

Equilibrium and Kinetic Studies of Reactive Black 8 Adsorption onto Crosslinked Chitosan Beads

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Abstract: Environmental pollution problems by the discharge of effluent containing various contaminations from textile, paper and paint industries have become a serious issue in recent years. Dye removal from wastewater has received considerable attention for several adsorbents and several classes of dye. Reactive black 8 is an environmentally hazardous dye and most applicable in textile industries. Chitosan is a non-toxic, biodegradable and biocompatible and acts as an efficient adsorbent because of the amino functional groups. In the present work, the crosslinked chitosan beads were synthesized by using glutaraldehyde as a crosslinker and the adsorptive removal of reactive black 8 by the beads from an aqueous solution was investigated. The effect of contact time and initial dye concentration was evaluated. The adsorbent dosage was retained as 1 g/L and initial dye concentration values were varied from 30 to 150 mg/L. Equilibrium isotherms were analysed by Langmuir, Freundlich, Dubnin–Radushkevich, and Temkin isotherm. Freundlich isotherm model was found fit effectively for the reactive black 8 adsorptions. Kinetic adsorption data were evaluated using the pseudo-first-order kinetic model, the pseudo-second-order kinetic model and the intraparticle diffusion model. The adsorption followed pseudo second order kinetics. Overall, this study indicates chitosan beads as an efficient, eco-friendly and low-cost adsorbent for the removal of reactive black 8 dye from aqueous solutions.

Key words: Adsorption, chitosan, kinetics, reactive black 8.

1. Introduction

It is known that significant amount of wastewater which contains textile dyes used in various industries such as dyeing, coloring, etc. is released into the environment without any treatment unconsciously. Such as, discharge of the effluent into streams and rivers results in a major threat to the aquatic environment as well as human health. Textile dyes used in textile dyeing processes are stable and have complex aromatic structure. There are many different dyestuffs according to their chemical structure. Reactive dyes are in the group of azo dyes and useful for textile industries due to its practical, bright and fast coloring behaviour and ease of application [1]. Reactive black 8 (RB8, $C_{19}H_{11}ClN_8Na_2O_{10}S_2$, FW 656.5 $g \cdot mol^{-1}$) is an environmentally hazardous dye and most applicable in textile industries. Fig. 1 shows

the chemical structure of the RB8 dye.

Chitin is one of the most abundant polymers available naturally [3]. Chitosan is obtained by deacetylation of chitin, and is synthesized by crustacean shells, insects, etc. [4]. Chitosan has many superior features such as non-toxic nature, biodegradability, biocompatibility [5-7]. It acts as an efficient adsorbent because of the amino ($-NH_2$) functional groups. Chitosan with a cationic structure is effective in the removal of anionic dyes from aqueous solution. Otherwise, chitosan exhibits unstable behavior in low pHs and does not show adsorption property. In low pH mediums such as dye-containing effluents, chitosan must be structurally stabilized to use as an adsorbents. Crosslinking is known as a good way to ensure stability and strength the structure. Certain reagents have been used to crosslink chitosan such as glutaraldehyde, tripolyphosphate, ethylene glycol.

In this work, chitosan beads were synthesized by using glutaraldehyde as a crosslinking agent to adsorp

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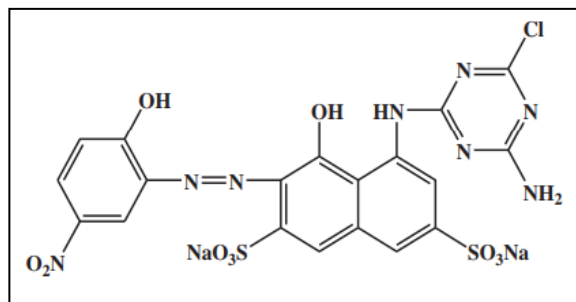


Fig. 1 Chemical structure of RB8 [2].

hazardous RB8 dye from aqueous water. The effect of contact time and initial RB8 dye concentration was evaluated to explain the adsorption process. Equilibrium and kinetic studies of the adsorption process were also discussed.

2. Materials and Methods

2.1 Materials

Chitosan (Aldrich, a degree of deacetylation 75-85%), acetic acid (Merck) and crosslinker agent, glutaraldehyde (Fluka, 50%) were used for the synthesis of the adsorbent. RB8 was purchased from a dye factory in Bursa, Turkey. All chemicals were of analytical grade and used without further purification.

2.2 Synthesis of Crosslinked Chitosan Beads

The aqueous acetic acid solution was used to dissolve chitosan as mixing 1 g chitosan in 75 mL acetic acid. The solution was dropped into a slowly stirring 1 M NaOH solution by using a syringe. The system was allowed to stir overnight. After that, the mixture was washed with distilled water until the mixture reached neutral pH. The sample was mixed with 2.5% w glutaraldehyde ethyl alcohol solution and left for crosslinking at 60 °C for 15 h in a shaker. After the reaction was completed, the crosslinked beads were washed with distilled water to eliminate excess glutaraldehyde. The resulting material was shown in Fig. 2.

2.3 Adsorption Experiments

The adsorbent dosage was retained as 1 g/L and



Fig. 2 The crosslinked chitosan beads.

initial dye concentration values were varied from 30 to 150 mg/L. All the experiments were carried out without any pH adjustment and at room temperature. And 50 mL of conical flasks was used to shake the solution and beads at 120 rpm. The effect of contact time and initial dye concentration was evaluated. The concentrations of RB8 in aqueous solution were determined using a UV-vis spectrophotometer (Agilent Cary 60 UV-Vis) at wavelength 589 nm. The adsorption capacity was determined using Eq. (1) given below:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where q_e was the equilibrium adsorption capacity (mg/g), C_0 and C_e were the initial and equilibrium concentrations (mg/L) of RB8 dyes, respectively. V was the volume (L) of the solution and W was the weight (g) of the adsorbent.

Equilibrium isotherms were analysed by Langmuir, Freundlich, Dubnin-Radushkevich, and Temkin isotherm. Kinetic adsorption data were evaluated using the pseudo-first-order kinetic model, the pseudo-second-order kinetic model and the intraparticle diffusion model.

3. Results and Discussion

3.1 Effect of Contact Time and Adsorption Kinetics

The kinetic study of RB8 adsorption onto crosslinked chitosan beads was performed to determine the effect of the contact time on the adsorption process. Remaining

dye concentrations were determined for the various time intervals by UV–vis spectrophotometer. The adsorption process was attained equilibrium at 23 hours. The parameters for the kinetic study were 1 g/L adsorbent dosage, natural pH of the dye solutions. The experiments were carried out at room temperature. Fig. 3 shows the removal efficiency of the process. The figure is plotted for all concentrations of RB8. The maximum removal was obtained as approximately 70% for the dye concentration of 30 ppm. Dye removal percentages was achieved for 30, 60, 90, 120 and 150 ppm as 68.94, 40.3, 39.83, 34.15, 30.85% respectively. Besides this, adsorption capacities for all dye concentrations were plotted in Fig. 4. The highest capacity value was calculated as 46.28 mg/g for 150 ppm RB8 dye concentration.

Pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models were used to model adsorption kinetics mathematically. Linearized forms of the model equations (Eqs. (2)-(4)) were given below [8]:

Pseudo-first-order kinetic model:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

Pseudo-second-order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Intra-particle diffusion kinetic model:

$$q_t = k_{\text{diff}} t^{1/2} + C \quad (4)$$

where q_e is the amount of the dyes adsorbed at equilibrium (mg/g), q_t is the amount of the dyes adsorbed at time (mg/g), k_1 is the rate constant of pseudo-first order kinetic (hour^{-1}), k_2 is the rate constant of pseudo-second-order kinetic ($\text{g}/(\text{mg} \cdot \text{hour})$), k_{diff} is the intraparticle diffusion rate constant ($\text{mg} \cdot \text{g}^{-1} \cdot \text{hour}^{-1/2}$) and C is a constant related with boundary layer thickness.

Adsorption kinetics of the process were studied for all initial dye concentrations (30-150 mg/L) and adsorbent dosage was 1 g/L without pH adjustment for 23 hours at room temperature. The plots of the

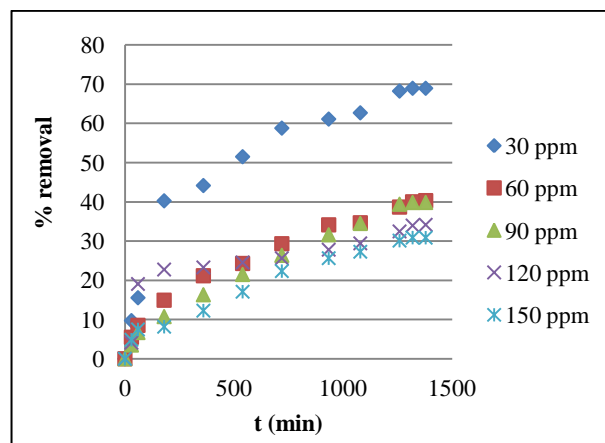


Fig. 3 Effect of time on dye removal efficiency of the crosslinked chitosan beads (adsorbent dosage: 1 g/L; 25 °C; 120 rpm; 23 h).

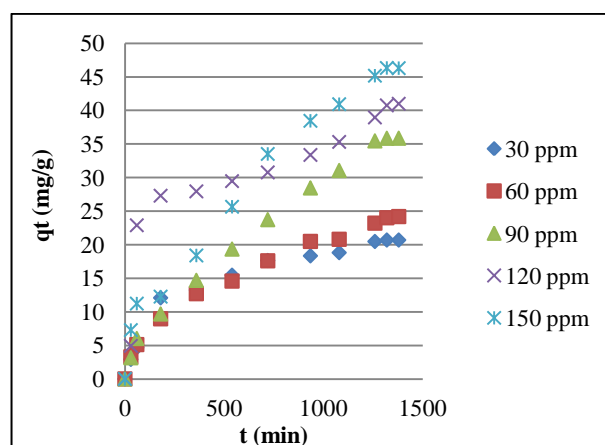


Fig. 4 Effect of time on adsorption capacity of the crosslinked chitosan beads (adsorbent dosage: 1 g/L; 25 °C; 120 rpm; 23 h).

pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models were illustrated in Figs. 5-7, respectively. Table 1 shows the kinetic parameters for the RB8 adsorption onto crosslinked chitosan beads.

From a comparison of the regression coefficients (R^2) more higher values were obtained for the pseudo-second-order kinetic model from the pseudo-first-order model. And also experimental and calculated q_e values were determined as close to each other for the pseudo-second-order kinetic model [9]. Therefore the pseudo-second-order model was found in best fit with the adsorption process. R^2 values for the intra-particle diffusion model was also determined

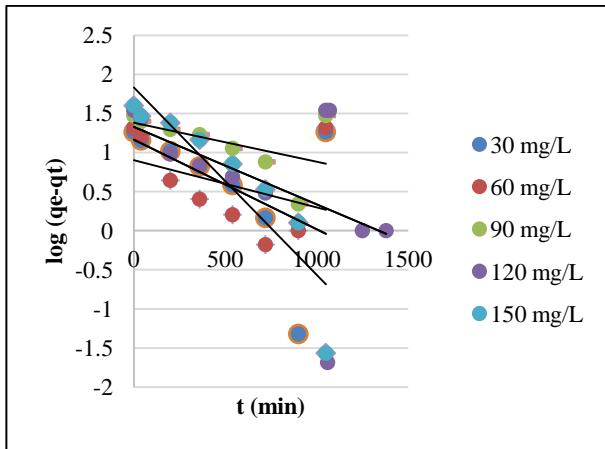


Fig. 5 Pseudo-first-order kinetic model for dye by adsorption onto crosslinked chitosan beads (adsorbent dosage: 1 g/L; 25 °C; 120 rpm; 23 h).

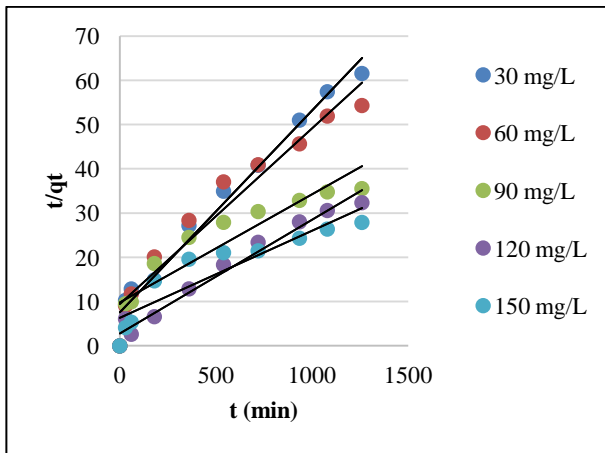


Fig. 6 Pseudo-second order kinetic model for dye by adsorption onto crosslinked chitosan beads (adsorbent dosage: 1 g/L; 25 °C; 120 rpm; 23 h).

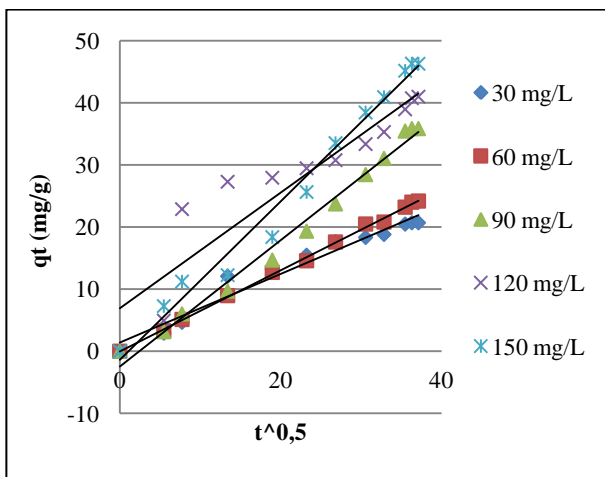


Fig. 7 Intra-particle diffusion study for dye by adsorption onto crosslinked chitosan beads (adsorbent dosage: 1 g/L; 25 °C; 120 rpm; 23 h).

as higher than > 0.9 . This model gives information about the rate-limiting step of the process. Depending on the state of the plot, if the plot passes through from the origin (if the C value is zero), intraparticle diffusion solely rates limiting step of adsorption rate. the shape of the plots for this model also shows the stages of the adsorption process. Two or more straights show that the adsorption occurs in multi-stages [10]. As can be seen from Fig. 7, plots for all dye concentration appear to be linear and do not pass through from the origin. Thus, intraparticle diffusion is effective but not solely rate-limiting step for the RB8 adsorption process.

3.2 Equilibrium Isotherms

Adsorption equilibrium isotherms for the RB8 adsorption process were explained by Langmuir, Freundlich, Dubnin–Radushkevich and Temkin isotherms. The isotherms exhibit relation between adsorbent and adsorbate and coverage of adsorption multilayer or monolayer at equilibrium [11]. Linearized forms of the isotherm equations Eqs. (5)-(10) were given below [9, 12]:

Langmuir isotherm equation:

$$C_e/q_e = C_e/q_m + 1/(q_m \cdot K_L) \quad (5)$$

Freundlich isotherm equation:

$$\ln q_e = \ln K_F + (1/n) \cdot (\ln C_e) \quad (6)$$

Temkin isotherm equation:

$$q_e = B \ln K_T + B \ln C_e \quad (7)$$

Dubnin–Radushkevich isotherm equation:

$$\ln q_e = \ln (q_D) - (K_{DR} \varepsilon^2) \quad (8)$$

$$\varepsilon = RT \ln (1 + 1/C_e) \quad (9)$$

$$E = (1/\sqrt{2KDR}) \quad (10)$$

where C_e is the equilibrium concentration (mg/L) in solution, q_e is the equilibrium adsorption capacity (mg/g), q_m is the maximum adsorption capacity (mg/g), K_L is the Langmuir constant (L/mg), K_F is the Freundlich constant $[\text{mg/g L/g}]^{1/n}$, n is surface heterogeneity

Table 1 Kinetic parameters for the RB8 adsorption onto crosslinked chitosan beads.

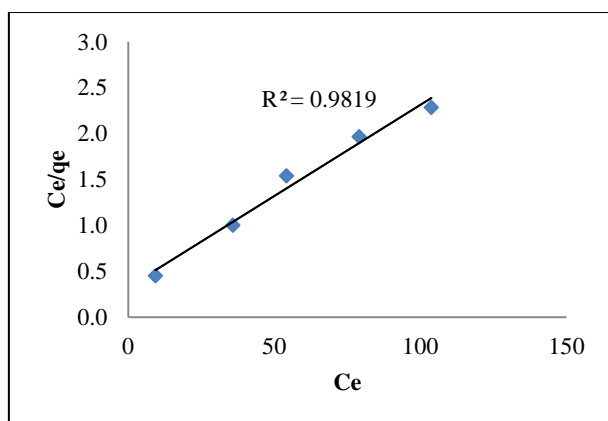
$C_{\text{onc.}}$ (mg/L)	Pseudo-first order model				Pseudo-second order model			Intraparticle diffusion model		
	$q_{e,\text{exp.}}$ (mg/g)	$q_{e,\text{cal.}}$ (mg/g)	k_1 ($\times 10^3$) (hour $^{-1}$)	R^2	$q_{e,\text{cal.}}$ (mg/g)	k_2 ($\times 10^3$) (hour $^{-1}$)	R^2	k_{diff} (mg/g hour)	C	R^2
30	20.6822	11.4657	2.0727	0.2693	22.7790	1.9272	0.9914	0.553	1.3893	0.9594
60	24.1775	18.2852	2.9939	0.1533	27.3224	1.3395	0.943	0.6536	-0.0321	0.9983
90	35.8504	31.5500	2.7636	0.2622	45.2488	0.4884	0.8629	1.0167	-2.4486	0.9881
120	40.9813	0.2999	-16.4178	0.252	42.1941	0.5617	0.9687	0.9306	6.922	0.8618
150	46.2803	42.1890	2.9939	0.816	55.5555	0.3240	0.864	1.2746	-1.3639	0.9821

factor, B Temkin constant (J/mol), K_T Temkin adsorption potential (L/mg), q_D theoretical maximum capacity (mg/g), K_{DR} Dubinin–Radushkevich isotherm constant (mol^2/J^2), ϵ is the Polanyi potential, R is the gas constant (J/mol K), T is the temperature (K), E is the adsorption energy (kJ/mol).

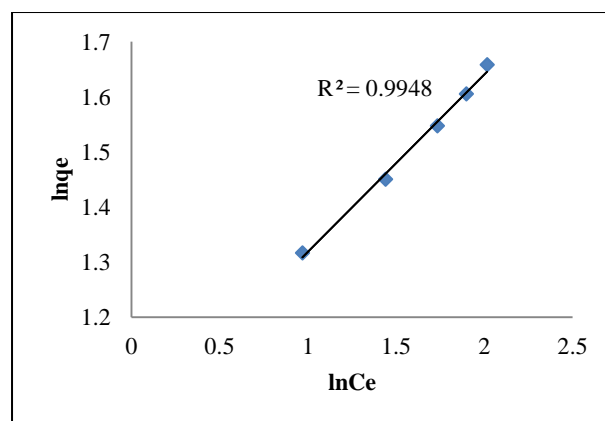
Isotherm parameters for the adsorption process were listed in Table 2. Regression coefficient for Freundlich isotherm is 0.9948 which is higher than

Langmuir (0.9819), Temkin (0.9398) and Dubinin–Radushkevich (0.8164) coefficients. Therefore, the adsorption fitted better with Freundlich isotherm to describe RB8 adsorption onto chitosan beads. Freundlich isotherms confirm that a multilayer adsorption occurs on heterogeneous surfaces between the adsorbate and adsorbent [13].

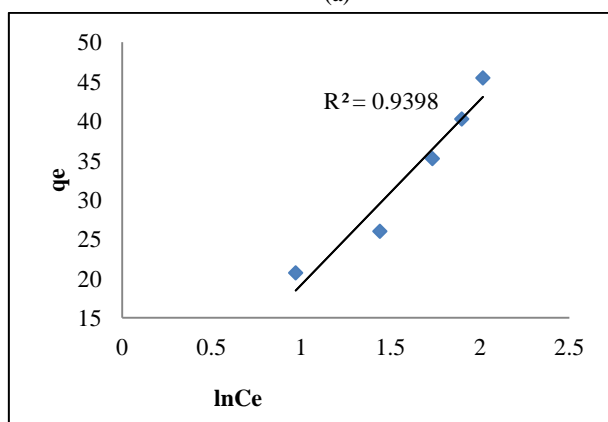
Fig. 8a shows the Langmuir isotherm plot for the adsorption process. The Langmuir isotherm model



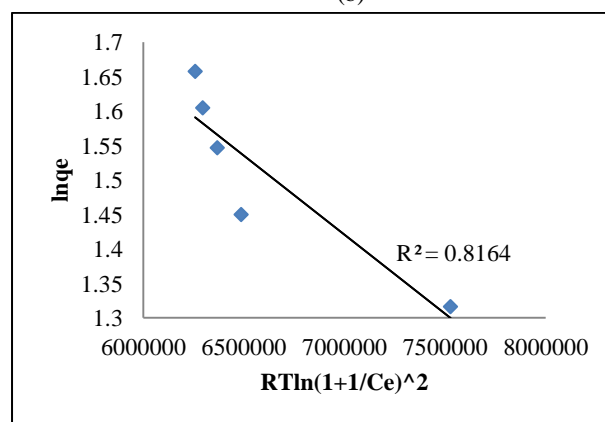
(a)



(b)



(c)



(d)

Fig. 8 (a) Langmuir isotherm, (b) Freundlich isotherm, (c) Temkin isotherm, (d) Dubnin–Radushkevich isotherm for dye by adsorption onto crosslinked chitosan beads.

Table 2 Langmuir, Freundlich, Temkin and Dubnin-Radushkevich isotherm constants for the adsorption of dye on the chitosan beads.

Langmuir Adsorption Isotherm			Freundlich Adsorption Isotherm			Temkin Adsorption Isotherm			Dubnin-Radushkevich Adsorption Isotherm		
q_m (mg/g)	K_L	R^2	K_F [$\frac{\text{mg/g}}{(\text{L/g})^{1/n}}$]	n	R^2	K_T (L/mg)	B (J/mol)	R^2	q_D (mg/g)	$K_{DR} \cdot 10^7$ ($\frac{\text{mol}^2}{\text{J}^2}$)	R^2
52.63	0.058	0.9819	2.709	3.107	0.9948	0.8334	23.465	0.9398	20.6	2	0.8164

exhibits that adsorption occurs on active sites as a monolayer. The isotherm parameters q_m and K_L were calculated as 52.63 mg/g and 0.058 for the adsorption process, respectively. Freundlich isotherm plot is illustrated in Fig. 8b. This isotherm presents that adsorption is affected both physically and chemically [13]. $1/n$ factor for the Freundlich isotherm indicates that the adsorption process is favourable. The n value was calculated as 3.107 for the RB8 adsorption onto chitosan beads, so the process is described as favourable [14]. In Fig. 8c, the Temkin isotherm model indicates the interactions between the adsorbate and adsorbent [15]. Temkin adsorption potential and Temkin constant were calculated as 0.8334 L/mg and 23.465 J/mol, respectively. Fig. 8d belongs to the Dubnin–Radushkevich isotherm which applied to present adsorption energy of the process [16]. The parameters were found as q_D 20.6 mg/g and $K_{ad} 2 \times 10^{-7} \text{ mol}^2/\text{J}^2$. According to this isotherm the adsorption energy, E was calculated as 1.58 kJ/mol.

4. Conclusions

In the present study, crosslinked chitosan beads were used to remove RB8 dye from the aqueous water and adsorption mechanism of the process was revealed by controlling some parameters such as contact time and initial dye concentration. The resulting inferences can be listed as follows:

- Percentages of RB8 removal from aqueous solutions were increased with time for 23 hours.
- A maximum adsorption capacity of 46.28 mg/g has been obtained for the initial dye concentration of 150 mg/L.
- The regression constants demonstrated that the adsorption kinetics of RB8 was more compatible with

the pseudo-second-order model and intra-particle diffusion model.

- Freundlich isotherm model was found fit effectively for the RB8 adsorption.
- The Freundlich constant ($1/n$) is smaller than 1, indicating a favourable process.
- This study convinced that the crosslinked chitosan beads proved to be an alternative, economic, and environmentally friendly adsorbent for dye removal from aqueous solution.

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