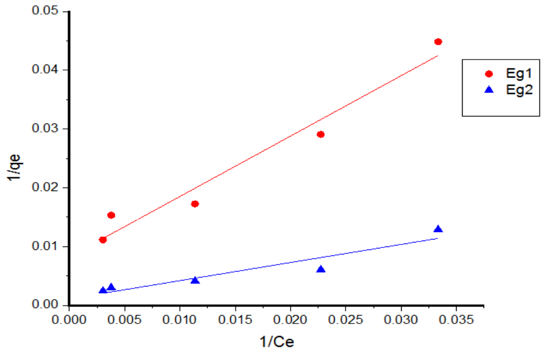

Fig. 7. Langmuir isotherm for Eg1 and Eg2

Table 4: Summarize adsorption kinetics laws

Adsorption kinetics	General formula	Linear Form	Represent of linear form	Parameters	Ref
First order	$\frac{dq_t}{d_t} = k_1(q_e - q_t)$	$\log(q_e - q_t) = \log q_e - (\frac{k_1}{2.303})t$	Time vis log(a-x)	K_1, q_e(mg/g)	(30)
Second order	$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e{}^2}$	Tim vis t/q_e	K_2, q_e^2, q_e	(31)

The adsorption process of copper ions on eggshell and coated eggshell were deeply investigated considering the adsorption kinetics. Pseudo-first-order, and pseudo-second-order have been applied, Table 2 shows general and linear formulas. The fitting of Cu^{2+} kinetic models to Eg1 and Eg2 equilibrium data are shown in Fig. 8 and 9 whereas the results of respective kinetic parameters in Table 3. The pseudo-second-order model well described the Cu^{2+} on to Eg1 and Eg2 their R^2 value (0.993) and (0.961) respectively. In addition, the value of calculated q_e of the pseudo-second-order model of Eg1 is higher than pseudo-first order model by 18.7 times, while in Eg2 19.4 times. Therefore, the pseudo-second-order compose chemisorption which involving valence forces by sharing of electrons between adsorbent and adsorbate.[32]

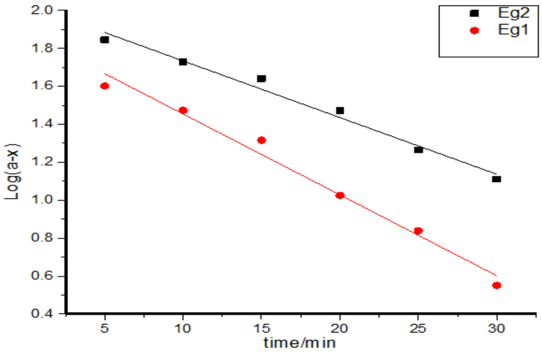

Fig. 8. first order of Eg1 and Eg2

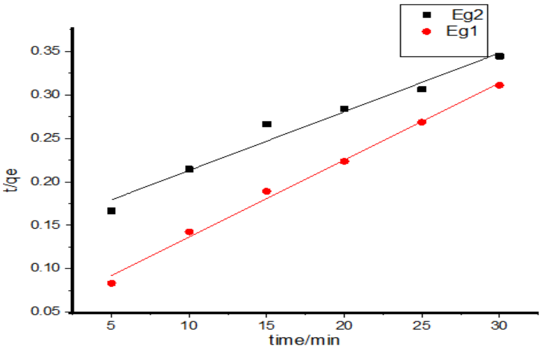

Fig. 9. second order of Eg1 and Eg2

The Effect of activation

The result showed that the activation of an eggshell coated by ferrite has a good ability to remove copper ions from its solution at 500ppm and 80min. This result is illustrated by finding the concentration of Cu^{2+} at this time closed to zero because the iron oxide coating results in an increase in the percentage adsorption of solute due to increasing of the surface area.

CONCLUSION

In this study the biosorption of Cu^{2+} from aqueous solution onto eggshell was investigated. The contact time, pH and isotherms were studied to perform the ability of the eggshell to remove Cu^{2+}. The maximum adsorption was found at pH 6, 80 minutes and 500 ppm. Because of its large surface area, eggshell coated with iron oxide outperforms eggshell in terms of copper removal. The prepared eggshell was suitable for removing heavy metals from both drinking water and waste water at a low cost and on a large scale.

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Conflict of interest

Sahl Yasin *et al.,* declare that I have no conflicts of interest related to the publication of this article. The research presented here was conducted in an objective and unbiased manner, and the findings and conclusions are based solely on the data collected and analyzed.

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