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Removal of synthetic reactive dyes from textile wastewater by Sorel's cement

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ABSTRACT

Removal of some reactive dyes (RY-145, RR-194 and RB-B) from textile wastewater effluents using Sorel's cement is described. Parameters affecting dye uptake including contact time, reagent dosage and pH are examined and optimized. Dye adsorption equilibrium data are fitted well to the Langmiur isotherm rather than Freundlish isotherm. The adsorption isotherm indicates that the adsorption capacities are 107.67, 120.89 and 103.14 mg dye per gram of Sorel's cement for RY-145, RR-194 and RB-B reactive dyes, respectively. The adsorption isotherms, including Langmuir constant (Q° and b) and Frendlich constant (K_F and n), for the dyes decrease with the increase of temperature. The values of enthalpy change (ΔH) for RY-145, RR-194 and RB-B dyes are −146.96, −49.23 and −264.86 kJ mol^{-1}, respectively, indicating that the removal process is exothermic. The sorption of the dyes is enhanced by increasing the pH, reaching a maximum at pH 6–11. Experimental runs conducted to measure the chemical oxygen demand (COD) of textile wastewater loaded with reactive dyes, reveal ∼96% removal of the COD contents within 30 min under optimized conditions.

1. Introduction

Wastewater from textile dyeing and finishing factories is a significant source of environmental pollution [1]. Reactive dyes are extensively used in textile industry, fundamentally due to the ability of their reactive groups to bind to textile fibers through covalent bonds [2]. These characteristics facilitate the interaction with the fiber and reduce energy consumption [3]. The major environmental problem associated with the use of reactive dyes is their loss in the dyeing process since the fixation efficiency ranges from 60 to 90% [3]. Consequently, substantial amounts of unfixed dyes are released in the wastewater displaying a high organic loads as indicated by high chemical oxygen demand (COD), low biodegradability and high-salt content of the textile wastewater. The European Union (EU) directive 91/271 imposes limits on wastewater colour, as it reduces light penetration in receiving water bodies.

A wide range of wastewater treatment techniques have been suggested. Biosorption and aerobic and anaerobic treatment [4–7] are probably of the most inexpensive approaches. However, the dyes inhibit bacterial activity and thus a pre-treatment step is often necessary to increase the biodegradability [8]. Physico-chemical processes have been also proposed including coagulation with alum, ferric chloride, magnesium chloride, lime and polymers [4]. Adsorption on activated carbon, polymers, mineral sorbents and biosorbents [9,10] have been also suggested. Chemical oxidation [11,12], photolysis [12,13], suspended or supported photocatalysis degradation [14–16] and electrophoto-catalysis [17] have been utilized. Among these, the adsorption process gives reliable results as it can be used to remove different types of colouring materials.

Although activated carbon is a preferred adsorbent for colour removal, its widespread use is restricted due to its high cost. Alternative adsorbents, including peat [18], plum kernels [19], wood [20], coal [21], resin [22], coir pith [23] and chitosan fibers [24], have been used with various industrial wastewaters [25,26]. Some of these alternative adsorbents, though easily available and cost effective, do not effect complete dye colour removal compared with activated carbon [18–20,24]. A promising approach for effective colour removal from composite wastewater of cotton textile mill involved catalytic thermal treatment accompanied with coagulation has been suggested [27,28].

In the present study, Sorel's cement is used for removal of reactive dyes in textile wastewater. Advantages offered by using Sorel's cement are low cost, good efficiency, fast removal kinetics and simple preparation.

2. Experimental

2.1. Materials

Pure references reactive dye samples (RY-145, RR-194 and RB-B) were obtained from local textile factories. Aqueous solutions

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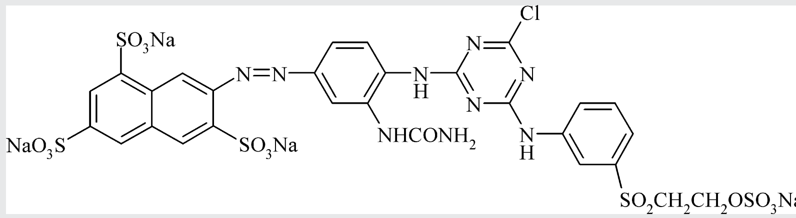
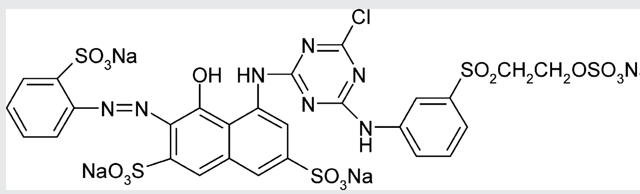
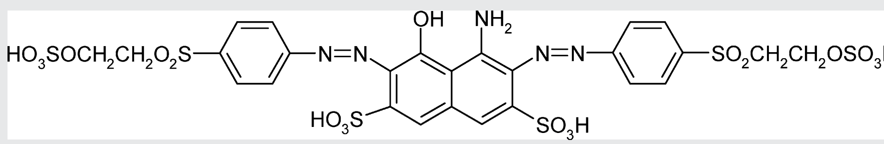
Table 1
Chemical structures and absorbance maxima of the examined reactive dyes

Dye	Mol. mass	Structure	λ_{max}
RY-145	1025.5		418
RR-194	863.5		514
RB-B	893		580

of the dyes were freshly prepared. The structures of the dyes and their maximum wavelengths of absorbance (λ_{max}) are shown in Table 1.

Sorel's cement was prepared using commercial grade of MgO and $MgCl_2$ (supplied by ADWEC, Egypt). Magnesium oxide (2.4 g) was dissolved in 8 ml of aqueous 1.78 M $MgCl_2$ solution at 75 °C to neutralize the free hydrogen ions formed by the hydrolysis of $MgCl_2$ and to increase the pH value of the solution. A 1.0 g portion of $FeCl_3$ was added, to increase the hardness of cement and to improve the synergism with $MgCl_2$ for removal of the dyes, and the mixture was stirred for 10 min. The paste was separated by centrifugation and washed thoroughly with ethanol as previously described [29,30]. The solid product was dried under IR lamp, stored in a desiccator and kept at 75 °C for 4 h. The dry solid paste was ground and sieved to a particle size of 35 mesh. The structure of the cement as previously verified [31] can be represented by Fig. 1 [32].

2.2. Equipment

All spectrophotometric measurements of the reactive dyes were done with a Shimadzu 160A UV–vis spectrophotometer using 1.0 cm matched quartz cuvettes at λ_{max} 418, 514 and 580 for RY-145, RR-194 and RB-B dyes, respectively.

An Orion digital pH/mV meter (Model SA 720) in conjunction with a combination glass electrode (Orion 81-02) was used for all pH measurements.

FTIR spectrometry was carried out with a PerkinElmer model 1725X using KBr discs.

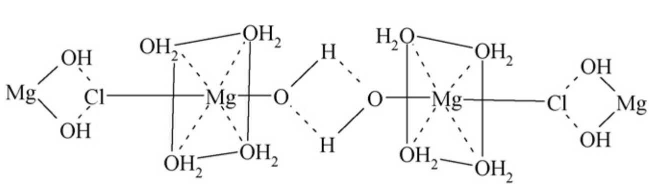


Fig. 1. Structure of Sorel's cement.

2.3. Procedure

2.3.1. Adsorption studies

Experiments for adsorption equilibrium were conducted at 20 and 40 °C temperature by shaking 20 mg of Sorel's Cement with 25 ml of dye solution in the concentration range of 2×10^{-1}–1×10^{-2} mM for in the equilibrium contact time. After the sorption experiment, the mixture was centrifuged and the residual dye concentration in the supernatant was determined spectrophotometrically using the calibration curves.

Adsorption isotherms were determined by shaking 0.02 g of Sorel's cement (0.8 g/l) with 25 ml of dye solutions of concentrations ranging from 2×10^{-4} to 1×10^{-5} M solution adjusted to pH 6 with dilute HCl for an equilibrium time. The solutions were thermostated at different temperatures (20, 40 °C). After shaking, the supernatant solution was separated from Sorel's cement precipitate by centrifugation. The remaining concentrations of RY-145, RR-194 and RB-B dyes in the solution were spectrophotometrically determined by monitoring the absorbances at λ_{max} 418, 514 and 580 nm, respectively.

In all experiments, the difference between the initial dye concentration (C_o) and the equilibrium concentration (C_e) was calculated and used to calculate the adsorptive capacity (q_e) as follows:

$$q_e = \frac{V}{m}(C_o - C_e)\text{mol/g}$$

where V, is the total volume (in liter) of dye solution (l); m, is the mass of cement adsorbent used (g); C_o, and C_e are the initial and residual molar concentrations (mmol) of the dye, respectively.

3. Results and discussion

3.1. Effect of Sorel's cement dosage on adsorption

Adsorption of some reactive dyes as a function of Sorel's cement dosage at pH 6 was investigated. Sorel's cement dosage was varied from 0.4 to 2 g/l of the dye solution and equilibrated for 30 min.

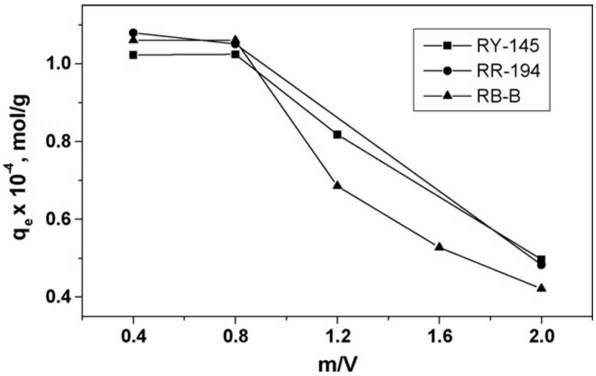


Fig. 2. Effect of adsorbent (Sorel's cement) dosage on the removal of some reactive dyes. Conditions: C_o, 10^{-4} M; time of contact, 30 min.; pH, 6 and temperature, 20 °C.

Adsorption of the dyes increased with increasing adsorbent dosage and equilibrium was established with 0.02 g of the sorbent (Fig. 2). For this purpose, the volume/mass of adsorbent (V/m) was plotted as a function of q_e. The optimum cement dosage for maximum dye removal was 0.8 g/l for an initial dye concentration of 0.1 mmol/l. Maximum colour removal of the dye solution (25 ml of 10^{-4} M) was achieved with a minimum cement dosage of 0.02 g. The removal efficiency and mechanism have previously been demonstrated [32].

3.2. Effect of contact time

Adsorption of a fixed concentration of the reactive dyes at (10^{-4} M) on Sorel's cement was studied as a function of contact time in order to determine the equilibration time for a maximum adsorption (Fig. 3). The standard deviations in the residual dye concentration in the supernatant solution after 20, and 40 min contact time with the cement are 2.1 and 1.7%, respectively. Half an hour was enough for adsorption equilibrium of all tested dyes. This revealed that Sorel's cement is a good adsorbent with fast kinetics for removal of reactive dyes compared with other previously suggested adsorption materials which take a much longer time as indicated in Table 2.

3.3. Effect of pH

The effect of pH on the removal of reactive dyes by Sorel's cement is shown in Fig. 4. Sorption at different pH values was conducted by adjusting the pH of the dye solution at different values with dilute HCl before treatment with Sorel's cement. The distribution coefficient K_d was computed from the relation:

Table 2
Optimum contact time for different adsorption materials

Adsorbent	Minimum contact time (min)	Reactive dye	References
Metal hydroxide sludge	50	RR-141	[33]
Zeolite	120	RR-239	[36]
Calcined alunite	120	RY-64	[37]
Sorel's cement	30	RY-145, RR-194, RB-B	This work

$$K_d = \frac{(C_o - C_e)V}{MC}$$

where C_o and C_e are the initial and final concentrations of the dye (mmol), V (l) is the test volume and M (g) is the weight of Sorel's cement. Maximum adsorptive capacity of the dyes was obtained at pH 6–11. Below pH 5, Sorel's cement dissociates. The obtained pH range suits for waste treatment plants without further addition of chemicals or any side effects on the pH of the effluent after the treatment process. These results agree with the effective pH range obtained by other workers for removal of some reactive dyes by metal hydroxide adsorbate sludge [33].

3.4. Adsorption isotherms

The adsorption isotherms of RY-145, RR-194 and RB-B reactive dyes on Sorel's cement reflects the relationships between the amount of adsorbed dye per weight unit of adsorbent (q_e) and the equilibrium concentration (C_e), at two different temperatures. It is evident that the adsorption of RY-145, RR-194 and RB-B dyes on the Sorel's cement decreases with an increase in temperature indicating that the process is exothermic. The linear plots of the Langmuir model (C_e/q_e vs C_e) are shown in Fig. 5. The maximum adsorption capacities (Q°) and the (b) constants were calculated from the slope and interception of the Langmuir plots, respectively, using the equation:

$$\frac{C_e}{q_e} = \frac{1}{bQ^\circ} + \frac{1}{Q^\circ}C_e$$

The linear plots of Freundlich model ($\log q_e$ vs $\log C_e$) are shown in Fig. 6. The Freundlich constants (n and K_F) were calculated from the slope and interception of the Freundlich plots, respectively, using the equation:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$

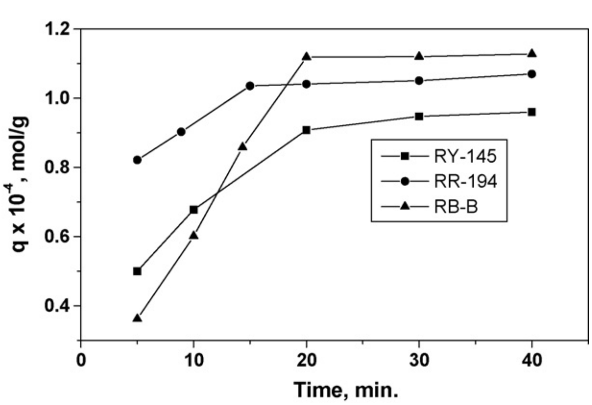


Fig. 3. Effect of contact time on the removal of some reactive dyes by Sorel's cement. Conditions: C_o, 10^{-4} M; dose of Sorel's cement, 0.02 g; pH, 6 and temperature, 20 °C.

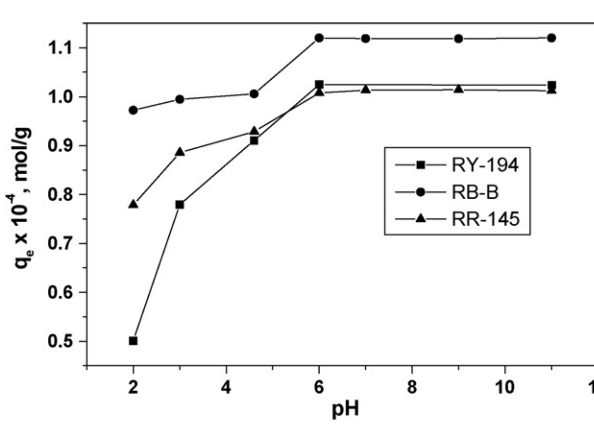


Fig. 4. Effect of pH on the removal of reactive dyes by Sorel's cement. Conditions: C_o, 10^{-4} M; dose of Sorel's cement, 0.02 g and temperature, 20 °C.

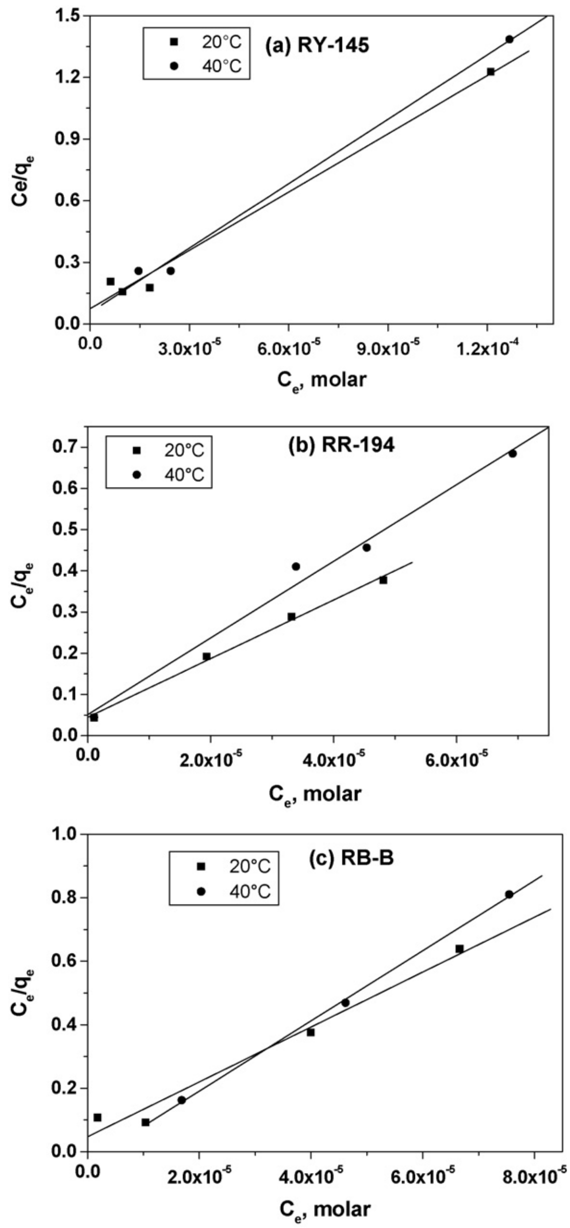


Fig. 5. Langmuir plots for the adsorption of (a) RY-145, (b) RR-194, and (c) RB-B dyes by Sorel's cement at different temperatures.

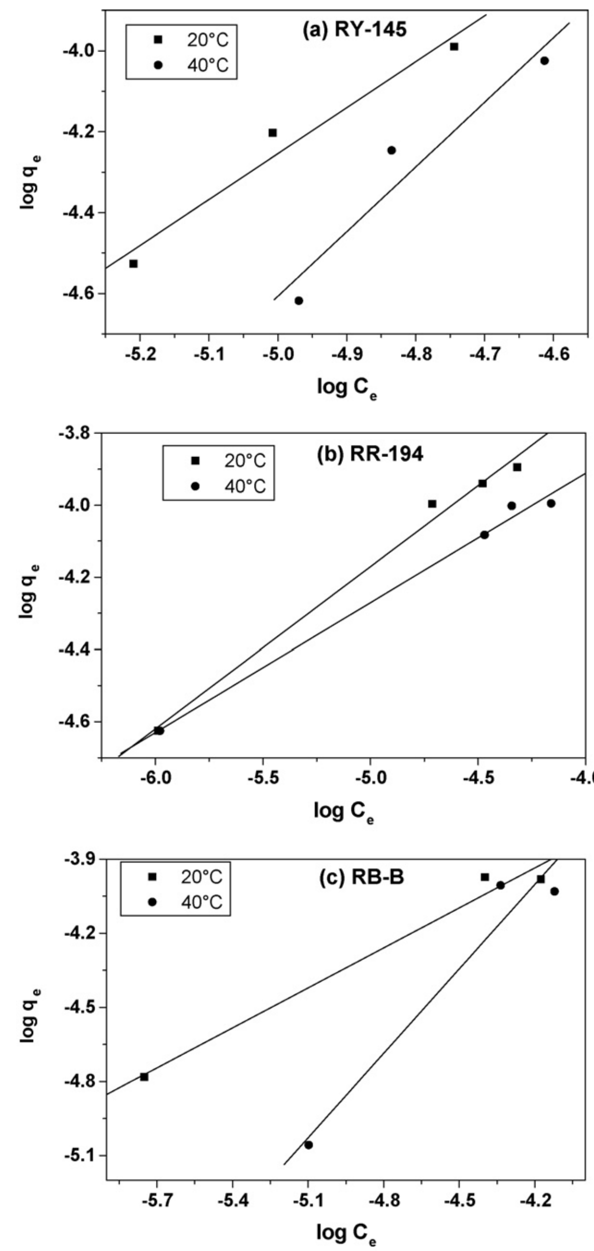


Fig. 6. Freundlich plots for the adsorption of (a) RY-145, (b) RR-194, and (c) RB-B dyes by Sorel's cement at different temperatures.

Table 3
Constant values of Langmuir and Freundlich isotherms for adsorption of RY-145, RR-194 and RB-B dyes by Sorel's cement

Dye	Temp. (°C)	Freundlich's		Langmuir			
		$\log K_F$	n	Q°		b (l/mol)	R_L
				(mol/g)	(mg/g)		
RY-145	20	1.426	0.880	10.50×10^{-5}	107.67	125496.6	0.0738
	40	3.388	0.625	9.57×10^{-5}	98.14	184469.9	0.0514
RR-194	20	1.922	2.220	14.00×10^{-5}	120.89	159587.4	0.0589
	40	2.472	2.780	10.80×10^{-5}	93.25	181572.3	0.0522
RB-B	20	1.669	1.850	11.55×10^{-5}	103.14	184055.3	0.0515
	40	0.783	0.877	9.04×10^{-5}	80.72	368500.0	0.0264

All calculated constants obtained by both models are listed in Table 3.

The influence of adsorption isotherm shape has been previously discussed in connection with the favorable adsorption in terms of R_L [34], a dimensionless constant referred to as the separation factor. R_L is calculated using the equation [35]:

$$R_L = \frac{1}{1 + bC_o}$$

where b is Langmuir constant (l/mol) and C_o the initial concentration (M). The values of R_L are presented in Table 3. All R_L values are between 0 and 1. These data indicate that Sorel's cement is a favorable adsorbent for removal of reactive dyes from aqueous effluents.

3.5. Thermodynamic studies

The free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were evaluated using the following equations:

$$\Delta G^\circ = -RT \ln b$$

$$\ln\left(\frac{b_2}{b_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where R is the universal gas constant (8.314 J K^{-1} mol^{-1}) and T (K) is temperature. The results are depicted in Table 4.

The enthalpy changes (ΔH°) of adsorption of RY-145, RR-194 and RB-B dyes by Sorel's cement were −146.96, −49.23 and −264.86, respectively. This indicates that the adsorption proceeds through an exothermic process. The negative ΔG° values show spontaneous adsorption process and the positive ΔS° values indicate the affinity of the adsorbent for the dyes.

3.6. Spectroscopic studies

The infrared (IR) spectra of Sorel's cement before and after impregnated in the reactive dyes (Fig. 7) show that the peak of ν(O–H) at 3407 cm^{-1} in Sorel's cement is shifted after adsorption of the dyes to 3432 cm^{-1} due to a Vander Waals interaction between the azo groups (–N=N–) of the reactive dyes and hydroxyl groups (–OH) of Sorel's cement. In addition, two new peaks are found at 1050 and 1410 cm^{-1} due to the sulphonic substituents and triazine ring of the azo dyes RY-145 and RR-194, respectively. This confirms the attachment of the dyes on Sorel's cement. Other much weaker absorption bands due to C–C, C–N, C–O and C–S bending vibrations at 1100–1450 cm^{-1} are also detected. All absorption peaks display less absorption intensity after interaction with the cement sorbent.

Table 4
Thermodynamic parameters for adsorption of dyes on Sorel's cement at different temperatures

Dye	Temp. (°C)	ΔG° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})	ΔH° (kJ mol^{-1})
RY-145	20	−286.19	0.464	−146.96
	40	−315.00	0.527	
RR-194	20	−292.05	0.828	−49.23
	40	−315.34	0.849	
RB-B	20	−295.52	0.104	−264.86
	40	−333.78	0.220	

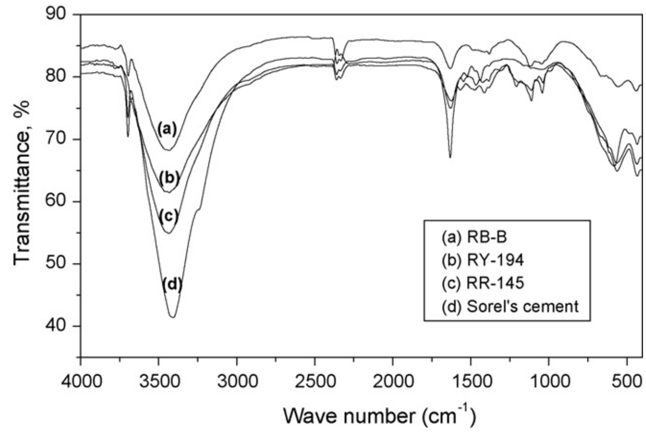


Fig. 7. IR spectra of Sorel's cement before and after adsorption of the reactive dyes.

3.7. Removal of reactive dyes from textile wastewater

Some wastewater samples were collected from the drain of some textile factories during dyeing process with reactive dyes. The released effluents containing reactive dyes and detergents displayed chemical oxygen demand values of 415–618 mg O_2/l. The pH of the effluent was adjusted at pH 6 and the solution was allowed to contact for at least 30 min with stirring at ambient temperature with Sorel's cement in a settling tank. The supernatant solution was almost colourless and displayed a chemical oxygen demand of 15–35 mg O_2/l indicating an efficiency of dye removal exceeding 96%. The method is inexpensive because 1 kg of Sorel's cement cost ~US$ 3 and is sufficient to remove 100 g of the reactive dyes from wastewater effluents. Regeneration of Sorel's cement involves heating at 650 °C for 4 h to form $MgCl_2$ and MgO mixture which can be recycled in the process of cement preparation.

4. Conclusions

Sorel's cement is effectively used for the removal of reactive dyes from wastewater. The adsorbed amounts of the reactive dyes increases with the increase of the contact time and adsorbent dosage reaching a maximum equilibrium for 10^{-4} M of the dye at 30 min and 0.02 g adsorbent. The adsorbed amounts of reactive dyes decrease with increasing of temperature. Thermodynamic

Table 5
Adsorption capacities of different adsorbents used for removal of reactive dyes from wastewater

Adsorbent	Reactive dye	Q° (mg/g)	Ref.
Metal hydroxide sludge	RR-2	62.50	[33]
	RR-120	48.31	
	RR-141	56.18	
Sepiolite	RB-5	120.50	[36]
	RR-239	108.80	
Zeolite	RR-239	111.10	[36]
	RY-176	88.50	
	RB-5	60.50	
Calcined alunite	RY-64	5.00	[37]
Hydrotalcite	RY-208	47.80	[38]
Rhizopus arrhizus biomass	RB-19	90.00	[39]
Yeasts	RB-5	88.50	[40]
Chitosan	RR-141	67.93	[41]
Sorel's cement	RY-145	107.67	This work
	RR-194	120.89	
	RB-B	103.14	

studies indicate that the adsorption process follows an exothermic route due to negative value of enthalpy change. The adsorption follows Langmuir isotherm and the adsorption capacities are 107.67, 120.89 and 103.14 mg dye per gram of Sorel's cement for RY-145, RR-194 and RB-B dyes, respectively. A comparison of the adsorption capacity (Q°) of Sorel's cement with different adsorbents previously used for removal of reactive dyes from wastewater effluents (Table 5) reveals its remarkable efficiency over many other treated and untreated natural and synthetic adsorbents.

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