Adsorption performance of graphene quantum dots for cadmium (II) removal from synthetic wastewater

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Abstract

Graphene quantum dots (GQDs) was synthesized by a simple pyrolysis method. The as-prepared adsorbents were characterized by various techniques including energy dispersive X-ray spectroscopy (EDX) and scanning electron microscope (SEM). The adsorption performance of GQDs for cadmium (II) removal from synthetic wastewater was evaluated via batch adsorption technique. All supernatants were detected by atomic absorption spectrophotometer (AAS). The influence of initial concentration, contact time and pH were investigated. The optimum conditions for the removal of cadmium (II) ions were 20 mg/L, 30 minutes and 7 for initial concentration, contact time and pH of solution, respectively. With maximum adsorption capacity for cadmium (II) being 40.00 mg/g. The adsorption isotherms of GQDs fit well with the Langmuir models. It is exhibited that GQDs can be high performance adsorbent for cadmium (II) ion removal from wastewater.

Keywords: Graphene quantum dots adsorbent; Cadmium removal; Adsorption performance

Introduction

Cadmium is an important element used in various industries. However, it is a poisonous element that affects the health of plants, animals and humans alike. Therefore it's very important to remove this element from contaminated waters (Al-Qahtani, K.M., 2017). Nowadays, adsorption technique is one of the most promising process for metal ions removal from wastewater. This technique is basically relied on interactions between adsorbent and adsorbate (Nuengmatcha et al., 2014). Several kinds of adsorbents were applied for heavy metals removal such as orange peel and iron oxide nanoparticles (Gupta et al., 2012), activated carbon, carbon nanotubes, carbon nanofibers, and carbon fly ash (Al-Khaldi et al., 2013). Particularly, graphene quantum dots (GQDs) have been attached lots of attention to wastewater treatment due to their great adsorption performances for heavy metals in various type of functional groups on their surface. Therefore, in our work, GDQs was prepared by a simple pyrolysis method and applied to remove cadmium (II) ions from synthetic wastewater. The adsorption performance of the GQDs for cadmium (II) removal in a batch adsorption study was performed. The influence of initial concentration, contact time and pH were investigated Langmuir and Freundlich isotherms were also investigated in detail to fit an adsorption model for cadmium (II) removal from synthetic wastewater.

Experimental

Preparation and characterization of GQDs adsorbent

GQDs adsorbents were synthesized using the pyrolysis method by the modified procedure described previously (Nuengmatcha et al., 2018). Briefly, 2.0 g of citric acid was added into a 5 mL vial. The vial was heated to 260 °C using a paraffin oil bath for about 10 min. The citric acid was slowly liquated to a yellow colour. The liquid was transferred into a beaker containing 100 mL of 0.25 mol/L NaOH with continuous stirring for 30 min. The obtained sample solution was neutralized to pH 7.0 with NaOH. The obtained adsorbent was dried at 90°C and kept in desiccator before use. All obtained samples were characterized using SEM and EDX techniques.

Adsorption study

The adsorption of cadmium (II) was performed by a batch method. Approximately 0.02 mg of GQDs was added into 25 mL of solution containing 20 mg/L cadmium (II) ions in 125 mL conical flask. Then the solution was stirred at 150 rpm by using orbital shaker for 3 h. After that the solution was removed and analyzed the amount of cadmium (II) ions by flame atomic absorption spectrometry (FAAS). To study the influence of initial concentration (1-50 mg/L), contact time (10-180 min) and pH (1-8) were investigated. All experiments were conducted in triplicate. The adsorption capacity (q_e, mg/g) of cadmium (II) at an equilibrium state was determined as follows equation 1. The equilibrium nature of the adsorption of cadmium (II) onto GQDs was described by both Langmuir and Freundlich adsorption models.

$$q_e = V(C_o - C_e)/m \tag{1}$$

Where, C_o, C_e, V and m are an initial concentration (mg/L) of cadmium (II) in solution, cadmium (II) concentration at the equilibrium state, solution volume (L) and GQDs adsorbent mass (g), respectively.

Results and Discussion

Characterization of GQDs

The SEM and EDX techniques were performed to determine the major elements of GQDs. An SEM micrograph of GQDs and its associated EDX spectrum is shown in Fig.1. The spectrum shows the presence of C and O, as major elements; indicating that the GQDs was successfully synthesized. The contents of C and O in the synthesized GQDs adsorbent were 58.9 and 41.1%weight, respectively.

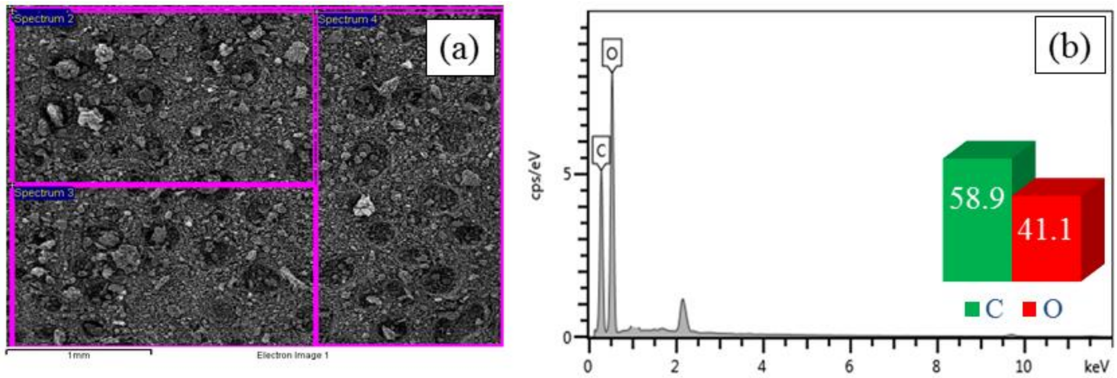

Fig. 1. (a) SEM image and (b) EDX spectrum of GQDs adsorbent

Optimum conditions for the removal of cadmium (II)

The pH of solution is very important parameter on the adsorption capacity of adsorbent. The results from Figure 2(a) showed that the adsorption capacity of cadmium (II) increased with the pH of solution at pH 1-5 and was constant in the range of 6-8. The maximum adsorption capacity was at pH 7 (11.57 mg/g). Figure 2(b) shows the effect of incubation time of cadmium (II) adsorption onto the GQDs with 10 mg/L of cadmium (II) concentration at pH 7. It can be well seen that at the beginning the rate of adsorption went up with increasing incubation time with equilibrium time observed within 30 min. We, therefore, subjected our further experiments with an incubation time of 30 min. Figure 2(c) shows the effect of the initial cadmium (II) concentration. It is demonstrated that the equilibrium adsorption capacity increased with increasing initial cadmium (II) concentration. The optimal concentration is 20 mg/L cadmium (II). The GQDs adsorbent can remove cadmium (II) ion via their surface complexation due to the surface of GQDs consisted of various functional groups including carboxyl, hydroxyl and epoxy group (Upadhyay et al., 2014).

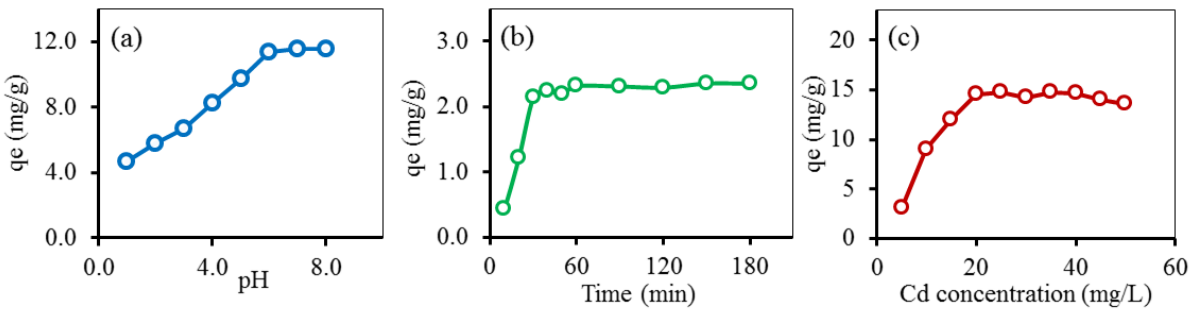

Fig. 2. Effects of (a) pH, (b) time and (c) initial concentration of cadmium (II)

Adsorption isotherm study

Langmuir isotherm and Freundlich isotherm models are used to describe the adsorption isotherms**.** The linear form of both Langmuir and Freundlich isotherms are given by the following Eq**.** (2) and Eq**.** (3)**:**

$$C_e/q_e = C_e/q_m + 1/q_m K_L \quad (2)$$

$$\text{Log } q_e = \log K_F + 1/n (\log C_e) \quad (3)$$

Where, q_m is the maximum quantity of cadmium (II) absorbed on GQDs adsorbent (mg/g), q_e is the quantity of cadmium (II) adsorbed on GQDs at equilibrium, and K_L is the constant value of Langmuir (L/mg), K_F and n are the constant value of Freundlich and the adsorption intensity, respectively. The q_m and K_L values are designed from the slope and the intercept of the straight line plot of C_e/q_e versus C_e, respectively. The K_F and 1/n values can be found from a linear plot of log q_e versus log C_e. Table 1 shows the constant values that are obtained from the Langmuir and Freundlich adsorption isotherm models and their correlation coefficients (R^2)

Table 1 Adsorption isotherm parameters of cadmium (II) using GQDs as an adsorbent.

Adsorbent	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	q_{max} (mg/g)	K_L	R^2	K_F	*1/n*	R^2
GQDs	40.00	0.02	0.9867	35.05	0.43	0.8026

From Table 1, it was found that Langmuir isotherm ($R^2 > 0.98$) fitted with the experimental results better than those of Freundlich isotherm ($R^2 > 0.80$). This indicates that there is a high degree of homogeneity on the GQDs surface with monolayer coverage of cadmium (II) on it. The q_{max} of cadmium (II) was found to be 40.00 mg/g.

Conclusion

The results indicate the suitability and efficiency of GQDs as an adsorbent for cadmium (II) removal from wastewater. The optimum conditions for the removal of cadmium (II) ions were 20 mg/L, 30 min and 7 for initial concentration, contact time and pH of solution, respectively. With maximum adsorption capacity for cadmium (II) being 40.00 mg/g. The adsorption isotherms of GQDs fit well with the Langmuir models. Our experiments clearly showed that the as-prepared GQDs has a high potential as adsorbent for cadmium (II) removal.

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