Acid Activated Bentonite-La Crosslinked Sesbania Gum Beads for Efficient Congo Red Adsorption

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Abstract. In this study, to recycle acid activated bentonite (AAB), novel hybrid beads were prepared from AAB and sesbania gum (SG), which might be an efficient adsorbent for removing an anionic dye Congo red (CR). To gain the greatest adsorption conditions of AAB-SG-La beads, experiments were carried out to evaluate the effects of initial pH value, AAB-SG-La beads dosage on CR removal. The optimal pH value of AAB-SG-La beads for CR elimination was in the range 4.0 ~ 8.0, which can broaden the applications of beads. In addition, the adsorption isotherm datas were consistent with the Langmuir adsorption model and adsorption kinetics conformed to the pseudo-second-order model. Furthermore, the adsorption capacity of CR was 588 mg/g, which revealed a superior adsorption capacity to other materials used as sorbents for CR. This work accredits that AAB-SG-La beads have the ability to remove anionic dye as an economical adsorbent.

1 Introduction

Due to the development of industry, some industries involved in cosmetics, medicine, and textiles emission an abundance of dye wastewater. In particular, In particular, Congo red is a representative anionic dye. This dye was harmful to human health, for instance causing eyes damaging, gastrointestinal malaise and cancer [1].

Various techniques are being used to eliminate dyes from aqueous waste, for instance, biological degradation, membrane filtration, photocatalytic oxidation process, electrochemical method, ion exchange, and adsorption. Above all, adsorption is considered one of the most potential technologies. It has great superiority in its high efficiency, low cost, and easy operation.

It's known that clay minerals such as bentonite have a great adsorption effect on dyes, which are excellent adsorbents, mainly due to their physicochemical properties, high surface area, and ion-exchange process. However, bentonite exist negative charge, which is more beneficial to adsorb basic dyes than acid dyes. Surface modification of bentonite via acid activation enhances the adsorption efficiency of acid dye[2]. Nonetheless, when bentonite needs to be used in practical application, the main obstacle is to deal with solid-liquid separation[3].

Many researchers have studied recovery of acid activated bentonite (AAB) using to sodium alginate,which is the natural biopolymer[4]. Newly, natural polymers have the focus of interest in the field of aqueous treatment as a result of their distinctive advantages: numerous active groups for instance hydroxyls, biodegradability, and nontoxic nature to the environment. Sesbania gum (SG) regard as a natural polymer obtained from the endosperm of sesbania seeds. Its main structure involves D-galactose and D-mannose, which are composed of 1:2. and it has biocompatibility, biodegradability and water solubility. SG can be acted as a novel adsorbent for diverse toxic and harmful compounds due to the functional groups like plenty of hydroxyls[5]. Acid activated bentonite composition with Sesbania gum beads predigests solid-liquid separation disposal compared with the use of fine clay materials.

Herein, we invested objectives of this study that is to prepare an easy and green of composite beads from the combination of acid activated bentonite-sesbania gum beads via a simple fabrication method; to observed the effect of the removal of CR on adsorbent dosage, pH; moreover, to explore the adsorption performance toward CR containing adsorption kinetics as well as adsorption isotherm.

2 Materials and Methods

2.1 Materials

Bentonite was got from Sinopharm Chemical Reagent Co., Ltd, sesbania gum (SG), Congo red (CR), lanthanum nitrate were obtained from Macklin. The reagents used in this study were of analytical grade, and all solutions were made up with deionization water.

2.2 Preparation of AAB-SG-La beads

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AAB was prepared according to our previous research [6]. Briefly,1 g of AAB was added to 30mL of 2%(w/v) sesbania gum solution, then vigorous stirring for 4 h until homogeneous. The mixture was decant into the syringe, then dropped into 100 mL 4%(w/v) lanthanum nitrate solution to form beads at stewing 24 h. The bead surface had remain lanthanum ions, which was removed by rinsing with deionized water. Dried, stored in a clean bottle for further use, and named the sample as AAB-SG-La beads. The fabrication process of AAB-SG-La beads is given in Fig.1.

Fig. 1. The fabrication process of AAB-SG-La beads.

2.3 Characterization

The functional groups of the adsorbents were using KBr pellet technique and determined by Fourier transform infrared spectrometer (Nicolet Nexus 470 apparatus, Nicolet, United States) were recorded in a scanning range of 4000 ~ 400 cm^{-1}.

2.4 Adsorption experiments

Batch adsorption experiments on the removal of CR by AAB-SG-La beads dosage, which performed with 100 mL of CR solutions of predetermined concentration (20 ~ 800 mg/L) in a series of 250 mL flasks, solution pH values (4~10), AAB-SG-La beads dosage (0.1~0.1 g/L) and reaction times (0~4 h). In this study, 0.1 mol/L HCl and NaOH solutions were used to adjust the pH. After each adsorption experiment, a certain volume (approximately 3 mL) of the aqueous solution was filtered through the 0.45μm filtering membrane, and the concentration of non-adsorbed CR was measured on the UV-visible spectrophotometer (UV-2550) with the maximum absorbance wavelengths of 497 nm. The percentage of dyes removal and The adsorption equilibrium capacity qe (mg/g) was measured by using the following Eq.(1) and (2), respectively:

$$R = (C_0\text{-}C_e)/C_0 \times 100\% \quad (1)$$

$$q = (C_0\text{-}C_e)V/m \quad (2)$$

Where, C_0(mg/L) and C_e(mg/L) are the initial concentrations of CR and the remaining CR concentration in the solution after adsorption. Each experiment was repeated three times and mean values were considered in the fitting process.

3 Results and Discussion

3.1 Effect of AAB-SG-La beads dosage

The influence of adsorbent doses of AAB-SG-La beads on the adsorption of CR was indicated in Fig.2. It was observed that the effect of adsorbent dose on CR removal from aqueous solution using CR concentration 300 mg/L, contact time 240 min, and initial pH of CR solution 7 at 25 °C. The removal of CR from 15.56 up to 99.57% with an increase of adsorbent dose from 0.1 to 0.1 g/L. It is an ordinary appearance and is shown in this investigation[7].

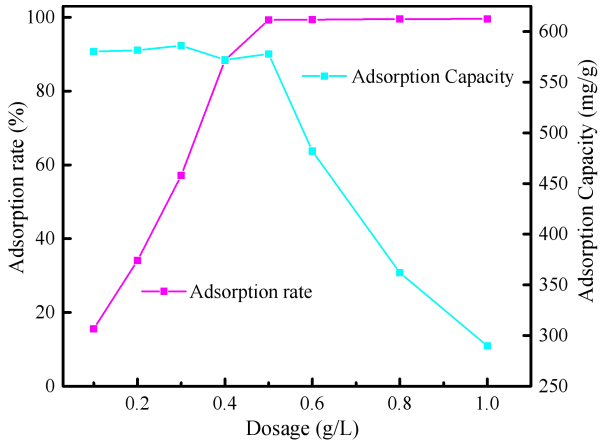

Fig. 2. Effect on various doses of AAB-SG-La beads on adsorption of CR.

3.2 Effect of adsorption on solution pH

Along with the surface properties of adsorbent in solutions will be effect by the initial pH value of CR. Fig. 3 described the role of pH on the adsorption of CR dye. For this, when the pH value on CR solution was grown from 4 up to 10, elimination of CR dropped to 99.65% from 19.45%. At high pH values, AAB-SG-La beads surface may be negatively charged, which lessened the adsorption of CR because of an electrostatic repulsion. On the contrary, AAB-SG-La beads surface may be positively charged in the acid region, making AAB-SG-La beads could be favorable to the adsorption of CR own to the electrostatic attraction. A similar report that holds this phenomenon in the literature[8].

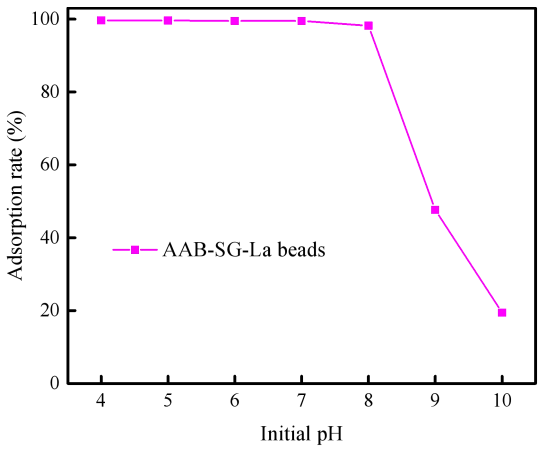

Fig. 3. Effect on the initial pH value on adsorption of CR on AAB-SG-La beads.

3.3 Adsorption isotherm studies

The Langmuir and Freundlich isotherm models are regarded as explaining the CR adsorption isotherm parameters onto AAB-SG-La beads as shown in Table 1. According to the correlation coefficient (R^2) and the adsorption capacity ($q_{m,cal}$ = 588 mg/g), CR adsorption onto prepared AAB-SG-La beads is fitting by the Langmuir model. It is recommend that the adsorption of AAB-SG-La beads are monomolecular layer and active sites are uniform.

3.4. Adsorption kinetics

As show in Table 2, the R^2 of the pseudo-second order kinetic model is higher than the pseudo-first-order as well as the adsorption capacity ($q_{m,cal}$ = 625 mg/g) derive from the pseudo-econd order kinetic model was similar to that gain experimentally ($q_{m,exp}$ = 597 mg/g). Therefore, the adsorption process is suitable to fit the pseudo-second order kinetic model. It is described that chemisorption may be predominantly command the CR adsorption rate by the AAB-SG-La beads.

The practical utilization of AAB-SG-La beads removes CR from to study. The maximum adsorption capacity of AAB-SG-La beads for CR is acquired to be 588 mg/g which shows that the adsorbent competes favorably with other related adsorbents as shown in Table 3.

Table 1. Adsorption isotherms parameters for CR dyes onto AAB-SG-La beads.

Adsorbent	Langmuir model			Freundlich model			$q_{m,exp}$/ mg·g^{-1}
	K_L/L·mg^{-1}	$q_{m,cal}$/ mg·g^{-1}	R^2	K_f/mg·g^{-1}	1/n	R^2	
AAB-SG-La beads	0.39	588	0.998	189.10	0.24	0.505	597

Table 2. Adsorption kinetic parameters for CR adsorption onto AAB-SG-La beads.

Adsorbent	Pseudo-first-order model			Pseudo-second-order model		
	k_1 ×0.01 /min^{-1}	$q_{m,cal}$/ mg·g^{-1}	R^2	k_2×0.001/g·mg^{-1}·min^{-1}	$q_{m,cal}$/ mg·g^{-1}	R^2
AAB-SG-La beads	1.24	138	0.660	0.17	625	0.997

Table 3. Contrast with the maximum adsorption capacities of several different sorbents for CR removal.

Adsorbent	Q_{CR}/ mg·g^{-1}	References
gelatin/bentonite beads	123	[9]
PAB hydrogel	42	[10]
Chitosan-Fe(OH)$_3$ beads	445	[11]
ZnO-clay-alginate beads	547	[12]
Alginate/natural bentonite beads	111	[13]
AAB-SG-La beads	**588**	**This study**

3.5. Adsorption mechanism

Fig. 4 showed the FTIR spectra of AAB-SG-La beads before and after CR adsorption. The band in spectra with wavenumber range 3410 cm^{-1} correspond to vibration stretching of O−H, peak at 2919 cm^{-1} which could be related to aliphatic C−H vibrations. The peaks at 1629 and 1379 cm^{-1} could be assigned to the stretching vibration of −OH, and the symmetric stretching of −COO−, respectively[14]. The corresponding peaks of −OH groups were also shifted from 3410 cm^{-1} to 3435 cm^{-1} for CR uptake. Moreover, the peak at 1379 cm^{-1} disappeared and a new peak at 1421 cm^{-1} onto AAB-SG-La beads after CR adsorption. These changes confirmed that the −OH groups and −COO− groups were involved in the adsorption of CR. The similar report that holds this result in the literature[15].

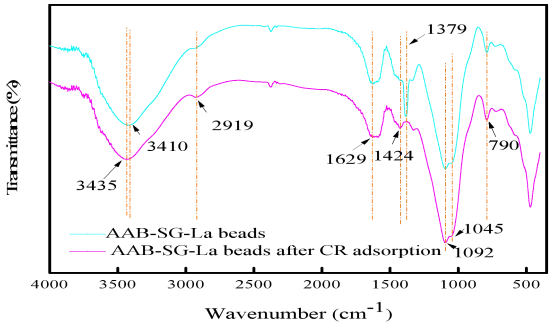

Fig. 4. FTIR spectra of AAB-SG-La beads before and after

CR adsorption.

4 Conclusions

We presented an inexpensive adsorbent based on composite AAB-SG-La beads via lanthanum nitrate solution crosslinking method, which was prepared from acid activated bentonite(AAB) and sesbania gum(SG). The optimum pH value for CR elimination by AAB-SG-La beads was broaden the applications of the beads. In addition, the adsorption isotherm data complied with the Langmuir adsorption model, the adsorption kinetics followed in the pseudo-second-order model. The maximum adsorption capacity was observed to be 588 mg/g. AAB-SG-La beads were used to anionic dye the adsorption capacity was comparably high compared with other synthetic materials. The results of FTIR spectral characterization of AAB-SG-La beads before and after CR adsorption indicated that the adsorption was mainly completed by hydrogen bonding. This work may provide new insight into the recovery of acid activated bentonite for environmental remediation, which would not cause secondary pollution.

Acknowledgments

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