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Removal of Textile Dye from Industrial Wastewater by Natural and Modified Diatomite

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Abstract**—**The textile industry produces high amount of colored effluent each year. The management or treatment of these discharges depends on the applied techniques. Adsorption is one of wastewater treatment techniques destined to treat this kind of pollution, and the performance and efficiency predominantly depend on the nature of the adsorbent used. Therefore, scientific research is directed towards the development of new materials using different physical and chemical treatments to improve their adsorption capacities. In the same perspective, we looked at the effect of the heat treatment on the effectiveness of diatomite, which is found in abundance in Algeria. The textile dye Orange Bezaktiv (SRL-150) which is used as organic pollutants in this study is provided by the textile company SOITEXHAM in Oran city (west Algeria). The effect of different physicochemical parameters on the adsorption of SRL-150 on natural and modified diatomite is studied, and the results of the kinetics and adsorption isotherms were modeled.

Keywords**—**Wastewater treatment, diatomite, adsorption, dye pollution, kinetic, Isotherm.

I. Introduction

EFFLUENTS from the dyeing industry contain highly colored species, and such wastes are not only aesthetically displeasing but also hinder light penetration and may in consequence disturb biological processes in water bodies. In addition, dyes are toxic to some organisms and hence harmful to aquatic animals [1]. Therefore, removal of dyes before disposal of wastewater is necessary. Currently, several physical and chemical processes are used to treat dye laden wastewaters such as dilution, adsorption, coagulation and flocculation, chemical precipitation, oxidation, ion-exchange, reverse osmosis, and ultra-filtration [2]. However, high cost, formation of hazardous by-products, intensive energy requirements, and inefficient reusability of adsorbents are still the limitations commonly countered during the application of these techniques [3]. Among treatment technologies, adsorption has been shown to be the most promising option for the removal of non-biodegradable organics from aqueous effluents, activated carbons being the most common adsorbent for this process due to its effectiveness and versatility. However, commercially available activated carbons are very expensive. The attention currently is being paid to develop low-cost and highly efficient alternative adsorbents. Among of these adsorbents, diatomite or diatomaceous earth is one of a siliceous sedimentary rock widely available in Algeria. It is made principally from a wide variety of shape and sized skeletons of aquatic plants called diatoms. It is usually pale colored, soft, and lightweight [4]. Based on low cost, environmental friendly nature, objectives of this investigation are (i) to describe the adsorptive removal of Orange Bezaktiv SRL-150 using native and modified diatomite and (ii) to determine some parameters affecting sorption of SRL-150 dye on the adsorbents used.

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II. Materials and Methods

A. Preparation of Adsorbents

The Diatomite used in this study was supplied by the National Company for Non-ferrous Mining Products ENOF from Sig deposit in Mascara (western Algeria). After grinding and sieving (250 µm), the diatomite was dried overnight at 100 °C. The material obtained has undergone at 500 and 600 °C for 2 h in programmable furnace with a heating rate of 5 °C/min. The obtained materials were noted reservedly D500 and D600.

B. Characterization Methods

The external morphology and microstructure of D500 and D600 samples were observed by Scanning Electron Microscope (SEM). The principal functional groups were identified by using Fourier Transform Infra-Red spectroscopy (FTIR), and the spectra were recorded in the range of 400–4000 cm^{-1}.

C. Adsorption Experimental Procedures

The adsorption experiments of the Orange Bezaktiv (SRL-150) textile dye onto D500 and D600 were carried out on batch mode. After agitation and centrifugation, the residual concentration of SRL-150 dye was measured by using UV-visible spectrophotometer (HACH-DR 2000) at 480 nm. The adsorption capacity Qe (mg/g) was determined by:

$$Q_e = \frac{(C_i - C_e) \cdot V}{m} . \quad (1)$$

where C_i and C_e are, respectively, the initial and residual concentration of SRL-150 in solution (mg/L), V is the volume of solution (L), and m is the mass of adsorbents (g).

D. Adsorption Kinetic Molding

In order to determine the best kinetic model which fits the adsorption experimental data, the pseudo-first order and pseudo-second order models were used. The linear expressions of these two models are described in Table I [5].

TABLE I
KINETIC ISOTHERM ADSORPTION MODELS AND THEIR LINEARIZED EXPRESSIONS

Model	Linear equation
Pseudo-first order	$\ln (Q_e - Q_t) = \ln Q_e - k_{1p}\, t$
Pseudo-second order	$t/Q_t = 1/ k_{2p} Q_t^2 + t/Q_e$

Q_t (mg/g) is the amount of adsorbed SRL-150 at t moment, and k_{1p} and k_{2p} are the adsorption rate constants of Pseudo-first order and Pseudo-second model.

III. RESULTS AND DISCUSSION

A. Characterization

The FT-IR spectra of diatomite show major adsorption bands at 3621, 1093 and 875 and 464 cm^{-1}, as depicted in Fig. 1. The band at 3621 cm^{-1} is due to the free silanol group (SiO–H) on the surface, the bands at 1094, 875, and 464 cm^{-1} attributed respectively to asymmetry, symmetric stretching, and deformation vibration of siloxane (–Si–O–Si–) links [6].

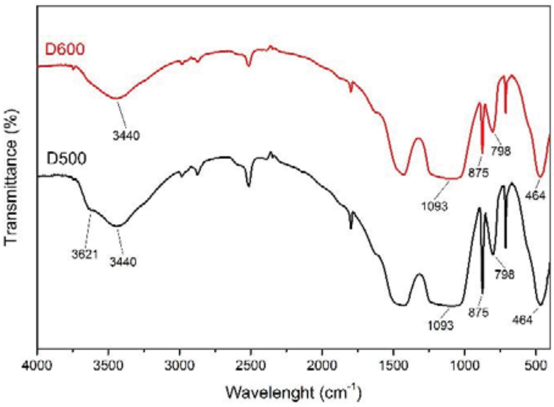
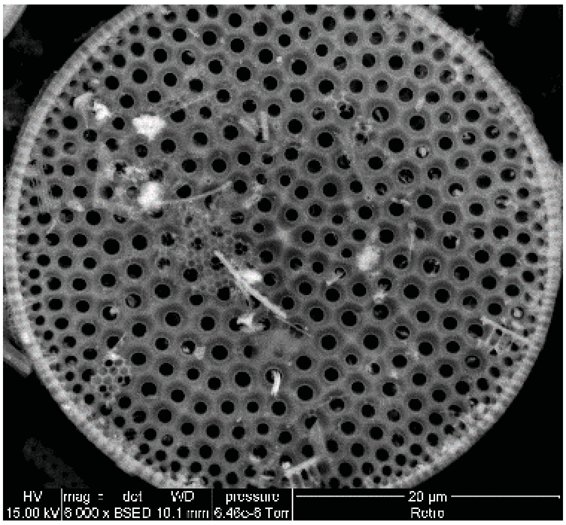
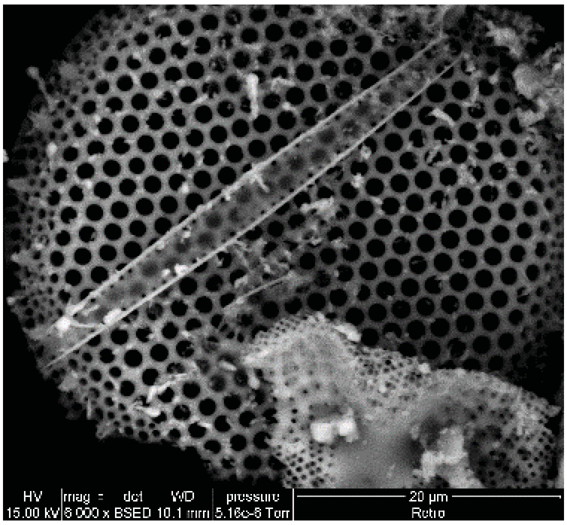


Fig. 1 FT-IR spectrum of D500 and D600 samples

The diatom shells of D500 and D600 are composed of plaque and circular-shape, and possess well-developed pores, and two types of macropores are exhibited in Figs. 2 (a) and (b). The macropores in the center of shells are not arrayed regularly, and their pore sizes are concentrated in the range of 1–2 µm (Fig. 2 (a)); the edge macropores show an ordered array with pore size in the range of 0.25–0.5 µm. After treatment at 600 °C, the structure has not collapsed and the diatomite still showed its multi-pore structure and the pores on the surface became larger. The impurity adhesion was almost gone, which made the pores on the surface of sieve tray larger than that of raw diatomite. The same observation was reported by Zhang et al. [4].



(a)



(b)

Fig. 2 SEM image of (a) D500 and (b) D600

B. Influence of pH Solution

The pH is an important parameter for adsorption studies and affects not only the adsorption capacity, but also the color and solubility of dye solutions. The maximum adsorption capacities of SRL-150 dye were plotted against the equilibrium pH using 50 mL of 50 mg/L initial dye solution and 0.1 g of adsorbent for a prefixed time period (60 min). As shown in Fig. 3, the equilibrium uptake capacity decreased from 23.7 to 1.27 mg/g when the solution pH was changed from 2 to 10 for D500 and from 22.6 to 2.31 mg/g when the solution pH was changed from 2 to 10 for D600. From this study, the optimum pH was determined as 2 at which the maximum adsorption capacity of SRL-150 dyes was determined as 23.7 and 22.6 mg/g respectively for D500 and D600 at 25 °C. This effect was largely related to the anionic characters of SRL-150 dye. Weak base groups on the surface were protonated and acquired a net positive charge with diminishing solution pH. This caused a significantly high electrostatic attraction between the surface of D500 and D600 and SRL-150 dye and as a result, a high adsorption capacity [7].

C. Influence of Contact Time

Fig. 4 shows the effect of contact time at initial dye concentration of 50 mg/L, pH 2, ratio 2, and temperature 25 °C. The adsorption capacity increases with an increase in contact time and reaches a plateau at 20 and 40 min for D500 and D600, respectively. Moreover, it is seen that the adsorption of SRL-150 is very rapid in the first 15 min and then slowly declines with time until equilibrium. The initial rapid phase may be due to an increase in the number of vacant sites available at the initial stage. Similar trends have been reported by serval authors [8].

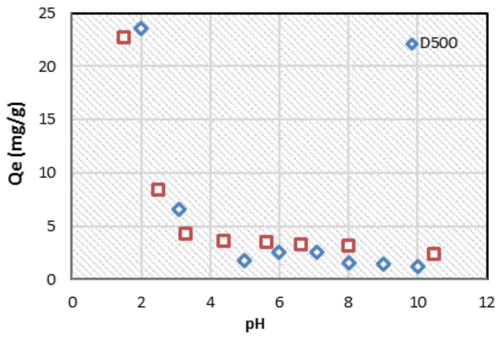


Fig. 3 Effect of pH for the adsorption of SRL-150 dye onto D500 and D600 at 25 °C

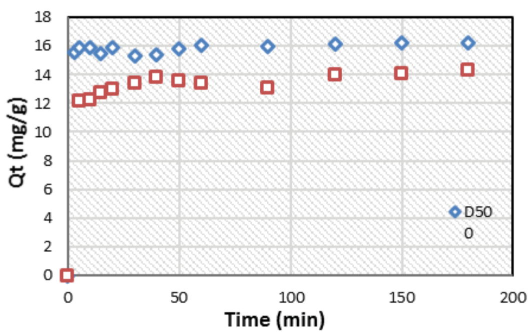


Fig. 4 Effect of contact time on the adsorption of SRL-150 by D500 and D600

D. Adsorption Kinetics

Kinetic studies are important to understand the dynamic of the reaction in terms of order of the rate constant since the kinetics parameters provide information for designing and modeling the adsorption process [9]. Two well-known kinetic models were used to examine the mechanism of the adsorption process: the pseudo-first-order model and pseudo-second-order model.

The study of the kinetics of adsorption results was shown in Figs. 5 (a) and (b), Table II.

TABLE II
KINETIC PARAMETERS FOR ADSORPTION OF SRL-150 BY D500 AND D600

		Pseudo-first order			Pseudo-second order		
	$Q_{e, exp}$	Q_e	k_{1p}	R^2	$Q_{e, cal}$	K_{2p}	R^2
D500	16,22	0,96	0,014	0,325	16,21	0,113	0,999
D600	14,23	2,04	0,011	0,374	14,18	0,028	0,998

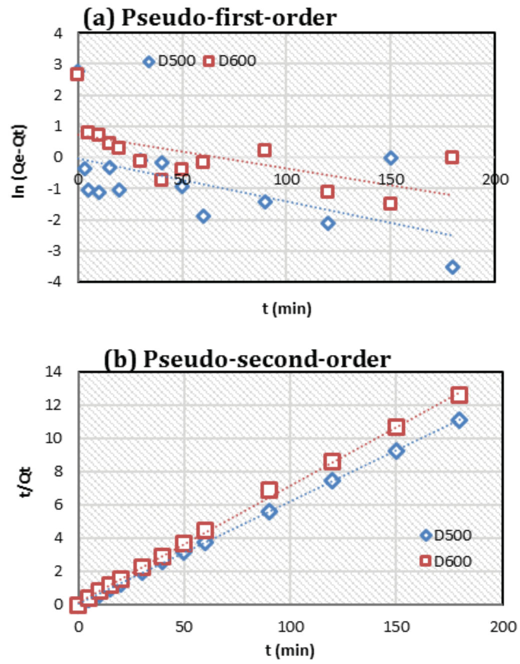


Fig. 5 Kinetic model plots (a) Pseudo-first-order and (b) Pseudo-second-order for adsorption of SRL-150 dye onto D500 and D600

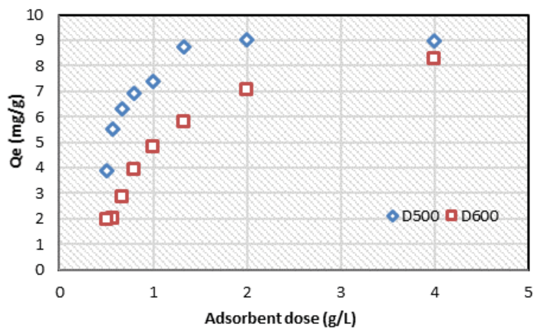


Fig. 6 Influence of adsorbent dosage on the adsorption capacity of SRL-150 dye onto D500 and D600

By plotting t/qt against t, straight lines are obtained (Fig. 5 (b)). The rate constants k_{2p} and calculated equilibrium adsorption capacities $Q_{e, cal}$ obtained from the intercepts and slopes of the plots are given in Table II. The correlation coefficients are close to unity. In addition, the values of $Q_{e, cal}$ show good agreement with the experimental data. Thus, the adsorption could be approximated more appropriately by the pseudo-second-order model, supporting the assumption of chemisorption as the rate-limiting mechanism through sharing or exchange of electrons between adsorbent and adsorbate

[10].

E. Influence of Adsorbent Dose

To investigate the effect of adsorbent amount, the adsorption of SRL-150 onto D500 and D600 was measured at eight different adsorbent concentrations at an initial dye concentration of 50 mg/L. The uptake values are given in Fig. 6. It is clear that, up to 1,5 g/L, an increase in the adsorbent concentration raises the adsorbed dye amount, which is reasonably coherent since the number of available active sites increases with an increase in adsorbent concentration and it, therefore results in the increase of adsorbed dye amount. Above the adsorbent concentration of 2 g/L, the equilibrium adsorbed amount remains constant since the saturation of the active sites does not allow an increase in the adsorption capacity in the studied initial dye concentration. Robinson et al. [11] reported the same findings.

IV. Conclusion

In this work, we examined the adsorption ability of diatomite treated at 500 and 600 °C toward complex textile dye: Orange Bezaktiv (SRL-150). It was shown that the highest dye removal capacity was found at pH 2. Adsorption equilibrium uptake was enhanced by increasing the adsorbent dosage up 10 g/L for an initial dye concentration of 50 mg/L. The pseudo-second-order kinetic is the most appropriate and satisfactorily describe the present adsorption phenomenon, assuming therefore a chemisorption process.

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The authors would like dedicate this work to Prof. Mohand Said Ouali.

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