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Kinetic Studies on the Removal of Reactive Blue 49 Dye from Aqueous Solution onto Chitosan-Activated Sludge Composite Particles

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Abstract: Nowadays, water contamination due to the textile dyeing residues is increasing and alarming. One of the most important decontamination techniques is considered to be adsorption due to its efficiency and low cost. Numerous adsorbent materials are prepared the last years to remove toxic dyes especially from contaminated waters. In this study, waste activated sludge produced in biological treatment systems were evaluated and the composites containing chitosan and the waste sludge were synthesized as an adsorbent. The adsorption characteristics of Reactive Blue 49 (RB49) from aqueous solution onto the chitosan-activated sludge composites have been investigated. The effects of contact time and solution pH for the adsorption of RB49 by the chitosan-activated composites was studied for a period of 27 h for initial dye concentrations of 60 mg/l at 25°C. The maximum adsorption capacities of the composites was 16.91 mg/g and obtained at pH 1. Three kinetic models (pseudo first order, pseudo-second order and intraparticle diffusion model) are employed to fit the experimental data and to elaborate the kinetic mechanism for the adsorption of RB49 on the chitosan-activated sludge composites. The pseudo-second-order kinetic model provided the best fit to the experimental data for the adsorption of RB49 dye. Overall, this study indicates the chitosan-activated sludge composites as an effective adsorbent for the removal of RB49 dye from the aqueous solutions. The usage of the composites as adsorbent in adsorption process can manage the environment and turn waste into treasure.

Keywords: Activated sludge, Adsorption kinetics, Chitosan, Composite

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1. Introduction

Textile industries and other dyeing industries such as paper, printing, leather, food, plastic and rubber are primary industrial wastewater sources. Dyes in these industrial wastewaters are generally toxic, carcinogenic, and non-biodegradable. Discharge of the coloured effluent into streams and rivers results in a major threat to the aquatic environment as well as human health. The main methods of removing dyes from wastewater are membrane separation [1], coagulation [2], biodegradation [3], photocatalytic oxidation [4], and adsorption [5-6]. Among these different physicals, chemical and biological treatment methods, adsorption is considered to be the most promising method due to its efficiency and low cost. The adsorption method has attracted the attention of researchers because of the high diversity of new promising adsorbents such as graphene composites [7], agricultural wastes [8], metal oxide based nanomaterials [9], polymeric materials [10], waste activated sludge [11] for this process.

Activated sludge is frequently applied to wastewater to remove organic compounds through the metabolic reactions of microorganisms [12]. The waste sludge is considered as one of the great kinds of solid wastes resulting from domestic wastewater treatment plants. For environmental and ecological reasons, the disposal of these sludges has become immensely important. There are worldwide interests in using inexpensive and commercially available waste materials as an adsorbent for contaminant removal in adsorption process [13]. However, there are a very limited number of studies in the literature that report preparation of adsorbent containing waste activated sludge for removal of dyes. This paper presents the synthesis of the polymeric composites containing waste sludge, which is not reported previously.

Chitosan is a biopolymer obtained chitin, low prices, friendly environment polymer, which is one of the excellent basic substances for the synthesis of new adsorbents. The presence of amino groups in the chitosan structure makes this cationic polymer more efficient in attracting anionic dyes than common adsorbents. However, chitosan needs to be crosslinked to improve poor stability in acidic conditions and low mechanical strength. Certain reagents such as epichlorohydrin, glutaraldehyde, tripolyphosphate, ethylene glycol, diglycidyl ether, and diisocyanate have been used to crosslink chitosan [14-15].

In this study, the chitosan-activated sludge composites were prepared by dropwise addition of gel containing chitosan and activated sludge into a precipitation bath and the composites crosslinked with glutaraldehyde. The synthetic process is simple, low cost, easy to operate and less pollution. Adsorption of Reactive Blue 49 (RB49) from aqueous solution onto chitosan-activated sludge composites have been investigated. The effect of contact time and pH for the adsorption of RB49 by the chitosan-activated sludge composites was studied for a period of 27 h. The pseudo first order, second order and intra-particle diffusion models were applied to investigate the kinetic data.

2. Materials and Methods

2.1. Materials

Chitosan (75-85 % deacetylated) was purchased from Aldrich Chemical Corporation, Germany. Aqueous acetic acid (Merck) solution was used as a solvent for the chitosan. Glutaraldehyde solution (Fluka, 50%) was used as a crosslinker. The pH of the experimental solutions was adjusted by adding 0.1 N NaOH (Merck, Germany) and 0.1 N HCI (Carlo Ebra, France) solutions. Sample of active sludge were collected from a membrane bioreactor (MBR) system. The active sludge (containing Trametes versicolor) was used for the decolorization of simulated textile wastewater in MBR. Reactive Blue 49 (purity of 99%) was obtained from a dye factory in Turkey. Reactive Blue 49 is a commercial anionic dye and used for cotton, viscose dyeing. Fig. 1 illustrates the molecular structure of the dye. All chemicals were of analytical grade, and no further purification was required.

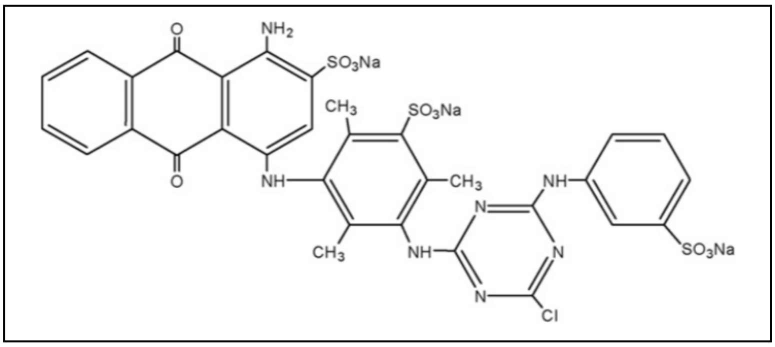


Fig. 1 The molecular structure of Reactive Blue 49.

2.2. Synthesis of Crosslinked Chitosan-Activated Sludge Particles

1 g of chitosan was dissolved in 75 mL of 5 % v/v acetic acid with constant stirring. Activated sludge was added in the weight ratio of chitosan/activated sludge 1:1 and the mixture was left overnight with continuous stirring on magnetic stirrer resulting in the formation of the dispersion. The solution was taken in a syringe and allowed to fall slowly and dropwise into 1 M sodium hydroxide solution with gentle stirring and kept with continuous stirring overnight. After the process, the mixture was washed many times with distilled water to attain a neutral pH. The sample was shaken in 2.5 % w glutaraldehyde ethyl alcohol

solution. After 15 h crosslinking reaction at 60 °C, the chitosan-activated sludge composites were washed with water again to remove excess glutaraldehyde and then dried.

2.3 Adsorption Experiments

The effect of contact time for the adsorption of RB49 by the chitosan-activated sludge composites was studied for a period of 27 h for initial dye concentrations of 60 mg/L at 25°C. The adsorbent dosage was 0.1 g/50 mL of the dye solution. The experimental studies were carried out at pH 1, 2, 3, 5 and 7. Using a UV–vis spectrophotometer, the concentrations of the dye in aqueous solution were determined at a maximum wavelength of 586 nm before and after the adsorption process. The adsorption capacity (qe) of the dye adsorbed onto the chitosan-activated sludge adsorbent was calculated using Equation (1):

$$q\ (mg/g) = \frac{(C_0 - C_e)V}{w} \tag{1}$$

where C_0 and Ce are the initial and the equilibrium concentrations of dye in the adsorption solution (mg L^{-1}), V is the volume of the adsorption solution (L), and W is the weight of the adsorbent (g).

The removal efficiency (%) of dye can be obtained using Equation (2):

$$Removal\ Efficiency\ (\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

3. Results and Discussion

3.1 Effect of contact time and pH

The effects of contact time on the dye removal efficiency of the chitosan-activated sludge composites were investigated and given in Fig. 2. Dye removal efficiency of the chitosan-activated sludge composites initially increases as the contact time is prolonged, and gradually reaches equilibrium.

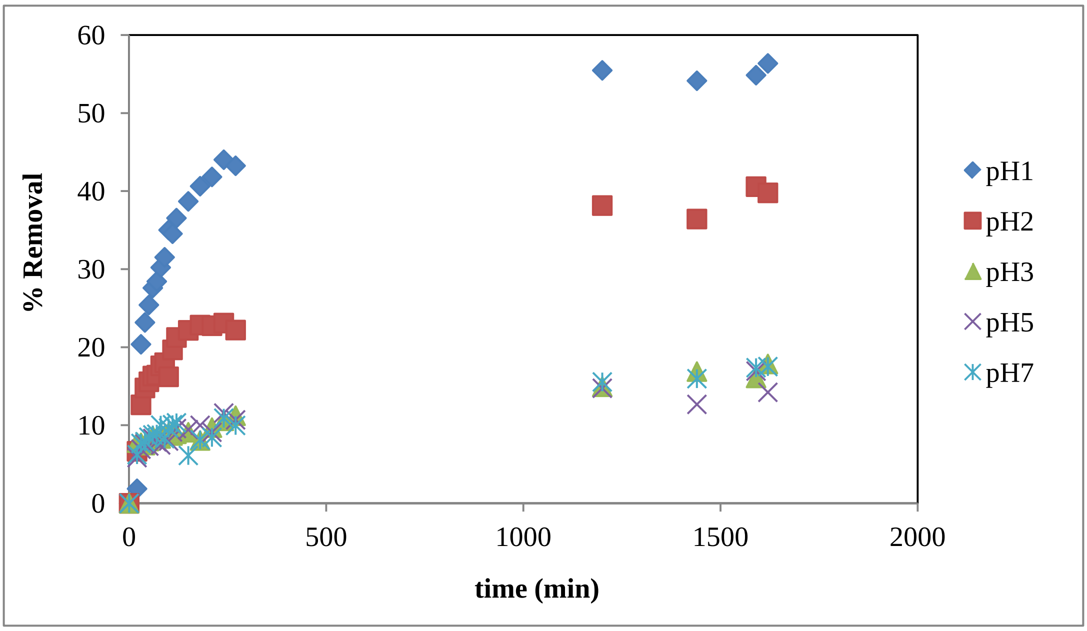


Fig. 2 Effect of contact time on dye removal efficiency of the chitosan-activated sludge composites (Adsorbent dosage: 0.1 g/50 ml; 25°C; 150 rpm; 27 h).

Solution acidity influences the adsorption behaviour of the chitosan-activated sludge adsorbent. The effect of contact time on the adsorption capacity of RB49 by the chitosan-activated sludge adsorbent at different pH values is shown in Fig. 3. The maximum adsorption capacity of the synthesized chitosan-activated sludge composites was 16.9 mg/g for dye RB 49 at pH 1. At pH = 7, the maximum adsorption capacity dropped to 5.26 mg/g, which is only 69 % of that at pH = 1. The ability of chitosan-based adsorbents to adsorb anionic dyes such as RB49 increases with decreasing pH due to an increase in the degree of amino groups protonation [16].

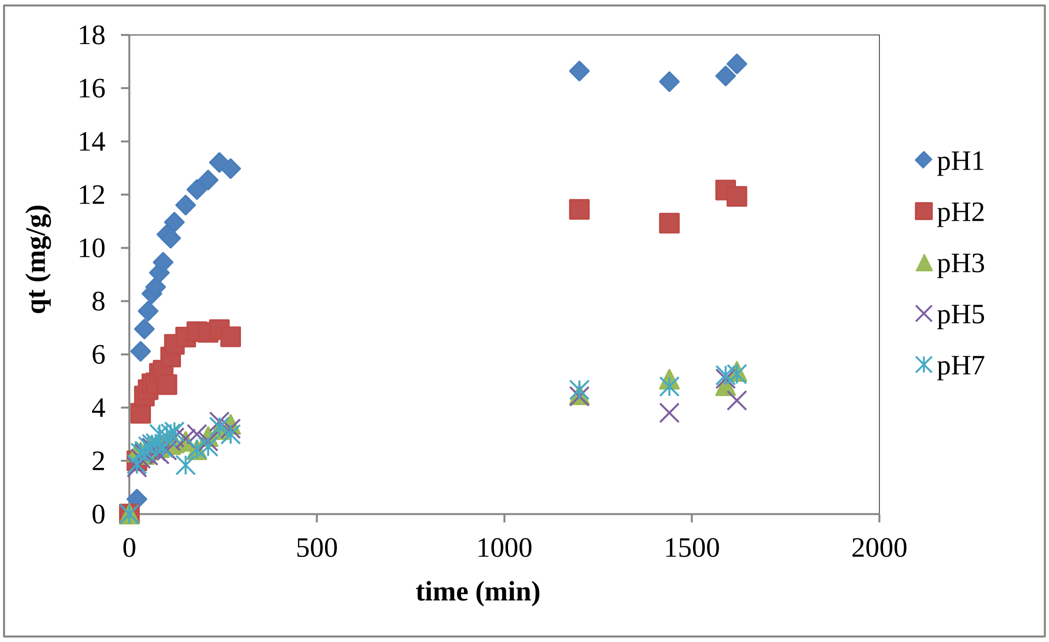


Fig. 3 Effect of contact time on the adsorption capacity of RB49 on the chitosan-activated sludge composites (Adsorbent dosage: 0.1 g/50 ml; 25°C; 150 rpm; 27 h).

3.2 Adsorption Kinetics

Kinetics of adsorption was determined by analyzing adsorptive uptake of the dye from aqueous solution at different pH values. In order to investigate the adsorption processes of RB49 on the chitosan-activated sludge composites at different pH values, three kinetic models were used including pseudo first order, pseudo-second order and intra-particle diffusion model.

Pseudo First Order Model [17]:

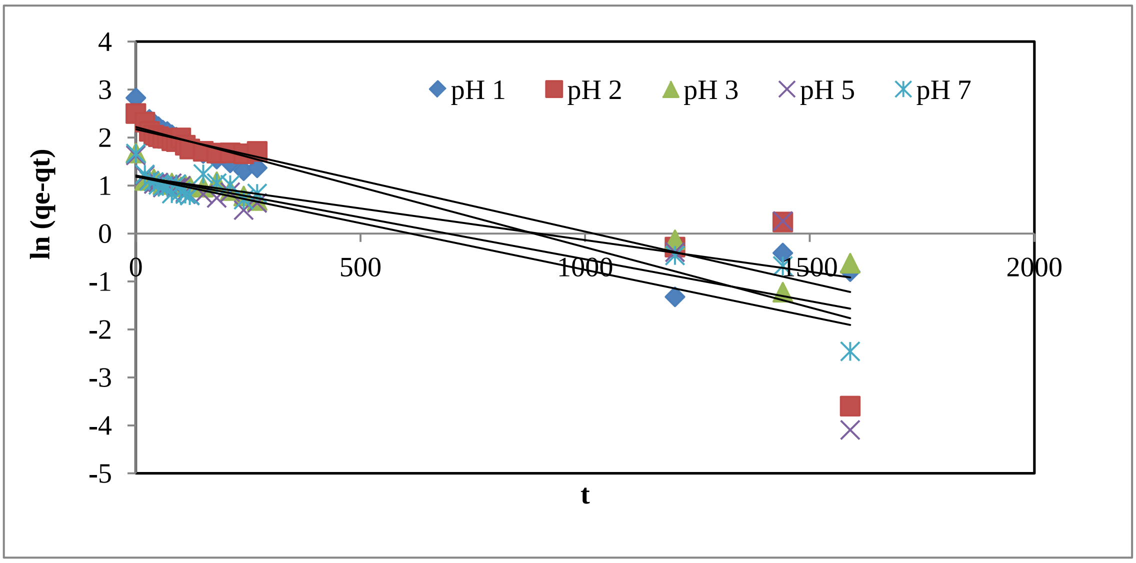
$$\ln(q_e - q_t) = \ln q_e - k_1 . t \qquad (3)$$

where q_e (mg/g) is the equilibrium adsorption capacity, q_t (mg/g) is the adsorption capacity at t time, t is the time of adsorption, k_1 (min^{-1}) is the pseudo-first-order kinetic adsorption rate constant. The plots of $ln(q_e-q_t)$ versus t represent straight lines with k_1 as the slope and *ln qe* as the intercept (Fig. 4 (a)).

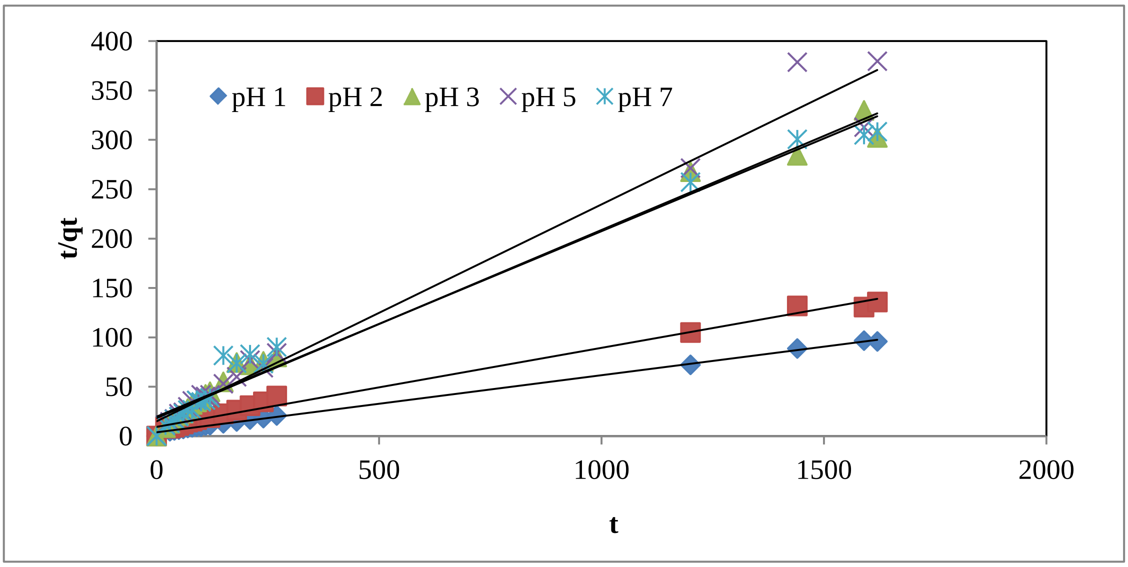
Pseudo Second-Order Model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

where k_2 is the rate constant of the pseudo-second-order equation. The plots of t/q_t versus t can be used to obtain the k_2 and q_e values (Fig. 4 (b)).



(a)



(b)

Fig. 4 Pseudo first order (a) and Pseudo-second order (b) kinetic plots for the adsorption of RB 49 dye onto crosslinked chitosan-activated sludge composites (Adsorbent dosage: 0.1 g/50 ml; 25°C; 150 rpm; pH 1; 27 h).

The kinetic parameters calculated by non-linear regression analysis using Eqs. (3) and (4) are presented in Table 1. It is obvious that the corresponding linear regression correlation coefficient (R^2) values for the pseudo-second-order model are relatively higher than those for the pseudo first order at different solution pH. Moreover, the calculated $q_{e,\ cal}$ values obtained from the pseudo-second-order kinetic model agree with the experimental data ($q_{e,exp}$) better than those obtained from pseudo-first order. It is demonstrated that the adsorption of the RB49 dye onto the chitosan-activated sludge composites can be described by the pseudo-second-order kinetic much better than the pseudo-first-order model. Therefore, the adsorption of RB49 on the chitosan-activated sludge is a chemical adsorption process and controlled by electrostatic attraction [18].

Table 1. Kinetic parameters for the adsorption of RB 49 dye onto the chitosan-activated sludge composites at different pH values.

		Pseudo-first-order			Pseudo-second order		
pH	$q_{e,exp}$ (mg/g)	$q_{e,\ cal}$ (mg/g)	$k_1(x10^3)$ (min^{-1})	R^2	$q_{e,\ cal}$ (mg/g)	$k_2(x10^3)$ (min^{-1})	R^2
1	16.9	8.80	2.1	0.8993	17.3	0.8860	0.9987
2	12.2	9.21	2.5	0.8134	12.5	0.6782	0.9901
3	5.36	3.26	1.3	0.9148	5.25	1.9923	0.9868
5	5.10	3.28	1.9	0.6491	4.55	3.2053	0.9806
7	5.30	3.36	1.7	0.8754	5.33	1.8032	0.9803

The intraparticle diffusion model describes the diffusion process of adsorbate in the particles. The model is first proposed by Weber-Morris, the formula is as follows [19]:

$$q_t = k_{id}\, t^{1/2} + C \qquad (5)$$

where k_{id} ($mg/g.min^{1/2}$) is the intraparticle diffusion rate constant, C is a constant related to the boundary layer thickness. The plot q_t versus $t^{1/2}$ enables to determine both the constants K_{id} and C (Fig. 5). The calculated parameters of K_{id} and C were listed in Table 2. The values of the regression coefficients (R^2) for the plots are higher than 0.97 and the C values are larger than zero. Initially, the dye ions are transported to the chitosan-activated sludge external surface through the film diffusion at a high rate. Once the surface is saturated, the RB49 dye ions enter inside the chitosan-activated sludge by intra-particle diffusion through the pores and internal surface diffusion until equilibrium is reached and this is represented by the second straight lines.

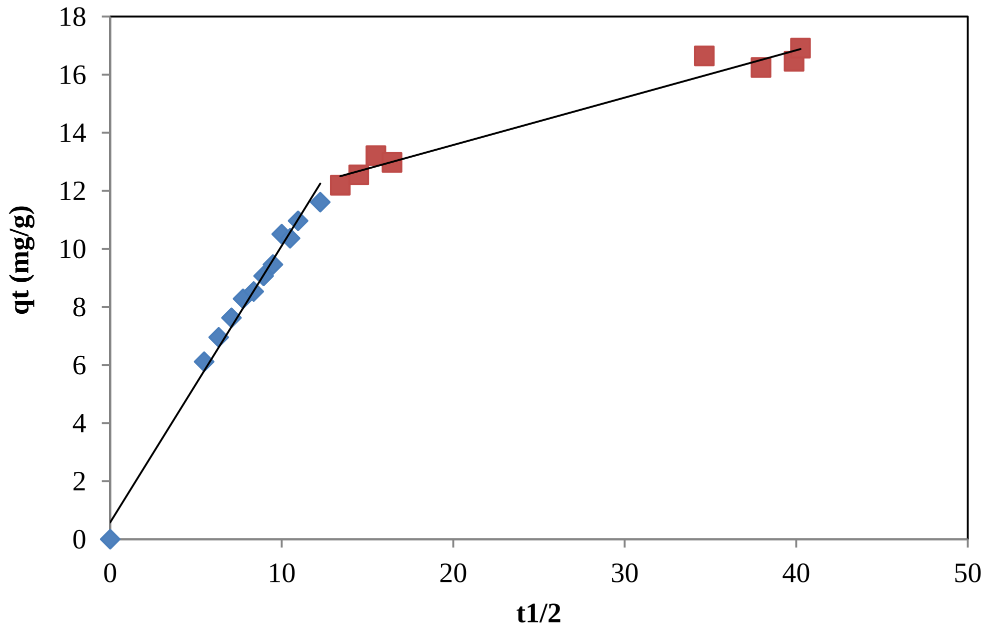


Fig. 5 Intra-particle diffusion model for the adsorption of RB 49 dye onto crosslinked chitosan-activated sludge composites (Adsorbent dosage: 0.1 g/50 ml; 25°C; 150 rpm; pH 1; 27 h).

Table 2. Kinetic parameters of the intraparticle diffusion model for the adsorption of RB 49 dye onto crosslinked chitosan-activated sludge composites.

$k_{i,1}$ (mg/g.min$^{-1/2}$)	$C_{i,1}$	R^2_1	$k_{i,2}$ (mg/g.min$^{-1/2}$)	$C_{i,2}$	R^2_2
0.9529	0.5778	0.9867	0.1631	10.315	0.97

4. Conclusion

In this paper, chitosan-activated sludge composites were prepared by dropwise addition of gel containing chitosan and activated sludge into a precipitation bath and used as adsorbents for RB49 dye. The effects of contact time and pH for the adsorption of RB 49 by the chitosan-activated sludge composites were studied for a period of 27 h for initial dye concentration of 60 mg/L at 25°C. The adsorption capacity of the synthesized adsorbents was 16.91 mg/g for RB49 dye. The pseudo-second-order kinetic model provided the best correlation to the experimental results. The contact time between the pollutant and the adsorbent has significant importance in the wastewater treatment by adsorption. In this study, Reactive Blue 49 dye was removed by crosslinked chitosan-activated sludge particles in a short time effectively. The adsorbent has a good application prospect in the treatment of wastewater and dye pollution.

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