Adsorption Studies on Reactive Black 5 by Varying the Composition of Sorel Cement

A. Bhaskaran¹, R. Hariharasuthan²

¹Professor and Head, Dept. of Applied Physics, Sri Venkateswara College of Engineering, Sriperumbudur 602 117, Tamil Nadu, India; ²Professor, Dept. of Chemistry, S.A. Engineering College, Chennai 600 077, India.

ABSTRACT

Search for new, cheaper and effective adsorbents especially for textile and leather dye effluents are in constant progress. Batch experiments were carried out for the adsorption of Reactive Black 5 by varying the composition of Sorel Cement. The composition of MgO and MgCl₂ are varied. Further the Sorel cement was doped with FeCl₃ and its adsorption capacity investigated. The effect of initial dye concentration, pH, and temperature and contact time were studied. The equilibrium data were fitted into Freundlich and Langmuir adsorption isotherms. The adsorption efficiency and adsorption capacity factor were calculated. The composition doped with FeCl₃ showed a higher adsorption capacity. Such composites can be used to remove other organic dyes also. The process is chemisorption which increased with temperature and so the rate and extent of adsorption increased. Kinetics studies were fitted into pseudo first order rate expression.

Key Words: Higher adsorption capacity, Thermodynamic parameters, Sorel cement

INTRODUCTION

Several effluents containing organic dyes are discharged into the water bodies and to the land from textile, leather and other industries (1). The stringent effluent treatment has become mandatory to avoid water or soil pollution. A cheaper, easily available, efficient adsorbent is in constant search (2 – 4). Several minerals, bio-waste and activated charcoal obtained from various biosources have been investigated. But an economical and efficient adsorbent need to be still identified. Sorel cement can be prepared (5) in larger quantities and contains Mg²⁺ or MgO which can act as a good adsorbent. In the present study the composition of Sorel cement has been modified with more MgO or doped with FeCl₃ and the adsorption capacity have been investigated. The effect of initial concentration, pH, and temperature has been studied and thermodynamic parameters evaluated. The kinetic of adsorption will be discussed.

EXPERIMENTAL

All the chemicals obtained are chemically pure. The adsorption experiments were performed by batch method where samples of 10 mg of Sorel's Cement X were equilibrated with 50 ml of solution containing various amount of Reactive dyes, with intermittent stirring. The initial pH of solution was adjusted to 7.0 using 0.1 M NaOH or NaCl. The effect of initial concentration of dyes was investigated for 20, 40, 60, 80, 100 and 120 min at pH 7.0 and 10 mg/50 ml sample dosage. The temperature of solutions (30, 40, 50 and 60°C) was controlled with a thermostatic bath. At the end of the adsorption period, the various samples were filtered using a filter paper and the supernatant liquid was analyzed for the remaining dye, using a UV – Visible spectrophotometer, by monitoring the absorbance changes at a wavelength of maximum absorbance of 550 nm. This procedure was repeated for various Sorel's Cement derivatives such as Sorel's Cement XA, Sorel's Cement XB, Sorel's Cement XC and Sorel's Cement XD.

Corresponding Author:

Bhaskaran A., Professor & Head, Sri Venkateswara College of Engineering, Sriperumbudur 602 117, Tamil Nadu, India.
Email: bhasdboss@gmail.com

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RESULTS AND DISCUSSION

Effect of Initial concentration of RB 5

Percentage of Reactive Black 5 adsorbed by Sorel's Cement X increases with temperature. When the initial concentration of Reactive Black 5 is above 75 mg/L, the percentage of dye, adsorbed by the adsorbent, reaches saturation (Table 1). At higher concentrations of the dye, the interactions between dye molecules enhance due to ion-pairs, hydrogen bonding or electrostatic. These interactions between the dye molecules decrease the extent of adsorption. Associated dye molecules become a "supramolecular" and so decrease the adsorption. At lower concentrations the interaction between the solute (dye) molecules will be lesser. At higher temperature and at higher concentrations, the extent of adsorption increases. At high temperature. The dye molecules move apart and the solvent sheath around the dye molecule is relaxed and the adsorption got enhanced. By decreasing the concentration of MgO in the Standard Sorel's Cement X, Sorel's Cement XA is produced. By addition of Sorel's Cement XA as adsorbent to the Reactive Black 5, it was observed that the initial rate of adsorption was rapid. If the phenolic OH group in the dye molecule is involved, effective adsorption takes place which demands a higher basic surface. When MgO is decreased the basic nature of the surface decreases and so the adsorption decreases.

By increasing the concentration of MgO in the Standard Sorel's Cement X, Sorel's Cement XB is produced. Addition of Sorel's Cement XB as adsorbent to the Reactive Black 5, it was observed that the extent of adsorption reaches to saturation level at room temperature. But at high temperatures, the extent of adsorption is relatively high. This is due to the ion-pair or solvent sheath breaks and enhances the adsorption apart from providing the activation energy for the chemisorption.

By decreasing the concentration of FeCl_3 in the Standard Sorel's Cement X, Sorel's Cement XC is produced. By addition of Sorel's Cement XC as adsorbent to the Reactive Black 5, there is a decrease in extent of adsorption. This suggests that the phenolic group interacts with Fe^{3+} and so adsorption increased when FeCl_3 is loaded. The extent of adsorption decreased in the Sorel's Cement XC when compared to Sorel's Cement X. As the Fe^{3+} decreases the adsorption decreased indicating coordinated interaction between Fe^{3+} and phenolic group of the dye decreased.

By increasing the concentration of FeCl_3 in the standard Sorel's Cement X, Sorel's Cement XD is produced. By addition of Sorel's Cement XD as adsorbent, to the Reactive Black 5, it was observed that the extent of adsorption is rapid. We expect an increase in the adsorption with increase in the concentration of FeCl_3 . But when the Cl^- in FeCl_3 may competitively adsorb and decreased the extent of adsorption compared with Sorel's Cement X or XA. When the values are compared with less FeCl_3 and more FeCl_3 samples (XC and XD), XD showed greater adsorption, due to possible Fe^{3+} interaction with the phenolic group, as explained. The process is chemisorption which increased with temperature and so the rate and extent of adsorption increased.

The Freundlich adsorption isotherms are given in Figure 1 and the Langmuir isotherm (6) is represented Figure 2 which can be arrived by

$$\frac{C_i}{Q_e} = \frac{1}{Q_m b} + \frac{C_f}{Q_m}$$

$$\text{The separation factor } R_L = \frac{1}{1 + bc_i}$$

The R_L values are found to be 0 and 1 and confirm that the ongoing adsorption process is favorable (7, 8).

Table 1: Percentage of Reactive Black 5 Dye removed by Sorel's Cement X

Sorel's Cement: X type [2.4 g MgO + 2.89g MgCl_2 + 1.0 g FeCl_3]

V = 50

Time: 80 mins

= 10 mg

C_i	C_e mg/L				$Q_e = (C_i - C_e) \times v/w$				% of dye removed			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
25	15.724	13.641	10.901	8.739	46.38	52.8	70.5	81.35	37.1	45.44	56.4	65.04
50	29.224	26.90	23.042	18.083	103.88	115.5	134.5	159.55	41.55	46.2	53.92	63.84
75	38.765	35.231	32.901	28.431	181.11	198.85	214.55	232.85	48.31	53.03	56.13	62.09
100	54.281	51.542	49.025	45.726	228.6	242.6	254.9	271.35	45.72	48.46	50.98	54.27

Figure 1: Freundlich Adsorption Isotherm of Reactive Black 5 Removed By XA.

Figure 2: Langmuir Adsorption Isotherm of Reactive Black 5 Removed By XA.

Effect of Contact time on Reactive Black 5

The amount of dye absorbed increased with time rapidly. The rate decreased significantly within half an hour and adsorption process reaches to saturation within 80 min.

The amount of dye adsorbed increased with increase in concentration of the dye. Under different conditions viz., concentration, adsorbent dose, temperature and pH, the pattern of the removal curves have been found to be the similar. Initial portion of the curve is linear and after a certain time the linear portion of the curve changes into a smooth curve and thereafter a plateau region is reached. It has been observed that an appreciable fraction of the total uptake of nearly 50% is completed within a short time of 20 minutes.

Adsorption efficiencies of the Sorel's Cement and its derivatives were studied for various contact times. The studies were carried out for different contact times viz., 20 min, 40 min, 60 min, 80 min, 100 min and 120 min. The initial concentration of Reactive Blue 4 for all adsorption studies was 50 mg/ L. The pH of dye solutions were adjusted to 7.1 by

adding HCl or NaOH. The particle size of the adsorbent was 35 μm with moisture of 1.75% and the density 0.7342 g/cc. The adsorption studies were also carried out by varying the dosage of the adsorbent from 10 mg/ 50 ml of dye solution to 50 mg/ 50 ml.

Adsorption of Reactive Black 5 by Sorel's Cement X increased with increase in contact time and increased with addition of adsorbent. Adsorption is 91% for contact time of 120 min. and with concentration of 50 mg/ 50 ml. It was observed that for the contact time of 80 mins, the adsorption of Sorel's Cement and its derivatives reached saturation in varied concentrations of Reactive Black 5. Almost 92% of the RB 5 has been removed by Sorel's Cement samples. This can be used effectively and efficiently to remove the dye and this class of dyes from the textile and leather effluents.

3.3 Effect of pH

The amount of dye adsorbed by Sorel's Cement and its derivatives as a function of time at different pH values is studied between pH values 3-12. The pH of the mixture was adjusted to the required pH value by adding 0.1 N of HCl or NaOH. The removal efficiency of dye increases with increase in pH from 3-12. The removal efficiency of Sorel's Cement for Reactive Black 5 was found to be higher at higher pH (Table 3).

At a higher pH or at higher alkalinity, deprotonation of phenolic, sulphonic, groups enhances the adsorption. Further FeCl_3 may become $\text{Fe}(\text{OH})_3$ and enhances the adsorption. At higher pH the adsorption is greater, because at lower pH the NH_2 group will get protonated and increase the adsorption over $\text{MgO} + \text{MgCl}_2$ surface. At higher pH the $-\text{OH}$ and SO_3H groups are deprotonated and so enhance the adsorption. This trend was also observed in Sorel's Cement XA, XB XC and XD.

Lagergren Pseudo-First-Order Kinetics

The pseudo-first-order kinetic model was used to predict the dye sorption kinetics. Pseudo-first-order equation of Lagergren is given by

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

Where q_e and q_t are the amounts (mol/g) adsorbed at equilibrium and at time t , and k_1 is the pseudo first order rate constant min^{-1} . The rate constant $k_1 \text{ min}^{-1}$ and q_e can be calculated (Fig.3, Table-2) from the slope and intercepts of $\log(q_e - q_t)$ vs. time (t)

Table 2: Kinetic data of Sorel's Cement XA – RB5

Concentration (10 mg/L)	First order rate constant (k_1 (1/min))	R ₂
10	3.66×10^{-2}	0.972
20	3.84×10^{-2}	0.957
30	3.42×10^{-2}	0.974
40	3.03×10^{-2}	0.968
50	3.10×10^{-2}	0.982

Figure 3: First order kinetics of Reactive Black 5 Sorel Cement X.

Table 3: Effect of pH on Reactive black 5 with Sorel's Cement XA

Particle size: 35 μ
Dosage : 50 mg/50 ml

Initial conc. C_i = 50 mg/L
Vol. of sol = 50 ml

pH	C_i mg/L	C_t after Time					
		20 min	40 min	60 min	80 min	100 min	120 min
3	50	48.3	45.3	43.6	42.2	413	39.2
4	50	47.2	43.1	41.2	40.1	38.9	37.6
5	50	46.6	42.4	39.1	38.0	37.2	35.3
6	50	44.3	40.6	38.1	36.3	35.4	34.1
7	50	42.3	39.2	37.3	35.0	34.1	33.4
8	50	41.1	38.3	36.4	34.6	33.2	31.6
9	50	42.9	40.6	38.2	36.1	34.6	32.2
10	50	44.8	42.1	39.9	38.1	36.0	34.9
11	50	46.1	44.9	43.0	40.1	38.7	37.6
12	50	48.0	46.2	43.6	41.2	39.3	37.9

CONCLUSION

Optimum concentrations of MgO and FeCl₃ are required for better adsorption. The composition Sorel cement XA has been found to be better among the composites. We have also studied the removal of other dyes like Rhodamine B, Reactive Yellow 17 and Reactive Blue 5 are removed efficiently by adsorption. Such inorganic composite cement materials therefore can be used as good adsorbents. The advantage is that they can be manufactured in large quantities and so become cheaper. They can be regenerated by heating or leaching methods.

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