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Chitosan/Graphene Oxide Composite Film for Adsorption of Cu^{2+} Ions

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Many materials have been studied to detect and remove pollution from the aqueous environment. In this study, chitosan (CH)/graphene oxide (GO) composite film was prepared with the intention of removal of copper ions (Cu^{2+}). The film adsorption capability of Cu^{2+} was analyzed at different parameters such as contact time, initial concentrations of Cu^{2+}, and CH to GO ratio. The film with a ratio of 1:5 showed the highest adsorption capability, with the film reaching equilibrium at 60 min. The initial concentration data fit well with the Langmuir isotherm model compared to the Freundlich isotherm model, showing that adsorption was the primary mechanism for removal. The maximum adsorption capacity recorded in this work was 39.96 mg/g. Hence, the CH/GO composite film has potential application in the removal of Cu^{2+} from wastewater.

topics: metal ion removal, chitosan composite, adsorption capacity, isotherm model

1. Introduction

Various methods for copper (Cu) removal from wastewater have been extensively studied. Chitosan (CH) was widely used as it can absorb heavy metals due to the presence of amino ($-NH_2$) and hydroxyl (-OH) groups which serve as chelating agent and reaction site [1]. Both the nitrogen and oxygen atoms in the amino and hydroxyl groups possess a lone pair of electrons capable of reacting with cations such as Cu^{2+} [2]. Chitosan can be used on its own or with other materials to further improve its function [3].

Graphene oxide (GO) is a specific product of graphene that undergoes the graphene oxidation. Due to the oxygen-based functional groups, GO is capable to absorb metal ions and dyes [4]. GO can be chelated with metal ions through coordinate and electrostatic interactions, forming a metal ion complex [5].

This work will examine the adsorption process of CH/GO composite film in the removal of Cu^{2+} ions from wastewater. The effect of parameters such as the CH/GO ratio, the initial concentration of Cu^{2+}, and the contact time on the adsorption capability was studied. A model of the adsorption isotherm of the composite was also investigated.

2. Experimental details

Now, 2 g of CH powder (75–85% deacetylated) was dissolved in 100 ml of 2% (v/v) acetic acid dilution for film preparation. The solution mixture was agitated for 24 h at 400 rpm and 50°C. To the homogeneous solution, 2 wt% of glycerol was added and stirred for 2 h. GO was added to the CH solution and agitated for another hour. The solution was then sonicated for 10 min at 55°C. The final solution was cast and dried in an oven for 24 h at 60°C. The dried films were immersed in 0.1 M of NaOH to neutralize the film before being washed with deionized (DI) water and dried well before use.

Batch adsorption tests were performed for various influencing variables such as CH to GO ratio, contact time, and initial Cu^{2+} concentrations. The studies were carried out using 0.1 g of prepared adsorbents in 100 ml of Cu^{2+} at pH 6. The Cu^{2+}

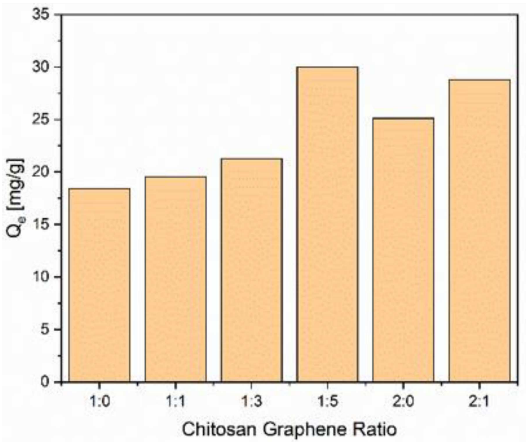

Fig. 1. Adsorption capacity for different ratios of the CH/GO composite film.

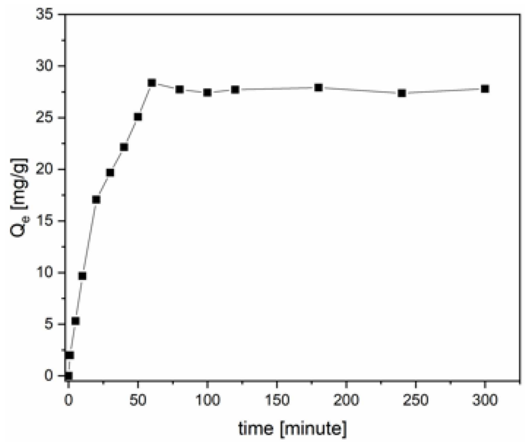

Fig. 2. Adsorption test for the 1:5 CH/GO composite film at different contact times.

concentration before and after the adsorption test was measured by inductively coupled plasma optical emission spectrometry (Optima 2000 DV, Perkin Elmer).

The adsorption capacity of the adsorbent (q_e) was calculated based on the formula

$$q_e = \frac{(C_i - C_e)}{m} V, \tag{1}$$

where C_i and C_e refer to the initial and final concentrations of Cu^{2+}, respectively, V is the volume of Cu^{2+} solution, and m is the mass of adsorbents.

The model of the adsorption isotherm can be determined based on the adsorption capacity results. The Langmuir isotherm model is given as

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}}\Big(C_e + \frac{1}{K_{\mathrm{L}}}\Big), \tag{2}$$

where $q_{\max}$ [mg/g] is the maximum Cu^{2+} adsorption amount, and K_{L} is the equilibrium adsorption constant.

The Freundlich isotherm model is given by

$$\log(q_e) = \log(K_{\mathrm{F}}) + \frac{1}{n}\log(C_e), \tag{3}$$

where K_{F} and n are Freundlich constants and all constants can be attained from the slope and intercept of the curve.

3. Results and discussion

To investigate the CH/GO films adsorption capacity, various CH to GO ratios were prepared at the ratio of 1:0, 2:0, 1:1, 1:3, 1:5 and 2:1. The mass of each film is fixed to 0.1 g, with the initial Cu^{2+} concentration of 100 mg/l. Figure 1 shows the adsorption capacity of the film at different CH/GO ratios.

It was observed that doubling the ratio of CH from 1:0 to 2:0 increased the adsorption capacity from 18.45 to 25.12 mg/g due to the more available active site. It was also observed that the adsorption capacity of the films increased linearly as the ratio of GO to CH increased. From the results, it can be concluded that films with the ratio of 1:1, 1:3 and 1:5 show higher adsorption capacity compared to 1:0, having values of 19.53 mg/g, 21.30 mg/g, and 29.99 mg/g, respectively. The 2:1 ratio film showed a slight increase in adsorption capacity to 29.77 mg/g compared to the 2:0 film.

These findings suggest that increasing the ratio of GO to CH in the film improved the adsorption capacity of the composite. The increase in adsorption capacity could be explained by the GO sheets' availability of oxygen-containing functional groups, facilitating the interaction with the Cu^{2+} ion [6]. Thus, adding more GO content increases the active sites for the chelating process by Cu^{2+}, which results in higher Cu^{2+} adsorption capacity in the CH/GO films. The 1:5 CH/GO films demonstrated the highest adsorption capacity, which means that more oxygen groups were formed due to their high GO content compared to other CH/GO film ratios.

The effect of the contact time on the film adsorptions capacity of Cu2+ was analyzed using the 1:5 film, as it has the highest adsorption capacity and shown in Figure 2. From the initial time to 20 min, the films' adsorption capacity increased drastically due to the large active site and the vast amounts of the Cu^{2+} ions available in the early stages of the experiment, which quickly caused the chelating process. After 20 min, the rate of adsorption capacity increases slowly with time. It is also observed that the adsorption of Cu^{2+} by the film reached equilibrium at 60 min. After 60 min, no noticeable change in the adsorption capability was observed. This can be attributed to the decreasing amount of Cu^{2+} and the available active site of the films, inferring that the chelating process is less likely to occur after 60 min of exposure.

Figure 3 demonstrated the adsorption capacity for different initial concentrations of Cu^{2+} solution of 1, 5, 10, 50 and 100 mg/l, measured at 60 min. The adsorption capacity increases with increasing initial concentrations of Cu^{2+}. This result can be

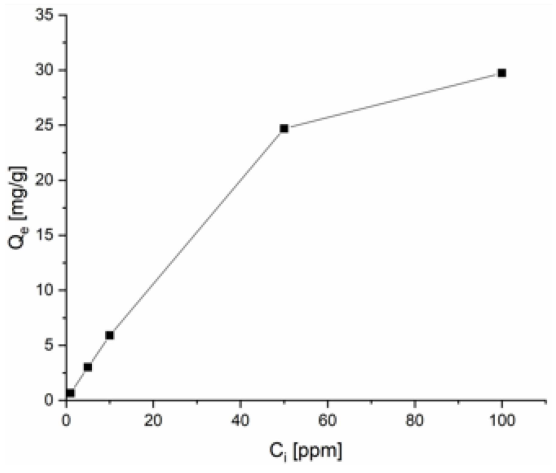

Fig. 3. Adsorption test for the CH/GO composite with a 1:5 ratio at a different initial concentration of Cu^{2+} ions solution.

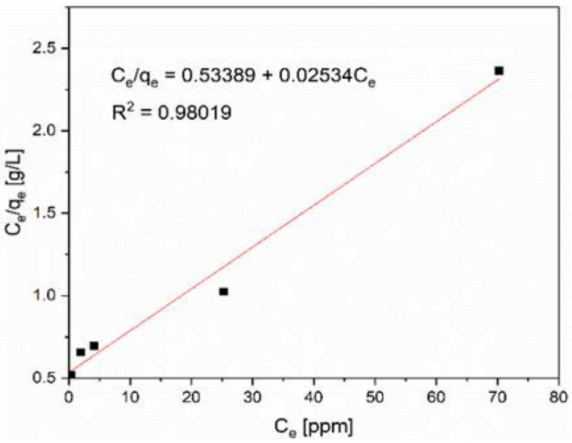

Fig. 4. The Langmuir model for adsorption of copper ions by the CH/GO composite film with a ratio of 1:5.

explained by the fact that more Cu^{2+} is available in the active site from the CH/GO adsorption site, which means a higher probability of the interaction between Cu^{2+} and CH/GO, and thus a higher adsorption capacity.

In Fig. 3, when the initial concentration of Cu^{2+} increases from 1 to 10 mg/l, the adsorption capacity increases gradually. However, there is a drastic increase in the adsorption capacity for C_i between 10 to 50 mg/l. This is attributed to the considerable difference in the value from 10 to 50 mg/l compared to the increment from 1 to 10 mg/l. The rate of adsorption begins to slow down as the initial concentration of Cu^{2+} increases from 50 to 100 mg/l. This is most likely due to the agglomeration of Cu^{2+} in the film, hence reduction of the film-specific surface area [7].

The Langmuir and Freundlich adsorption isotherms are shown in Figs. 4 and 5, respectively. The correlation coefficients (R^2) for Langmuir and

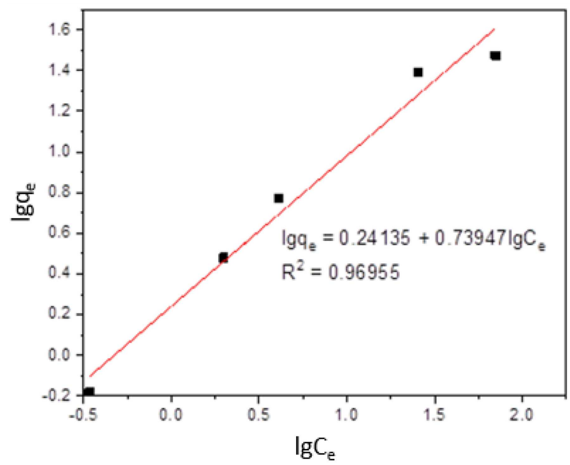

Fig. 5. The Freundlich model for adsorption of copper ions by the CH/GO composite film with a ratio of 1:5.

Freundlich isotherm models for a 1:5 ratio CH/GO composite film on Cu^{2+} adsorption were 0.98019 and 0.96955, respectively.

The data showed that the CH/GO composite film on Cu^{2+} adsorption fit well in the Langmuir isotherm model compared to the Freundlich isotherm model. The Langmuir model implies that the adsorption surface is homogeneous and all active sites have the same adsorption energy [8]. It also implies that monolayer adsorption happens on the surface of CH/GO composite films. Based on (2) and the Langmuir data plot, $q_{\max}$ for the films was found to be 39.960 mg/g.

4. Conclusions

The adsorption tests show that the best ratio for the adsorption test is 1:5, with the adsorption capacity of Cu^{2+} equal to 29.99 mg/g, and the adsorption capacity reaches equilibrium at 60 min. The film Langmuir isotherm model gave slightly better fits than the Freundlich isotherm model, suggesting that the adsorption of Cu^2+ is a monolayer on the film's surface. The maximum adsorption capacity of CH/GO composite film was 39.96 mg/g.

Acknowledgments

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