Removal of Reactive Brilliant Red X-3B and Co(II) Ion with Amino-EDTA Functionalized Silica Gel

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Abstract. Silica gel was modified with N-[3-(Trimethoxysilyl)propyl]ethylenediamine, following grafted with ethylenediaminetetraacetic acid (EDTA). The functionalized silica gel was used to readily absorb Co(II) ion from aqueous solution forming SG-Co, via the coordination of EDTA group on the surface of silica gel. The adsorption of Reactive Brilliant Red X-3B (X-3B) in aqueous solution with SG-Co was investigated under varying time, dye concentration, and adsorbent dosage. The results showed that the adsorption capacity of SG-Co for X-3B increased with increasing of time, initial concentration of the dye solution, and absorbent dosage. The adsorption process followed a pseudo second-order model and experimental data fitted Langmuir adsorption model.

Introduction

Industrial waste water is one of the major sources of aquatic environmental pollution. A huge volume of effluents with hazardous species, namely organic components, heavy metals and semimetals, is being discharged from industries into aquatic systems [1, 2]. Sustainable water supplies are vital for agriculture, industry, recreation, energy production, and domestic consumption. Thus, there is a requirement to improve the efficiency of water purification technology [3, 4]. Different materials were used for the removal of dyes by use of adsorption processes [5]. A number of workers have used different adsorbent systems, developed from various industrial waste materials, for the removal of toxic metals and organic waste pollutants [4]. This issue has been a matter of serious concern worldwide for the last few decades, and rigorous emphasis is being given to get rid of this unavoidable risk.

A number of agricultural wastes/by-products have been used for the dye removal from aqueous wastewater, such as rice husk and sugarcane bagasse to remove indigo carmine and methylene blue dye [6]. There are many other wastes which are being used to remove dye from waste water which are fly ash, sugarcane dust, cotton waste and orange peel etc. [7] Activated carbon adsorption is one such method which has great potential for the removal of dyes from aqueous waste [8].

According to one of the research simultaneous removal of dye and metal ions was done by using the heavy metal precipitant *N*,*N*-bis-(dithiocarboxy) piperazine. Here, the removal of the Cu^{2+} was done by the coordination polymerization reaction while the removal of dye was with the adsorption of $[CuBDP]_n$ precipitates [9].

As part of our ongoing research of simultaneous removal of metal ions and dyestuffs, in this paper, the applicability of functionalized silica gel derivative as absorbent for cobalt ions and Reactive Brilliant Red X-3B (X-3B) from water was studied. The effects of variables including the contact time, dye concentration and absorbent dosage were considered.

Experimental

Materials.

Silica gel with particle size in the range of 100−200 mesh was purchased from Qingdao Ocean Chemical Company, China. It was treated with nitric acid (HNO_3:H2O = 1:1) at 100°C for 3 hrs, and then hydrochloric acid (6 mol L^{-1}) at 100°C for 8 hrs. The treated silica gel was washed with doubly distilled water (DDW) and dried first at 120°C for 24 hrs, and finally calcined in Muffle furnace at 180°C for 2 hrs. Ethylenediaminetetraacetic acid (EDTA), N, N'-Diisopropylcarbodi-imide (DIC) and N-[3-(Trimethoxysilyl) propyl] ethylenediamine (95%) were obtained from Aladdin Reagent Co. Ltd, China. Cobalt sulfate ($CoSO_4 \cdot 7H_2O$), N, N-Dimethylformamide (DMF), Toluene, Methanol, Ether were purchased from Sinopharm Chemical Reagents Co. Ltd, China. These chemicals and reagents were used as supplied without further purification. Dry toluene was distilled under N_2 from CaH_2 and dry methanol from magnesium methoxide. All aqueous solutions for measurement experiments were prepared by using doubly distilled water, and the other reagents were of analytical grade (AR).

Preparation of functionalized silica gel and its adsorption for cobalt(II) ions.

Silica gel was modified with N-[3-(Trimethoxysilyl)propyl]ethylenediamine, following grafted with ethylenediaminetetraacetic acid (EDTA). The amino-EDTA functionalized silica gel was mixed with $CoSO_4$ solution (1.0 g of SiO_2-NH-NH-EDTA in 20 mL of 2 mmol $CoSO_4$). The yellowish brown silica gel turned to light red shortly, suggesting the fast adsorption of Co(II) ion onto the surface of silica gel forming cobalt (II) bound silica gel, SG-Co. Above processes are described in Figure 1.

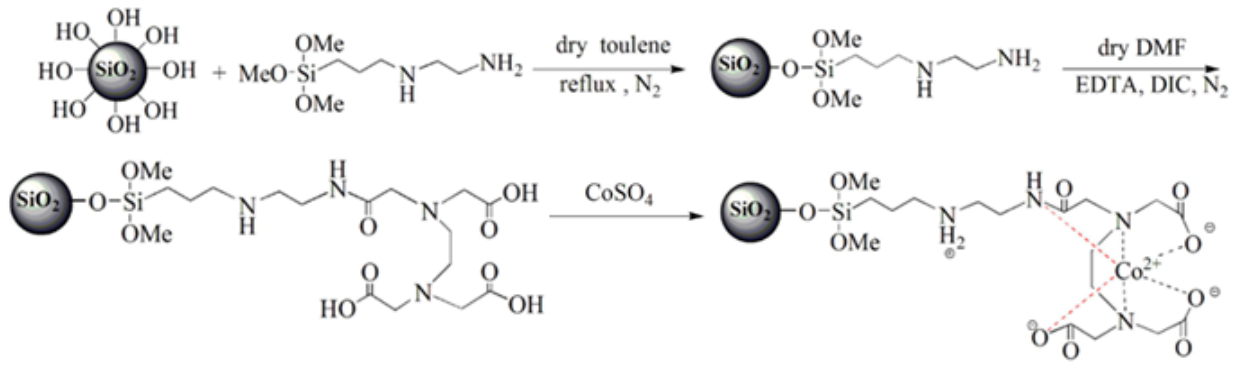

Fig.1. Preparation of functionalized silica gel and its adsorption of cobalt ions

Adsorption of Brilliant Red X-3B.

The SG-Co was added in the Brilliant Red X-3B (X-3B) solution, and the mixture was shaken at room temperature for 3 hrs. The dye adsorption capacity was calculated based on the absorbance (λ_{max}=538 nm) of the residue dye solution. The mechanism of the adsorption of anionic dye X-3B is depicted in Figure 2.

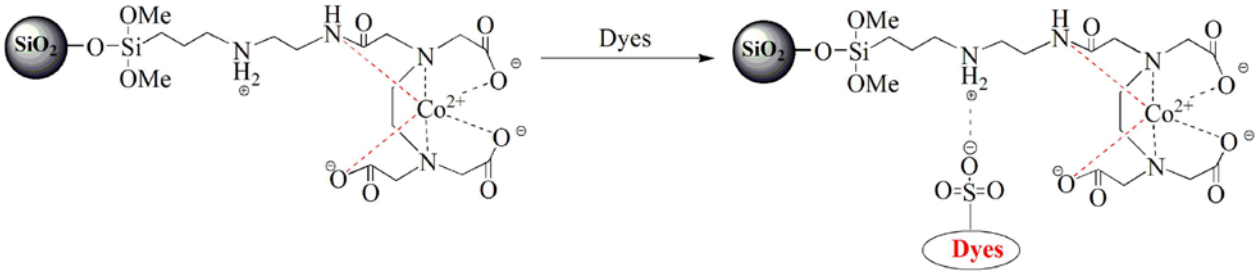

Fig. 2. Mechanism of dyestuff adsorption onto SG-Co

Results and Discussion

Effects of contact time.

The effects of contact time on the removal of X-3B by the SG-Co (30 mg of SG-Co in 30 mL of 50 mg L^{-1} of X-3B solution) are shown in Figure 3. Initially the X-3B dye amount (q_t) were

adsorbed quickly as shown in graph due to the many vacant adsorption sites. For SG-Co, all the active sites were occupied by the dye molecules within 1 hr after which the adsorption rate gradually decreased and became constant at equilibrium.

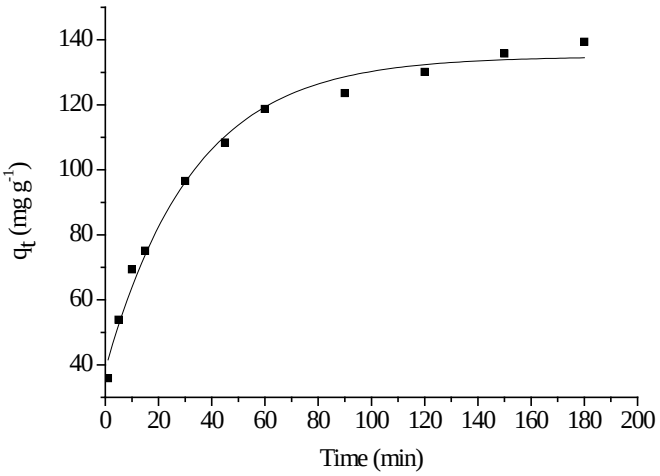

Fig. 3. Effect of contact time on the removal of X-3B by SG-Co

Effects of dye concentration.

SG-Co (30 mg) was added to the dye solution (30 mL) with various dye concentration in the range between 30 to 400 mg L^{-1}, and the effects of dye concentration on removal of X-3B by SG-Co are shown in Figure 4. It indicates that the adsorption capacity (q_e) of the SG-Co increases with increasing of dye concentration, and reaches to maximum value without equilibrium in the concentration range.

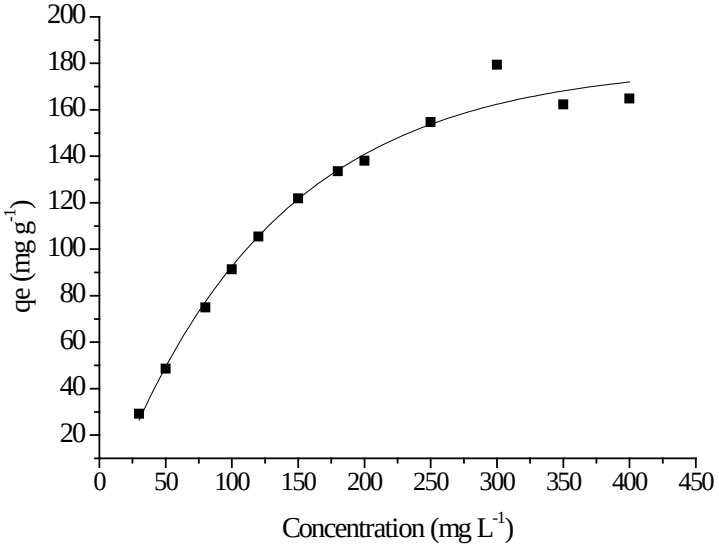

Fig. 4. Effect of dye concentration on the removal of X-3B by SG-Co

Effects of absorbent dosage.

SG-Co (20, 30, 40, and 60 mg) was added into the X-3B dye solution (30 mL of 80 mg L^{-1}), the effects of absorbent dosage on the removal of X-3B are shown in Figure 5. It reveals that the dye removal rate increases when the absorbent dosage increases, since the higher dosage absorbent supply more number of active sites for the interaction with anionic dyes.

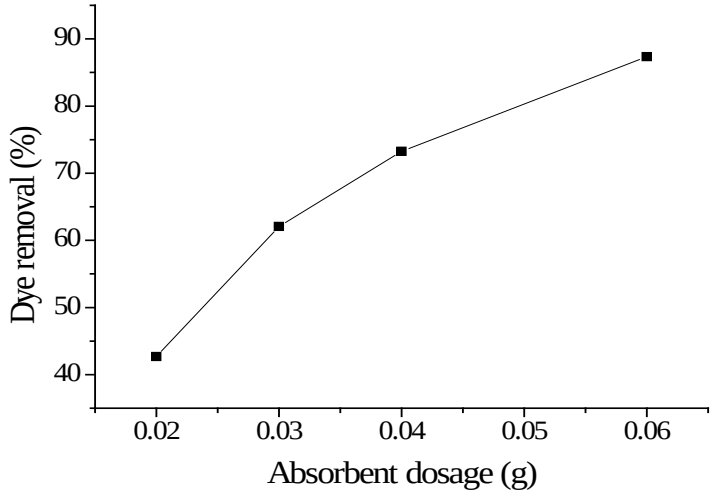

Fig. 5. Effect of absorbent dosage on the removal of X-3B by SG-Co

Adsorption kinetics.

The pseudo first (1) and second-order (2) models were used to describe the adsorption process of X-3B on SG-Co. The parameters of adsorption kinetics were calculated according to the research [10], and are listed in Table 1. The parameters of k_1 and k_2 are the pseudo first-order and second-order rate constant (min^{-1}) of adsorption; $q_{e\ (cal.)}$ (mg g^{-1}) values are the amounts of dye adsorbed per unit mass of absorbent at equilibrium. The value of pseudo first-order and second-order rate constant and regression coefficient (R^2) values are also in Table 1. The results show that correlation coefficient of pseudo second-order model is better than pseudo first-order model. The calculated qe ($q_{e\ (Cal.)}$) based on pseudo second-order model is similar to the experimental data $q_{e\ (Exp.)}$. Therefore, pseudo second-order model is more effective to represent the adsorption kinetics of SG-Co for X-3B.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

Table 1. Kinetic model parameters for the adsorption of X-3B on absorbent

$q_{e\ (Exp.)}$ (mg g^{-1})	Pseudo-first-order			Pseudo-second-order		
	k_1 (min^{-1})	$q_{e\ (Cal.)}$ (mg g^{-1})	R_1^2	k_2 (g mg^{-1} min^{-1})	$q_{e\ (Cal.)}$ (mg g^{-1})	R_2^2
134.47	0.02442	86.51	0.984	0.0006113	144.72	0.995

Adsorption thermodynamics.

Langmuir (3) and Freundlich (4) adsorption isotherms were used to evaluate the adsorption behaviour of SG-Co for X-3B. Table 2 shows R_L^2 values of the Langmuir isotherm model for the dye adsorption on SG-Co is higher than that of the Freundich isotherm model. The results indicate that the adsorption of X-3B on SG-Co fits Langmuir model better than Freundlich model.

$$\frac{C_e}{q_e} = \frac{C_e}{q} + \frac{1}{qK_L} \tag{3}$$

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \tag{4}$$

Table 2 Langmuir and Freundlich isotherm parameters

Langmuir			Freundlich		
q (mg g^{-1})	k_L(L mg^{-1})	R_L^2	k_F (mg g^{-1})	n	R_F^2
170.94	0.1298	0.995	42.440	3.509	0.900

Conclusions

The amino-EDTA modified silica gel was prepared and it was readily used to fast absorb Co(II) ions from aqueous solution, forming Co(II) bound silica gel, SG-Co. SG-Co were found to effectively adsorb X-3B from aqueous solutions. Its adsorption capacity increased with increasing of time, initial concentration of the dye solution, and the SG-Co dosage. The absorption was fast and reached adsorption equilibrium at about 60 min. The adsorption process of the X-3B on SG-Co followed a pseudo second-order model and experimental data fitted well with Langmuir adsorption model.

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