Scientific Research

Adsorption of Congo Red from Aqueous Solution Using CTAB-Kaolin from Bechar Algeria

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Abstract

Cetyltrimethylammonium bromide-modified kaolin (CTAB-kaolin or KC) was prepared and tested as an adsorbent for an anionic dye Congo red (CR) removal from aqueous solution in comparison with natural kaolin (K). The effect of various experimental parameters was investigated using a batch adsorption technique. In this manner, the adsorption isotherms and adsorption kinetics of CR on K and KC were examined. The isothermal data could be well described by the Langmuir equation and the dynamical data fit well with the pseudo-second-order kinetic model. The adsorption capacity of modified kaolin KC (24.46 mg/g) was found to be around 4 times higher than that of natural kaolin K (5.94 mg/g). The KC demonstrated the highest adsorption capacity by removing over 98% of CR after ten minutes of contact. These results indicate that CTAB-kaolin could be employed as low-cost alternative to activated carbon in wastewater treatment for the removal of colour which comes from industrial effluents of textile activities, tanning or printing.

Keywords

Adsorption, Congo Red Dye, Surfactant, Kaolin, Kinetics

1. Introduction

The wastewater disposed by textile industries is causing major hazards to the environment and drinking water due to presence of a large number of contaminants like acids, bases, toxic organic, inorganic, dissolved solids and colour [1]. In effect, the discharge of contaminants such as dyes in the environment is worrying for both

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toxicological and esthetical reasons as damaging the quality of the receiving streams and is toxic to food chain organisms [2]. These colored compounds are not only aesthetically displeasing but also inhibiting sunlight into the stream and reducing the photosynthetic reaction. Since many organic dyes are harmful to human beings, the removal of colour from waste effluents becomes environmentally important [3].

Congo red (CR) is a highly water-soluble diazo dye. It is an anionic acid dye used as a laboratory aid in testing for free hydrochloric acid in gastric contents, in the diagnosis of amyloidosis, as an indicator of pH, and also as a histological stain for amyloid. It has a strong affinity to cellulose fibers and thus is employed in textile industries. It is a derivative of benzidine and napthoic acid and metabolizes to carcinogenic products [4]. It is investigated as a mutagen and reproductive effector. It is a skin, eye, and gastrointestinal irritant. It may affect blood factors such as clotting, and induce somnolence and respiratory problems [5]. Therefore, an increased interest has been focused on removing of such dyes from the wastewater. Various physical, chemical and biological methods, including adsorption, biosorption, ozonation, coagulation/flocculation, advanced oxidation, membrane filtration and liquid-liquid extraction have been widely used for the treatment of dye-bearing wastewater [6]-[9]. Adsorption is a very effective separation technique and now it is considered to be superior to other techniques for water treatment in terms of initial cost, simplicity of design, ease of operation and insensitive to toxic substances [10]-[13]. A commonly-used adsorbent, activated carbon has a high capacity for the removal of dye/organics [14] [15]. But some of its disadvantages are the high price of treatment and difficult to regenerate which gives the increase in cost of the wastewater treatment. Consequently this cost problem has led to a search for cheap and efficient alternate materials including clays such as bentonite, sepiolite montmorillonite, alunite, and kaolinite [16]-[19]. In addition, clay minerals can be modified by either impregnation or grafting of organic/inorganic molecules on its surface to improve its properties, for example, bentonite or montmorillonite was modified with various quaternary ammonium cations for the removal of various organic contaminants from water and wastewater [20]-[22]. Kaolinite clays were also modified with tri-polyphosphate [23] [24], and 2-mercaptobenzothiazole impregnated clay surface was used for the removal of some heavy metal ions from water samples [25].

In this work, we modified kaolin with cetyltrimethylammonium bromide (cationic surfactant) to investigate kinetics and the mechanism of adsorption of Congo red dye onto organoclay (CTAB-kaolin). Comparative studies on the adsorption capacities of CR on both supports modified kaolin and kaolin was also established. Langmuir and Freundlich equations were used to determine the isotherm which gives the best correlation with experimental data. Pseudo-second-order model was used to evaluate the adsorption kinetics for both adsorbents.

2. Materials and Methods

2.1. Clay Minerals

Kaolin used was collected from a natural deposit, located in Tabelbala in province Bechar (Algeria). The average surface area and CEC of kaolin which were measured using methylene blue technique were 10.60 m^2/g and 8.01 meq/100g, respectively [18].

2.2. Reagents

Cetyltrimethylammonium bromide (CTAB) used for CTAB-kaolin (KC) preparation was of analytical grade and was purchased from Aldrich Chemical. Its chemical formula is $(C_{16}H_{33})N(CH_3)_3Br$ with molecular weight of 363.9 g/mol.

The Congo red obtained from Fluka, was used as received without any purification. The chemical formula of CR is $C_{32}H_{22}N_6Na_2O_6S_2$ with Colour Index 22120 and molecular weight of 696.663 g/mol. The chemical structures of the dye and CTAB are given in **Figure 1**.

2.3. Instrumentation

The pH of all solution was measured by a Titra Lab Instrument TIM800 Model pH meter. Congo red concentrations of solutions before and after adsorption were measured using a UV-VIS spectrophotometer (UV.1700 Pharmrspac) at wavelengths of 497 nm which corresponds to the maximum absorbance of the dye. The Fourier transform infrared (FT-IR) absorption spectra was recorded on KBr pressed pellets of the powdered sample in the range 4000 - 400 cm^{-1}, using a PerkinElmer FTIR 2000 spectrophotometer and the thermal analyses were performed using SETARAM SETSYS thermogravimetric apparatus.
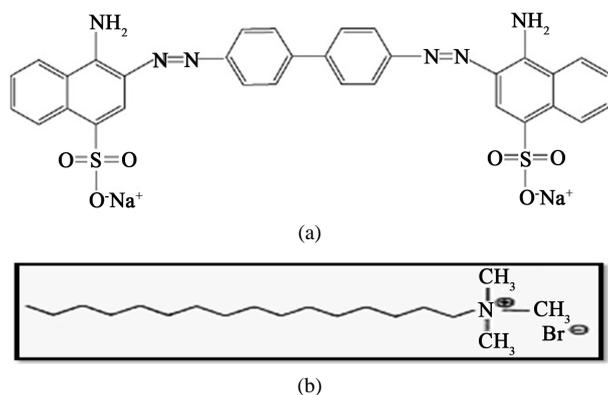
Figure 1. (a) Structure of CR; (b) Structure of CTAB.

2.4. Pre-Treatment and Organofunctionalization of Kaolin

Kaolin was initially saturated by ion exchange with excess sodium to eliminate the original cations from the interlayer region. Then, 20 g of kaolin was reacted with 500 mL of NaCl 1 N for 24 h at 343 K. The sodium kaolin (KNa^+) was separated using centrifugation and washed in distilled water until no residual halogen anions were detected by adding a 0.1 $mol \cdot L^{-1}$ of silver nitrate ($AgNO_3$) solution to the filtrate. The solid was dried at 373 K [26].

For CTAB-kaolin (KC) preparation, 10 g sample of the dried KNa^+ was added to 200 mL of distilled water containing 0.3 g of CTAB. The suspension was then shaken, at 70°C, for 24 h. The treated clay was then washed by shaking with 250 mL of water. The washing process was repeated several times until the washings were free from bromide ions as indicated by $AgNO_3$. The organokaolin was at last separated from water by centrifigation, dried at 80°C and gently ground with a mortar and pestle to break up aggregate particles [22].

2.5. Adsorption

Adsorption for CTAB-kaolin was undertaken in a batch equilibrium technique. The batch sorption studies were performed using different times of contact, initial concentrations of the dye and pH values. The effect of contact time on the adsorption capacity of modified kaolin was studied in the range 1 - 100 min at an initial concentration of 100 mg/L. Adsorption kinetics was studied using an initial concentration of 100 mg/L with the adsorbent dosage of 0.1 g/10mL at pH 6.9. Adsorption isotherms were studied at various initial concentrations of CR dye. The effect of pH was observed by studying the adsorption of the dye over a pH range of 5 - 13. The pH of the solution was adjusted with NaOH or HCl solutions. The amount of dye adsorbed per unit mass of CTAB-kaolin was calculated by using the mass balance equation given in Equation (1) [27].

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where q_e is the maximum adsorption capacity in mg/g, C_0 is the initial concentration and C_e is the concentration at equilibrium of CR dye solution in mg/L, V is the volume of the CR solution in mL and m is the mass of modified kaolin in grams.

The sorption capacity at time t, q_t (mg/g) was obtained as Equation (2) [27]:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{2}$$

where C_0 and C_t (mg/L) are the liquid phase concentrations of CR at initial and a given time t, V is the solution volume and m the mass CTAB-kaolin (g).

The percent adsorption of dye was calculated as follows Equation (3) [28]:

$$\text{Sorption \%} = \frac{C_0 - C_e}{C_0} \times 100\% \tag{3}$$

The same procedure was adopted to determine the retention of the dye on natural kaolin (K) [18].

3. Results and Discussion

3.1. Characterization of Modified Kaolin

3.1.1. FTIR Analysis

The presence of organic molecules in the clay layers can be determined by using infrared spectroscopy followed by TG.

In order to obtain complementary evidence for the intercalation of quaternary alkylammoniumcations into the silicate lattice, FTIR spectra were recorded in the region 400 - 4000 cm^{-1} (see **Figure 2**). New absorption band in spectrum of KC was detected around 3014 cm^{-1} which is due to stretching vibrations of CH$_3$-N. The symmetric and asymmetric stretching vibrations of methyl groups (CH$_3$) and the methylene (CH$_2$) of the aliphatic chain of the surfactant appear more strongly at 2850 cm^{-1} and 2920 cm^{-1} [29]. Additionally, the bending vibration of the methylene groups can be observed at 1467 cm^{-1}. A peak can be observed at 1394 cm^{-1} that arises from the C-N group of the organic modifier, verifying the intercalation of surfactant molecules between the silicates. The characteristic bands of the C-N bond which are between 910 and 1000 cm^{-1} (very strong for compounds of the type R-N$^+$(CH$_3$)$_3$) are hidden in complex inorganic-clay, by deformation vibrations of Al-OH (926 cm^{-1}).

3.1.2. TG Analysis

The TG curve of natural kaolin K (**Figure 3**) suggested a loss of mass over the temperature of 63°C - 205°C, which was attributed to the loss of adsorbed water, and an additional loss over the temperature range of 450°C -
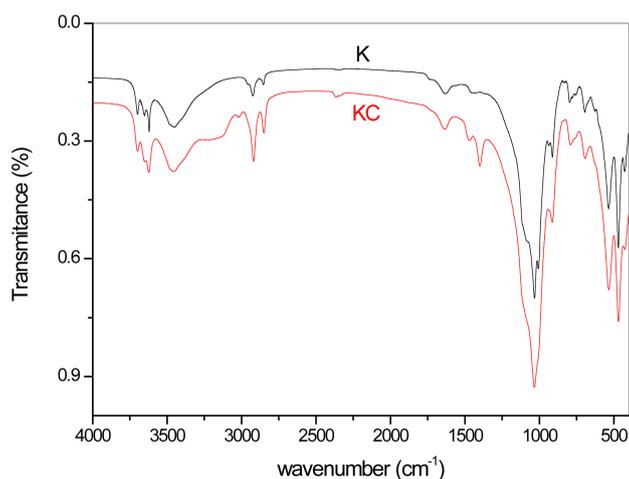

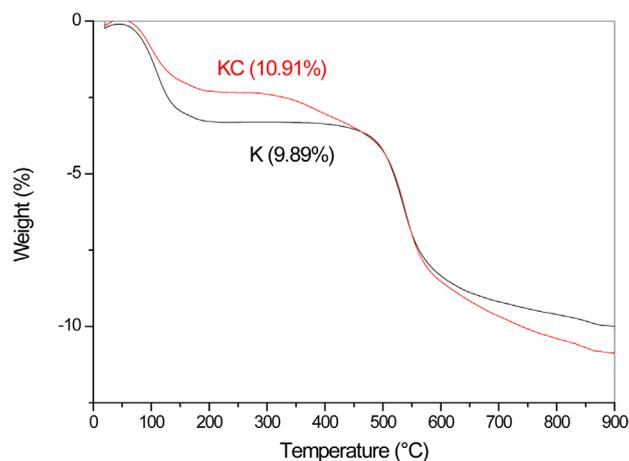**Figure 2.** IR spectra of CTAB-kaolin (KC) and kaolin (K).

Figure 3. TG analysis of CTAB-kaolin (KC) and kaolin (K).

900˚C due to both the elimination of coordinated water that become more strongly bonded to octahedral cations and the dehydroxylation of silanol [30].

The TG of CTAB-kaolin (KC) exhibited three stages of thermal decomposition. The first stage was due to adsorbed water and occurred over a temperature interval of 66˚C - 200˚C. The second stage was related to the coordinated water and the partial loss of organic moieties that were intercalated in the interlayer spacing over a temperature interval of 300˚C - 500˚C. The third loss over a temperature range of 500˚C - 900˚C was due to the elimination of the organic groups and the dehydroxylation of the silanol groups on the clay surface. The data exhibited a significant alteration in the thermal degradation.

The typical hydrophilic character of K was modified after the reaction with surfactant, which was evident by the drastic difference between the percentages of the first mass loss. An additional change was the increase in the total mass loss, which values were 9.89% and 10.91% for K and KC respectively, as observed in **Figure 3**.

3.2. Effect of Contact Time

As can be seen from the **Figure 4**, the adsorption rate of anionic dye in the first 10 min for KC is very fast. Highest amount of dye retained (98.16%) is occurred within the initial 10minutes of contact time. After reaching the saturation value in 10 min of contact, a continuous and smooth curve is obtained for KC adsorbent. Based on these results, 10 min was taken as the equilibrium time in batch adsorption experiments on KC. The adsorption of CR on natural kaolin K occurred quickly from the beginning of the experiments during the first 10min, then a slight increase until 40 min where the maximum adsorption of CR was observed (64.24%). Again as the results of this part of investigation clearly show, the uptake rate and adsorption amount of CR onto KC is much higher than that of K at any contact time. The difference in the equilibrium time for both adsorbents may be due to strong attractive forces such as electrostatic between the dye molecules and the surfactant-modified kaolin.

3.3. Effect of pH

It was observed that the adsorption is highly dependent on the pH of the solution, which affects the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate. As evident from **Figure 5**, with increase in pH of the solution the amount adsorbed increases (this is due to the neutralization of the charges at the surface of the adsorbents) till pH 10 but with further increase in the pH, percentage adsorption drops in case of both adsorbents (K) and (KC). The high negatively charged adsorbents surface sites did not favour the adsorption of deprotonated CR due to electrostatic repulsion. Also, an abundance of OH^- ions in basic solution creates a competitive environment with anionic ions of CR for the adsorption sites causing a decrease of adsorption [9] [31]. The high adsorption capacity of CTAB-kaolin is due to the strong electrostatic interaction between the $N^+(CH_3)_3$ and dye anions [32].
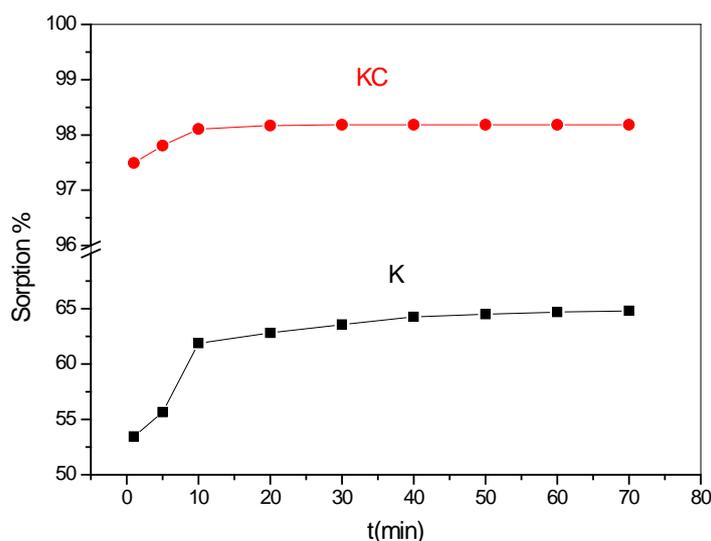

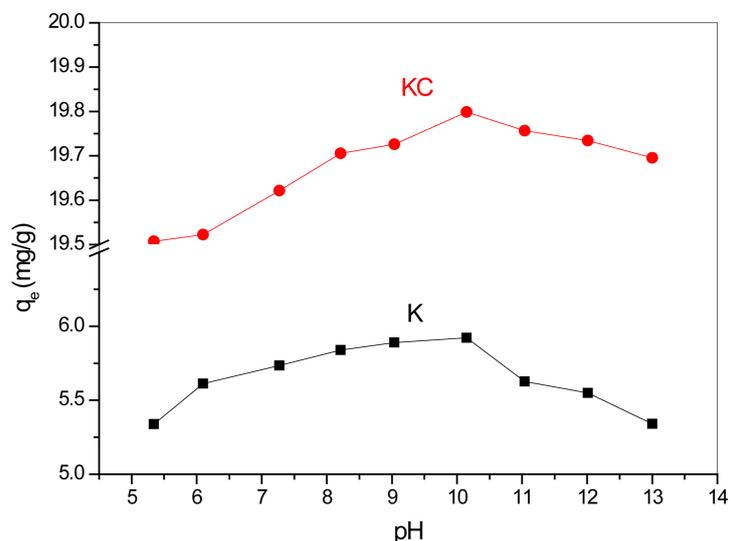**Figure 4.** Effect of contact time of CR adsorption by K and KC.

Figure 5. Effect of the pH on the q_e.

3.4. Adsorption Isotherm Studies

Several adsorption isotherm models have been employed to interpret the adsorption behaviors of dyes on solid adsorbents. In this study, the data collected have been fitted to the Langmuir isotherm [33] and the Freundlich isotherm [34], as described in Equations (4) and (5), respectively.

Langmuir equation

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{4}$$

Freundlich equation

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \tag{5}$$

In these equations, C_e is the concentration of the dye in solution (mg/L) at equilibrium with the adsorbed dye, q_e is the amount of the adsorbed dye (mg/g) at the solid/liquid interface, q_{max} is the monolayer capacity of the adsorbent (mg/g), K_L is the Langmuir adsorption constant (L/mg), K_f and $1/n$ are empirical parameters, K_f is the adsorption constant related to the bonding energy and $1/n$ is associated to the surface heterogeneity.

The adsorption isotherms of the dye onto K and KC were fitted by two models, as shown in **Figure 6** and **Figure 7**. The parameters predicted by the two different models are summarized in **Table 1**. In general, parameters were fit using the linear adjustment, whereas the correlation coefficients were fit better using the Langmuir model. As the data clearly show adsorption capacity of surfactant modified kaolin (KC) for CR dye is considerably higher than natural kaolin (at least 4 times).

3.5. Adsorption Kinetics

Many models were used to describe the adsorption processes. The most appreciated was Pseudo-second-order (Equation (6)) [35].

As shown in **Figure 8**, the data corresponded to Pseudo-second-order well. The parameters of Pseudo-second-order were listed in **Table 2**. The coefficients of determination (R^2) for two materials were good.

$$\frac{t}{q_t} = \frac{1}{2k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

where q_e (mg/g) and q_t (mg/g) are the adsorbed amounts of CR at equilibrium and time t (min); k_2 is the adsorption rate constants of Pseudo-second-order equation.
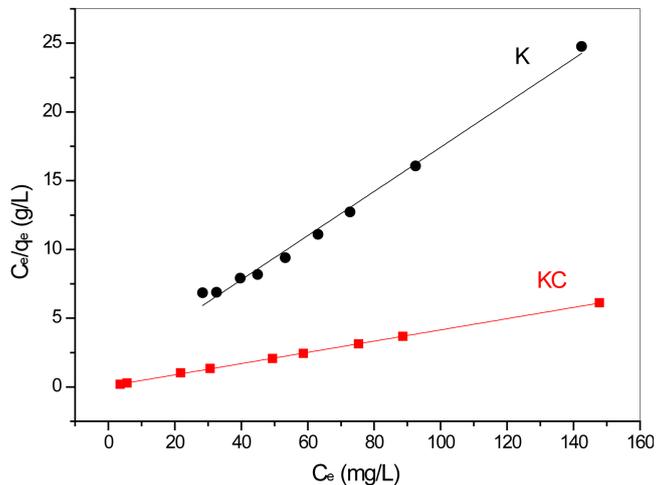
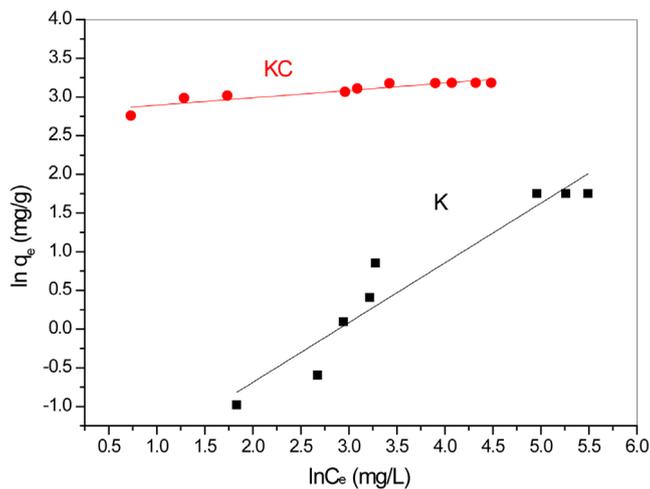**Figure 6.** Langmuir linear plot for CR adsorption on K and KC.

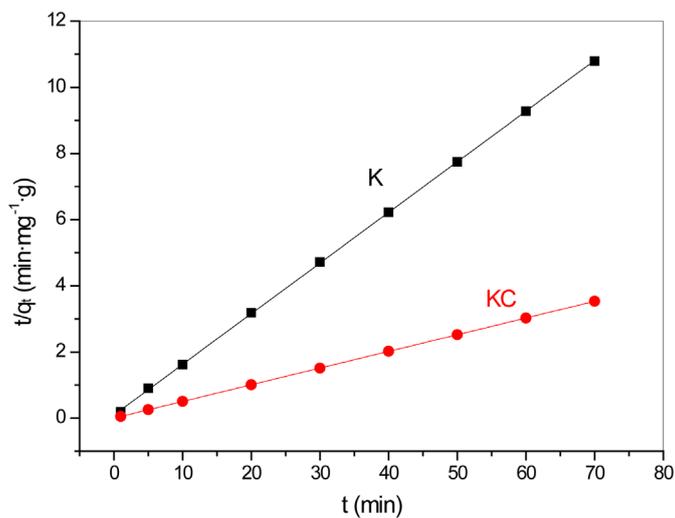**Figure 7.** Freundlich linear plot for CR adsorption on K and KC.

Figure 8. Pseudo-second-order parameters of CR adsorption onto kaolin (K) and modified kaolin (KC).

Table 1. Langmuir and Freundlich isotherms for the adsorption of CR on K and KC.

Adsorbent	Langmuir isotherm constants			Freundlich isotherm constants		
Parameters	q_m (mg/g)	K_L (L/mg)	R^2	n	K_f	R^2
K	5.94	0.18	0.997	1.295	0.107	0.908
KC	24.46	1.52	0.999	10.51	16.43	0.834

Table 2. Pseudo-second-order parameters of CR adsorption onto kaolin (K) and modified kaolin (KC).

Sample	k_2 (g/mg·min)	q_e (mg/g)	R^2
K	0.24	6.53	0.9999
KC	5.12	19.82	1

4. Conclusion

The surface of natural kaolin is not a more effective adsorbent for the removal of hydrophobicorganic compounds from aqueous solution. This is due to the electrically charged and hydrophilic characteristics of the surface. However, natural kaolin maybe modified with large organic cations (CTAB) in a manner that significantly improves its capability of removing hydrophobic contaminants from water. Despite the introduction of organic ions into the interlayer spacing, the layered structure is maintained. CTAB-kaolin showed a higher adsorption capacity toward CR than kaolin. Kinetics data of adsorption were well fitted by the pseudo-second-order kinetic model, while the isotherm data were well represented by the Langmuir model. We thus conclude that the modified kaolin clay may be used as very effective adsorbent for removal of anionic toxic dyes from aqueous media.

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