Adsorptive removal of copper (Cu) using magnetic nanoparticles alginate beads (SP-IONPs- ALG): characterization and optimization by response surface methodology (RSM)

Shymaa M. Shalaby[1*], Fedekar F. Madkour[1], Hala El-Kassas Y[2], Adel A. Mohamed[3], Mohamed A. Aly-Eldeen[4]

Abstract

Heavy metals consider one of the most hazardous contaminants released in the environment. The current study relates to use of factorial design software to evaluate efficiently factors influencing the adsorption capacity of iron oxide nanoparticles alginate beads (SP-IONPs-ALG) to remove copper from aqueous solution. The present study included prepared SP-IONPs- ALG and characterized by using EDX and SEM. The effects of operational parameters investigated by using response surface methodology (RSM). A 24 Central Composite Design (CCD) based on single-factor experiments and a four-variables, pH (x_1), contact time (x_2), initial dyes concentration (x_3) and adsorbent mass (x_4) to evaluate the efficiency of SP-IONPs- ALG for adsorption of copper from aqueous solution. Results revealed that pH, contact time and adsorbent dose had positive effect in dyes removal percentage but initial concentration had negative effect, with high removal percentage for copper (89.4 %) at pH 6, contact time 35 minutes and adsorbent dosage 0.06 g with maximum adsorption capacity mg g^{-1}.

Introduction

Heavy metals are concurrently becoming one of the main sources of serious environmental pollution that affect aquatic organisms [1]. Heavy metals are a growing global problem as they are persistent and non-biodegradable, metals are mobilized and carried into food web as a result of leaching from waste dumps, polluted soils and water. For this motive, many techniques for environmental remediation of heavy metals are being studied [2]. Organic pollutants are harmful to both the living organisms and the environment, which caused many problems in aquatic ecosystem and lead to a disturbance of the aquatic ecosystem [3]. Huge efforts have been made to improve wastewater treatment with different approaches [4-6]. The adsorption technique is currently widely used to remove contaminants from industrial wastewater owing to its many advantages, which include simplicity, high efficiency, and ease of use [7].

Nowadays, iron-based nanomaterials have shown amazing properties for adsorption activities because of their larger specific surface area, high porosity, and strong magnetic response, resulting in an extraordinary sorption capacity [8]. Naked magnetic nanoparticles have many problems such as the aggregation in water and chemical instability and oxidation. Controversially, it needs huge effort to well-dispersed completely from the water during the water treatment process and recycle in practical applications which have very small particles size. Moreover, they could cause secondary pollution due to leaching or leakage especially when applied in continuous-flow streams. To combat these problems coating it with a biocompatible shell as alginate [9]. Alginate is a renewable natural polysaccharide containing abundant many organic functional groups (e.g., carboxylic and phenolic) and is environmentally benign, because of these advantages' alginate has been applied as green adsorbents and has been often used as the supporting material to impregnate a variety of engineered nanomaterials to improve their stability and dispersion for environmental applications [10].

In order to ensure an efficient of adsorbent to removal pollutants from water and to maximize the adsorption yield, an optimization study should be conducted [11]. the optimization of the adsorption processes can be carried out by Response Surface Methodology (RSM), which considered as a combination between statistical and mathematical approaches [12]. In fact, RSM can be considered as an efficient tool to study the effect of process variables in the defined response as well as the interactions between all the factors [13]. The good point of this tool in the optimization process is to lower the experiment number, process time and the cost of the adsorption process [14].

Thus, the present work has two main objectives: First, develop a biological, cost effective and non-toxic adsorbent magnetic nanoparticles alginate beads (SP-IONPs- ALG). The characterization of the (SP-IONPs- ALG) carried out by Energy-Dispersive X-ray (EDX) and Scanning Electron Microscope. The second objective is examining the effectiveness of (SP-IONPs- ALG) in adsorption copper, tested the parameters contact time, pH, adsorbent dose and initial dye concentration by Response Surface Methodology (RSM) which help to determine the major factors and the mathematical model that predict the response as function of factor variations. The optimum conditions were determined using the model and its relative response surfaces.

Methodology

2.1 MATEIALS

In the present study was used the green biosynthesized magnetic nanoparticles using *Spirulina platensis* (SP-IONPs) by Shalaby et al. [15]. Nanoparticles were spherical in shapes, agglomerated and clustered with size average (5.1±1.8 nm). All chemicals were purchased from Merck (Germany). Copper standared obtained from L (Scharlau, Spain). All solutions were prepared by using deionized water (DW).

2.2 preparation of magnetic nanoparticles alginate beads (SP-IONPs- ALG)

Encapsulation method for nanoparticles in semipermeable alginate beads prepared according to EL-Kassas *et al.* [7]. The main propose was coated iron oxide nanoparticles were greenly biosynthesized by alginate to obtain spherical gel beads. SP-IONPs- ALG prepared by desired mass of SP-IONPs in 10 mL of 4% (w/v) sodium alginate solution. Stirred for 30 min, the solution extruded as small drops into a stirred solution of 3.5 % calcium chloride to obtain a homogeneous mixture, where spherical gel beads were formed with a size of 2.3 mm nearly. Finally, the beads formed allowed to harden and then rinsed with de-ionized water.

Physical and morphological characterization of SP-IONPs- ALG

The microanalysis structure of Fe_3O_4NPs- ALG was characterized by the Energy-dispersive X-ray (EDX) spectrum using an X-ray micro-analyzer (Module Oxford 6587INCA X-sight) to determine the elemental composition. The shape, surface morphology and size of the SP-IONPs- ALG was determined by using Scanning Electron Microscopy (SEM) JEOL (JSM-6510LV). the average diameter of pores, pore size distribution, and specific surface area of the produced adsorbent using the analysis of BET (Quantachrome NOVA 3200e). Zeta potential (pH $_{PZC}$) of the SP-IONPs- ALG was analyzed by using plotting a graph of ΔpH (pHeq – pH_0). 0.05 g of the adsorbent was mixed with 10 ml of 0.1 M NaCl for 24 hours with varying the (pH_0) between 1 to 12. The final pH (pH_f) was recorded and compared to the initial pH and the pH PZC corresponds to $pH_0 = pH_f$.

Preparation of copper solution

A stock solution of copper was prepared by diluted standard solution 1000 mg/L (Scharlau, Spain) by distilled water. Solutions in the range of required concentrations were prepared using a stock solution. The initial pH of each solution was adjusted to the required value with 0.1 M HCl and 0.1 M NaOH solutions before mixing the biosorbent into the solution.

Factorial Experimental Design

Response Surface Methodology (RSM) is a combination of statistical and mathematical methods, in the present study, Factorial Central Composite Design (CCD) based on single-factor experiments and a four-variables, pH (x_1) 2 - 10, contact time (x_2) 5- 65 minutes, the initial dyes concentration (x_3) 5 – 105 mg L^{-1}, adsorbent mass (x_4) 0.02 – 0.1 g, which considered as the independent variable used to evaluate the efficiency of SP-IONPs- ALG for adsorption of copper from aqueous solution. The batch adsorption experiments were conducted randomly at four different levels of independent variables coded as $+\alpha$, +1 and –1, $-\alpha$ for high and low values with six central points to give a total of 30 experimental runs can be performed at the same time. The low and high levels for the factors were selected according to preliminary experiments. The ranges and levels of these independent variables investigated are presented in Table (1). All possible combinations of these variables were used, and a matrix was established according to their high and low levels as described in Response Surface Methodology (RSM) (Table 1). For statistical calculations, the variables were coded as X_i according to the following equation [16].

$$Y = \beta 0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_i i X_i^2 + \sum_{i=1}^{k-1} * \sum_{i=1+1}^{k} \beta_i j X_i X_j$$

(3)

where Y indicates the variable of response (CV, MB and MO removal), X_i and X_j are independent coded variables and β_0, β_i, β_{ii}, β_{ij} are the intercept term, linear, quadratic, and interaction effects, respectively [17].

Results

3.1 Characterization of SP-IONPs- ALG

The SP-IONPs- ALG beads are formed have spherical and dark brown colour due to the presence of iron oxide nanoparticles. By comparison of the particle size of wet and dried beads, the SP-IONPs- ALG adsorbents displayed significant shrinkage after drying Figure (1). The diameters of wet and dry SP-IONPs- ALG beads is 3.5 mm and 2.3 mm, respectively, this results similar previous study [18]. The SEM images for the SP-IONPs- ALG beads are revealed in Fig. 2. a, as shown, a porous structure was clearly observed for all the beads. The composition of the magnetic alginate beads was also detected by the Energy-dispersive X-ray spectrum (EDS) (Fig. 2, b), where the iron (Fe), oxygen (O), carbon (C), sodium (Na), sulphur (S). The presence of iron (63.12 %) and Oxygen (18.03) is related to the present of iron oxide nanoparticles. Also, Sodium (0.72 %) is originated from sodium alginate precursors used in the formation protocol [19].

3.4 Optimization of copper uptake conditions by applying Response Surface Methodology (RSM)

Response Surface Methodology (RSM) is a combination of statistical and mathematical methods, as showed in Table 1, four independent variables (pH, contact time, initial concentration and adsorbent dosage) were segregated into five levels with a coded value $+\alpha$, +1 and –1, $-\alpha$ for high and low values with six central points to give a total of 30 experimental runs. These experimental runs were used to evaluate the efficiency of SP-IONPs- ALG for removal copper and the percentage removal (response) for each combination of the process variable, was involved in the RSM approach to recognize the interaction of each variable on the response. Amongst these 30 experiments, ……..????? experiments were repetition of the central point (run Nos. 1, 8, 11, 12, 15 and 17). The nearness of the responses of these 6 experiments can be confirmed the accuracy of the experiment process [19].

The experiments using the factorial designs enable all factors to vary simultaneously, this helps in determining the interaction of individual process variables on the response prediction. The experimental results for copper removal were fitted in Linear model which R^2 equal 0.97 and adjusted R^2 equal 0.922. ANOVA for Linear model statistical analyses values of Cu removal less than 0.0001, these results indicate these models' terms are significant, these results illustrated in Tables 2. The highest percentages of copper removal by the CCD method were obtained in run No. 18, which the percentages equal 89.4% but the lower removal percentage 41.8% was obtained in run 4, these results were shown in Table 1. In the run No.18 pH equal 6, contact time (t; 35 minutes), initial concentration (C_0; 5 mg L^{-1}) and adsorbent dosage was 0.06 g, the higher removal percentage of dyes in this run could be owing to the lower dyes concentration, these results will describe in 3.4.1 and similar to results described by Priya *et al.* [20].

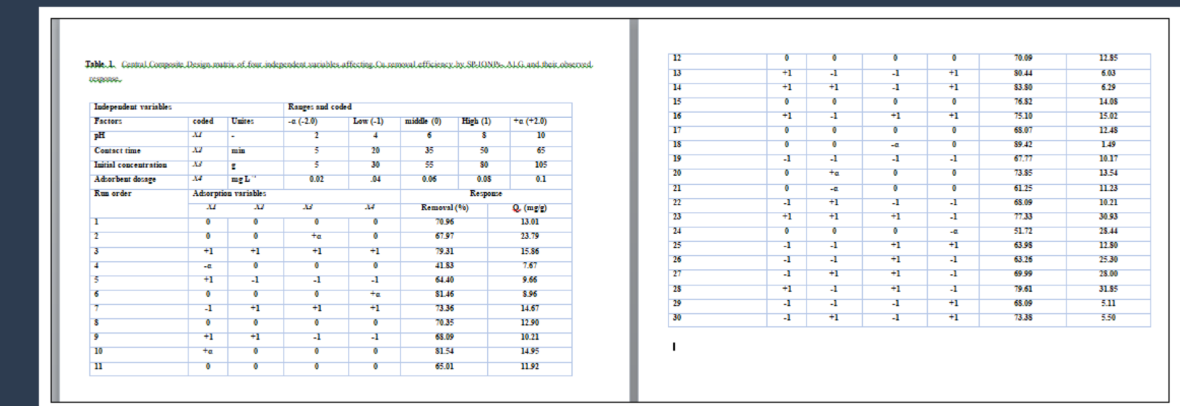
3.4.1 Response surface plotting for estimation of operating variables

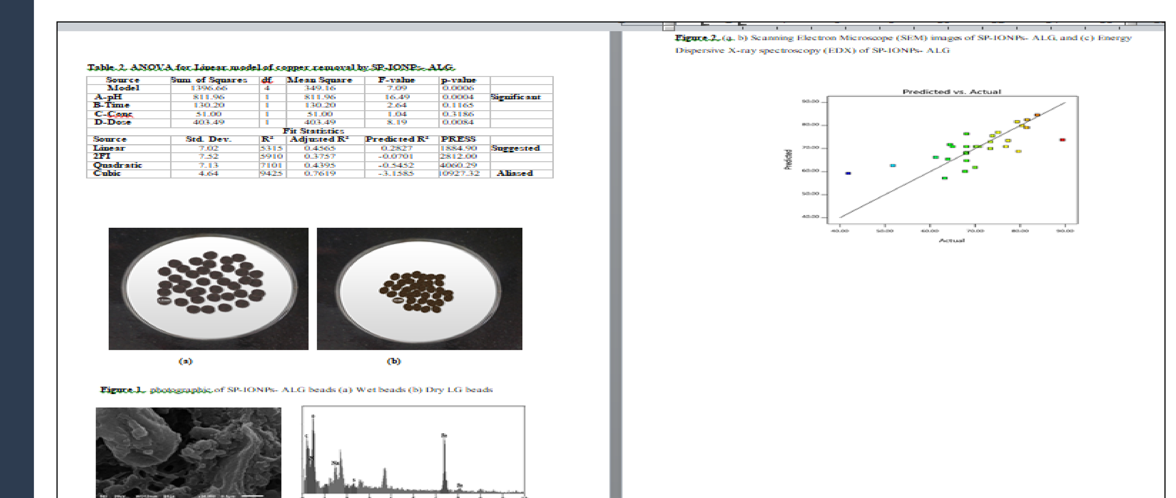
The actual visual predicted percentage for copper removal is presented in Figure 3 it was found that the actual values for Cu removal by SP-IONPs- ALG are well in line with the predicted values from the model equations (4):

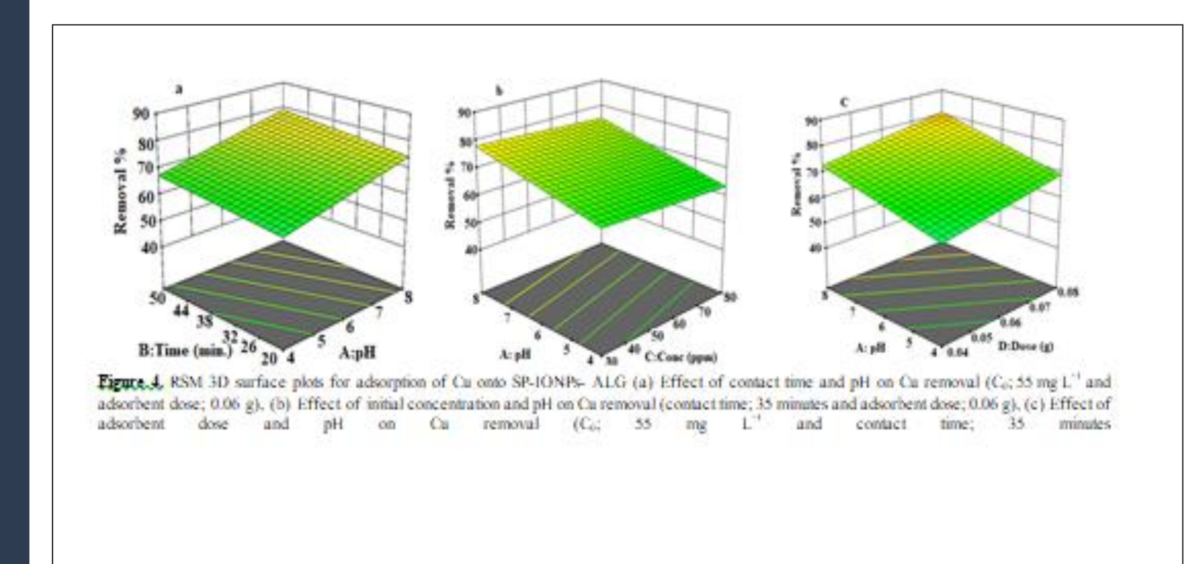
Y= +38.90039+2.90826ph+0.155277 time- 0.058312 conc +205.01226 dose (4)

The three-dimensional (3D) response surface plots provide information on the impact of interactions terms and their effects on the dependent variable. Hither, each plot is created by varying two individual variables in their corresponding experimental range while keeping the two-parameter constant. Fig 4 demonstrate the interaction of adsorption operating parameters of pH (A), contact time (B), initial concentration (C), and adsorbent dose (D) on removal efficiency for Cu. It was clearly noted that the combination pH with initial concentration and contact time with adsorbent dosage have a positive impact on Cu adsorption according to contour lines and multiple regression (Eq. 4).

As seen in Fig. 4 b, the increase in initial pH from 4 to 8 with contact time 35 minutes and adsorbent dose 0.06 g as constant leads to increase in the removal %, due to higher performance of the adsorbent in pH of more than pH_{ZPC} with determined pH_{ZPC} of 7.1 [21]. Fig 4e depicts the combined influence of the adsorbent dose and contact time with (C_0; 55 mg L^{-1}) and pH 6 as constant, it can be seen that the highest removal % was optimized with increasing in adsorbent dose and contact time together. Increased Cu removal with increasing adsorbent dosage is related to the larger reactive surface area and more active sites for the adsorption of adsorbate molecules [21]. From these results were predicted to pH 6, contact time 35minutes and adsorbent dosage 0.06 g, these consider optimal conditions for remove Cu with higher removal percentage (89.4%).







Conclusion

The present study proved that SP-IONPs- ALG can be used as an effective adsorbent for removal of the copper (Cu) from aqueous solutions. The produced SP-IONPs- ALG have been characterized using SEM and EDX revealing that morphology, size and chemical compassion with highly efficient characters. The effects of operational parameters investigated by using response surface methodology (RSM). A 2^4 Central Composite Design (CCD) based on single-factor experiments and a four-variables, pH (x_1), contact time (x_2), initial dyes concentration (x_3) and adsorbent mass (x_4) to evaluate the efficiency of SP-IONPs- ALG for adsorption of Cu from aqueous solution. pH, contact time and adsorbent dosage had positive effect in dyes removal percentage with high removal percentage for Cu (89.4 %). This study presents an eco-friendly method by using green SP-IONPs- ALG for removal Cu by RSM methodology.

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