

Comparative studies of Sorel's cement on selected dyes

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Abstract

Batch experiments are carried out for the adsorption of direct yellow 17, reactive blue 4 and rhodamine B dyes by Sorel's cement. The operating variables studied are initial dye concentration (C_i), pH, temperature and contact time. The equilibrium data are fitted to the Langmuir isotherm equations and the adsorption efficiency, adsorption capacity and dimensionless separation factor are calculated.

Keywords: Direct yellow 17, Langmuir isotherms, kinetic studies, pH effect, contact time.

Introduction

The discharge of untreated effluents into nearby water bodies or nearby land is not only aesthetically displeasing, but it also restricts light penetration, thus upsetting biological processes within a stream. In addition, many dyes are toxic to aquatic communities; some of them can cause allergic dermatitis, skin irritation, cancer and mutation in man. Approximately 12% of synthetic textile dyes used each year is lost during manufacture and processing operation and 20% of these dyes enter the environment through effluents that result from the treatment of residual industrial waters (Weber & Stickney, 1993). Effluents from dyeing industries are released into nearby land or rivers without any treatment because the conventional treatment or methods are not cost effective in the Indian context. On the other hand, low cost technologies never allow an effective colour removal and also have certain disadvantages. The adsorption is one of the most effective methods and Sorel's cement is used as adsorbent to treat effluent containing different classes of dyes, recognizing the economic drawback of commercial Sorel's cement.

Many researchers have studied the feasibility of using inexpensive alternative materials like coconut husk (Anurudh & Sreedhar, 1999), pearl millet husk, date pits, saw dust, buffing dust of leather industry, coir pith, crude oil residue, tropical grass, olive stone and almond shells, pine bark, wool waste, etc., as carbonaceous precursors for the removal of dyes from contaminated water (Sekaran *et al.*, 1995; Senthikumar *et al.*, 2005). The present study is undertaken to evaluate the efficiency of Sorel's cement (combination of $MgCl_2$, MgO and $FeCl_3$), for removal of dye in aqueous solution. In order to design adsorption treatment system, knowledge on kinetic and mass transfer processes is essential. In this paper, we report the applicability of kinetic models for the adsorption of direct yellow 17 (DY17), reactive blue 4 (RB4) and rhodamine B (RDB) onto Sorel's cement.

Materials and methods

The properties of the Sorel's cement used are given in Table 1. All chemicals used were of high purity,

commercially available Analar grade. Stock solutions of 1g/l of dyes were prepared using doubly distilled water.

2.4 g of MgO is dissolved in 8 ml of 1.78 M $MgCl_2$ solution at $75^\circ C$, then added 1 g of $FeCl_3$; stirred the mixture for 10 min. The paste was removed; centrifuge and dried in IR lamp for 4 h. The dried powder was sieved in 35 μm dia. mesh.

Direct yellow 17 (DY 17), Reactive blue 4 (RB4) and Rhodamine B (RDB) dye solutions were made to a known concentration. From that, 50 ml of 25 mg/l, 50 mg/l, 75 mg/l and 100 mg/l dye solutions were taken and loaded with the 100 mg of Sorel's cement. The samples were agitated with 200 rpm at $30^\circ C$, $40^\circ C$, $50^\circ C$ and $60^\circ C$ in definite time intervals and then withdrawn from the agitator for filtration. The filtrates were analyzed in UV-VIS 1700 spectrophotometer (Shimadzu make).

Results and discussion

Effect of contact time & initial dye concentration

The experimental results of adsorptions of direct yellow 17 (DY17), reactive blue 4 (RB4) and rhodamine B (RDB) on the Sorel's cement at various initial concentrations (25 mg/l, 50 mg/l, 75 mg/l and 100 mg/l) with known contact time are shown in Fig. 1-3 and Table 2. The equilibrium data are collected in Table 2 reveal that the percent adsorption decreases with the increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of Sorel's cement increased with increase in dyes concentration. It means that the adsorption is highly dependent on the initial concentration of dyes. This is because at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low, subsequently, the fractional adsorption become independent on the initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence, the percentage removal of dye is dependent upon the initial concentration. The equilibrium is established within 40 min for all concentrations. Fig.1-3 reveals that the curves are smooth, continuous and leading to saturation,

Table 1. Properties of Sorel's cement.

Size	0.035 mm
Density	0.7342 g/cc
Moisture	1.75% (98.25% dried)
Loss on drying	80%
Water soluble matter	0.80%
pH of aqueous solution	8.2

Table 2. Equilibrium parameters for the adsorption of dyes on to Sorel's cement.

Ci	Cf				Qe				% dye removed			
	30	40	50	60	30	40	50	60	30	40	50	60
Direct yellow 17												
25	5.344	4.906	4.642	4.404	98.27	100.46	101.39	103.91	78.62	80.37	81.43	82.39
50	14.301	12.002	10.121	9.973	178.49	190.00	198.46	201.35	71.40	75.99	79.36	80.06
75	28.431	26.171	22.234	17.432	232.84	244.10	263.90	289.40	62.09	65.11	70.36	76.76
100	49.821	45.712	39.416	31.441	250.90	271.44	302.90	342.80	50.68	54.28	60.58	68.56
Reactive blue 4												
25	7.421	6.219	5.061	4.230	87.85	93.90	99.70	103.85	70.32	75.13	79.26	83.10
50	16.944	14.631	12.900	10.093	165.28	176.85	185.50	199.54	66.11	70.74	74.2	79.80
75	36.144	30.208	26.419	23.174	194.28	223.96	242.92	259.14	51.81	59.23	64.77	69.10
100	53.560	47.409	39.170	34.644	232.70	263.00	304.10	329.20	46.54	52.60	60.83	65.86
Rhodamine B												
25	4.725	4.013	3.914	3.522	171.38	184.95	197.43	204.39	81.10	83.15	84.35	85.91
50	11.143	9.931	8.945	7.321	194.30	200.34	205.28	213.40	77.72	80.14	82.11	85.36
75	37.141	34.153	33.987	32.931	206.30	217.24	229.15	240.35	50.48	54.47	54.69	56.09
100	51.971	45.454	41.519	37.421	240.45	272.73	292.25	312.90	48.03	54.55	58.48	62.58

Fig. 1. Direct yellow 17 Vs Sorel's cement.

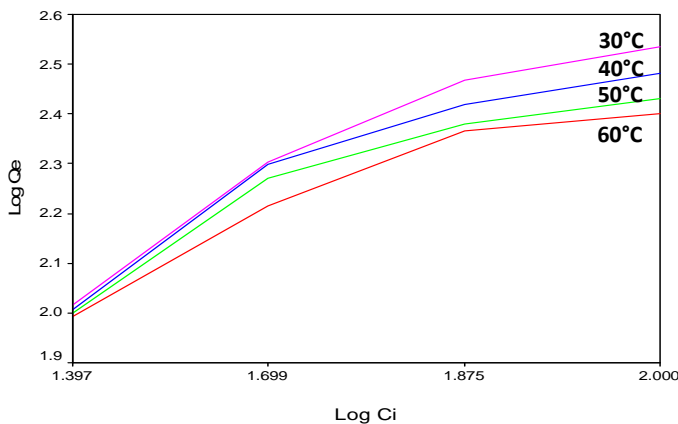


Fig. 1. Reactive blue 4 Vs Sorel's cement.

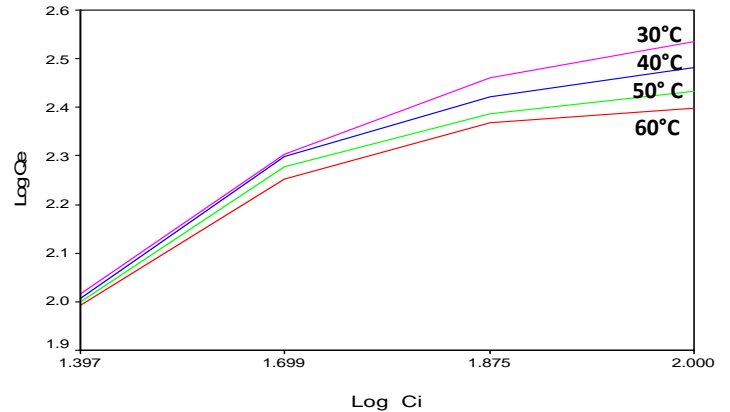


Fig. 3. Rhodamine B Vs Sorel's cement.

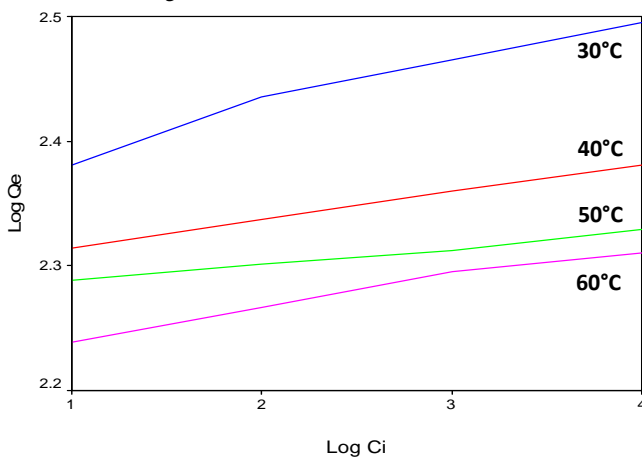


Fig. 4. Langmuir isotherm for the adsorption of DY17 by Sorel's cement.

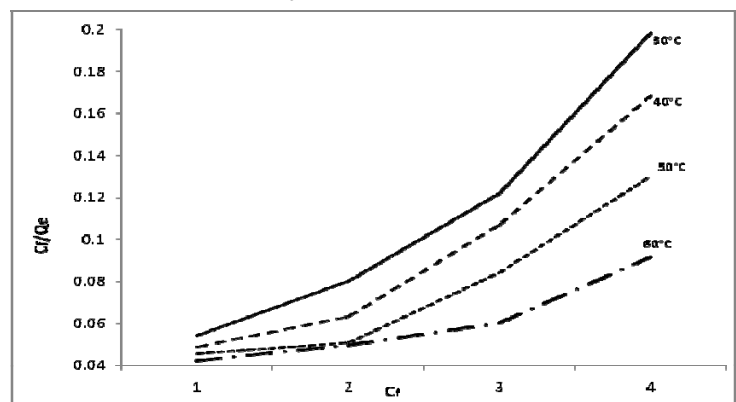
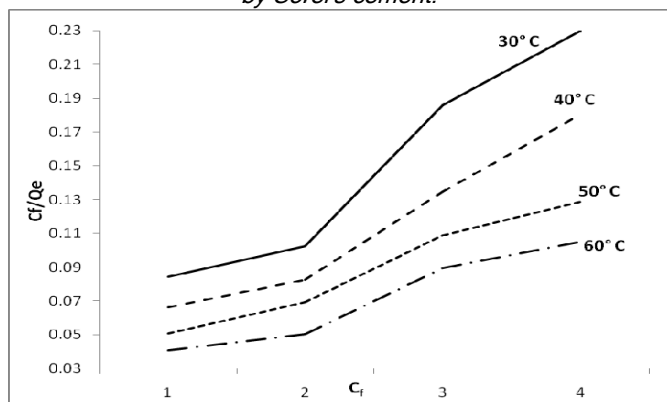


Fig. 5. Langmuir isotherm for the adsorption of RB4 by Sorel's cement.



suggesting the possible monolayer coverage of the dyes on the Sorel's cement (Senthikumar *et al.*, 2005).

Adsorption isotherm

The experimental data are analyzed according to the linear form of the Langmuir isotherms. The Langmuir isotherm is represented by the following equation (Langmuir, 1918).

$$C_f/Q_e = 1/Q_m b + C_f/Q_m \quad (1)$$

Here C_f is the equilibrium concentration (mg/l), Q_e is the amount adsorbed at equilibrium (mg/g) and Q_m and b are Langmuir constants related to the adsorption efficiency and energy of adsorption respectively. The linear plots of C_f/Q_e versus C_f suggest the applicability of the Langmuir isotherms (Fig. 4-6). The values of Q_m and b are determined from the slope and intercept of the plots and are presented in Table 3. From the results, it is clear that the values of adsorption efficiency Q_m and adsorption energy b of the Sorel's cement vary with increasing the temperature. From the values we can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on an adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface occurs. The trend shows that the adsorbent prefers to bind acidic ions and that speciation predominates on sorbent characteristics,

Fig. 6. Langmuir isotherm for the adsorption of RDB by Sorel's cement.

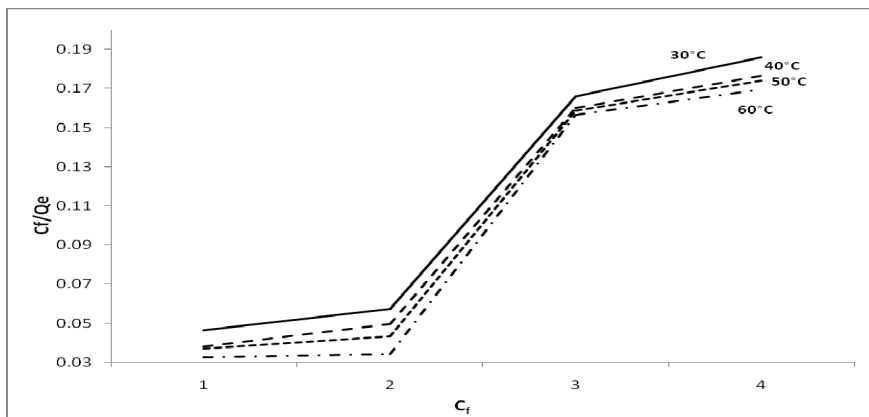
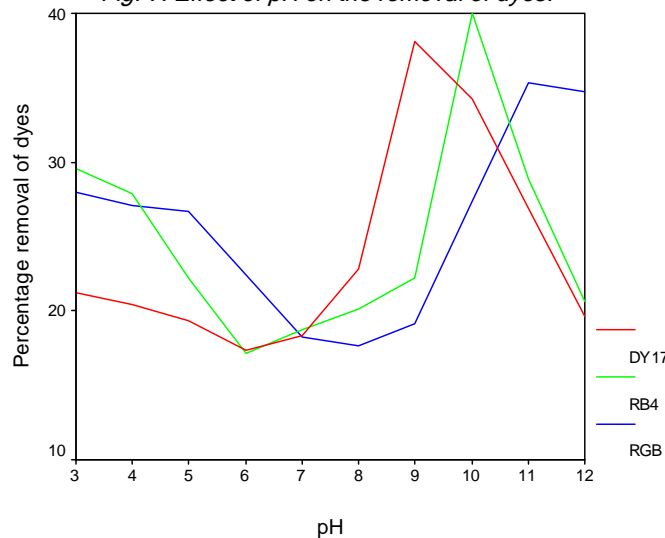


Fig. 7. Effect of pH on the removal of dyes.



when ion exchange is the predominant mechanism. Further, it confirms the endothermic nature of the processes involved in the system. To confirm the favorability of the adsorption process, the separation factor (R_L) is calculated and presented in Table 4. The values are found to be between 0 and 1 and confirm that the ongoing adsorption process is favourable (Namasivayam & Yamuna, 1995; Khattri & Singh, 1999). $R_L = 1 / (1 + bC_i)$ (2) Here, b is the Langmuir constant and C_i is the initial concentration of dye.

Effect of Sorel's cement concentration

The adsorption of the dyes on Sorel's cement is studied by varying the Sorel's cement concentration from 10 mg/l to 50 mg/l for direct yellow 17 (DY17), reactive blue 4 (RB4) and rhodamine B (RDB).

Effect of pH

The experiments carried out at different pH show that there is a change in the percent removal of dyes over the entire pH range of 3 to 9 shown in the Fig. 7. This indicates the strong force of interaction between the dyes and the Sorel's cement that, either H^+ or OH^- ions could influence the adsorption capacity. Here the interaction is larger at pH 6 due to the competence of acidic H^+ ion with dye cation for the sorption sites. The percentage of sorption increases above this pH value due to the presence of ionic COOH groups. The adsorption of dyes on the activated Sorel's cement does involve ion exchange mechanism. Due to this mechanism there should be an influence on the dye adsorption while varying the pH. This observation is in line with the type I isotherm shown in Fig. 6. Adsorption and

Table 3. Langmuir isotherm results $C_f/Q_e = 1/Q_m b + C_f/Q_m$.

Dyes	Temperature °C	Statistical parameters/constants		
		r	Q_m	b
Direct yellow 17	30	0.9719	9.3777	0.045
	40	0.9669	9.6016	0.039
	50	0.9524	9.5939	0.030
	60	0.9407	9.6953	0.023
Reactive blue 4	30	0.9742	10.2378	0.052
	40	0.9813	10.4312	0.039
	50	0.9874	9.5376	0.027
	60	0.9741	10.4076	0.023
Rhodamine B	30	0.9859	9.8639	0.0712
	40	0.9745	9.9153	0.0862
	50	0.9564	10.0178	0.0728
	60	0.9334	10.2212	0.0882

recycling of the spent adsorbent and the dyes. If the adsorbed dyes can be desorbed using neutral pH water, then the attachment of the dyes on the adsorbent is weak. If sulphuric acid or alkaline water desorption of the dyes, then the adsorption is by ion exchange. If organic acids, like acetic acid desorption of the dyes, then the dye is attached to the adsorbent through chemisorptions (Namasivayam & Yamuna, 1995). The effect of various reagents used for desorption studies shows that hydrochloric acid is a better reagent for desorption, because we could get more than 90% removal of adsorbed dyes. The reversibility of adsorbed dyes in mineral acid or base is in agreement with the pH dependent results obtained. The adsorption of dyes by mineral acids and alkaline medium indicates that the dyes are adsorbed onto the activated Sorel's cement by physisorption.

Table 4. Dimensionless separation factor (R_L), $R_L = 1/(1+bC_0)$.

Do (mg/l)	Temperature (°C)			
	30	40	50	60
Direct yellow 17				
25	0.46468	0.50633	0.57143	0.63492
50	0.30769	0.33898	0.40000	0.46512
75	0.22857	0.25478	0.30769	0.36647
100	0.18182	0.20428	0.25000	0.30301
Reactive blue 4				
25	0.43478	0.50633	0.59701	0.63492
50	0.27778	0.33898	0.42553	0.46511
75	0.20408	0.25478	0.33058	0.36697
100	0.16129	0.20408	0.27027	0.30303
Rhodamine B				
25	0.35971	0.31696	0.35461	0.31201
50	0.21929	0.18832	0.21552	0.18484
75	0.15773	0.13396	0.15479	0.13132
100	0.12315	0.10395	0.12077	0.10183

Conclusion

The experimental data correlated reasonably well with the Langmuir adsorption isotherms and the respective isotherm parameters are calculated. The amount of dyes adsorbed increases with increase in pH and temperature.

The amount of the adsorbed DY17, RB4 and RDB slightly decreased with increasing ionic strength. The dimensionless separation factor shows that the Sorel's cement can be used for the removal of DY17, RB4 and RDB from aqueous solution.

Acknowledgement

The authors thank Mr. P. Venkatesh Raja, Director, S.A. Engineering College and Dr. S. Suyambazhahan, Principal, S.A. Engineering College, Chennai-56 for immense support to carry out the research work.

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