

Adsorption Studies On Reactive Blue 4 By Varying The Concentration Of Mgo In Sorel's Cement

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-----ABSTRACT-----ABSTRACT-----

Batch experiments are carried out for the adsorption of Reactive Blue 4 by Sorel's cement with varying the composition. 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. From this the adsorption efficiency, adsorption capacity and dimensionless separation factor are calculated.

Key words: Reactive Blue 4, Various types of Sorel's Cement, Langmuir isotherms, Kinetic studies, pH effect, Effect of contact time.

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I. 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 some organisms causing direct destruction of aquatic communities. Some dyes can cause allergic dermatitis, skin irrigation, cancer and mutation in man. Recent estimates indicate that, 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 ^[11]. 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 color 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^[2], pearl millet husk, date pits, saw dust, buffing dust of leather industry ^[3], 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 water and wastewater ^[3,4]. The present study is undertaken to evaluate the efficiency of Sorel's cement by varying the concentration of MgO by keeping the constant strength of MgCl₂ and FeCl₃, for removal of Reactive Blue 4 dye in an aqueous solution. In order to design on adsorption treatment system, knowledge of the kinetic and mass transfer processes is essential. In this paper, we report the applicability of kinetic models for the adsorption of Reactive Blue 4 (RB 4) onto Sorel's cement by varying concentration of MgO.

Materials

II. Materials And Methods

Sorel's cement X: 2.4 g m of MgO is dissolved in 8 ml of 1.78 mol MgCl₂ solution at 75 °C, then add 1 gm of FeCl₃ and stir the mixture for 10 minutes. Remove the paste and centrifuge and dry the paste in IR lamp for 4 hrs. Sieve this powder in 35 μ m dia mesh. 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. The same procedure is repeated with 1.8 gm of MgO for Sorel's cement A type and 3.0 gm of MgO for Sorel's cement B type adsorbents.

Methods

Reactive Blue 4 (RB 4) dyes solutions were made to a known concentration of 25 mg/L, 50 mg/L, 75 mg/L and 100 mg/L. 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 adsorbents viz, Sorel's cement X, Sorel's cement A and Sorel's Cement B. Then the samples were agitated at 30° C, 40° C, 50° C and 60° C in definite time intervals. After that samples were withdrawn from the agitator and filtered. Adsorption studies were carried out using the various types of Sorel's cement X. The Sorel's cement X, A and B loaded with RB 4 were separated and gently washed with distilled water to remove any unabsorbed dye. Each of the dye-laden Sorel's cement was agitated with 50 ml of water.

III. Results And Discussions

Effect of contact time and initial dye concentration:

The experimental results of adsorptions of Reactive Blue 4 (RB4) on the Sorel's cement X at various initial concentrations (25 mg/L, 50 mg/L, 75 mg/L and 100 mg/L) with known contact time are shown in Figure 7. The equilibrium data are collected reveal that the percent adsorption decreases with the increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of all types of Sorel's cement increased with increase in dye concentration. It means that the adsorption is highly dependent on the initial concentration of dye. 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 in 60 min for the Sorel cement B with high concentration of MgO is showing more efficiency in removing RB4 whereas same condition is reached in 80 mins in the case of the other types of Sorel Cement adsorbents. Figure 7 reveals that the curves are smooth, continuous and leading to saturation, suggesting the possible monolayer coverage of the dyes on various types of Sorel's cement ^[5].

IV. 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 ^[6].

$C_{f}/Q_{e} = 1/Q_{m}b + C_{f}/Q_{m}....(1)$

Here C_f is the equilibrium concentration (mg/L), ' Q_e ' is the amount adsorbed at equilibrium (mg/g) and ' Q_m ' and 'b' is 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 (Figure 4 to Figure 6). The values of ' Q_m ' and 'b' are determined from the slope and intercept of the plots and are presented in Table 4. From the results, it is found that, for all combinations of Sorel's Cement, the values of adsorption efficiency ' Q_m ' and adsorption energy 'b' are varying with increase in the temperature. From the values we can conclude that the maximum adsorption corresponds to a saturated mono-layer 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, 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 5. The values are found to be between 0 and 1 and confirm that the ongoing adsorption process is favorable [^{7,8}].

$$R_L = 1 / (1 + bC_i)....(2)$$

Here, 'b' is the Lang mu ir constant and ' C_i ' is the initial concentration of dye.

V. 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 Figure 8. This indicates the strong force of interaction between the dyes and the various types of 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. The observation shows that by varying the MgO concentration in the Sorel Cement, the adsorption efficiency can be increased.

VI. Conclusions

The experimental data correlated reasonably well with the Langmuir adsorption isotherms and the respective isotherm parameters are calculated for various types of Sorel's cements vs RB4. The amount of dyes adsorbed increases with increase in pH of the medium. Further the efficiency of the adsorbent increase with change in MgO concentration. The amount of the adsorbed RB4 slightly decreases with increasing the ionic strength and increase with the increase in temperature. The dimensionless separation factor shows that the Sorel's cement can be used for the removal of RB4 from aqueous solution.

VII. .Acknowledgement

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

Table 1Properties of Sorel's Cement X

Table 2 Equilibrium parameters for the adsorption of Reactive Blue 4 by various concentrations of MgO in Sorel's Cement

| Gi | Cf | | | Qe | | | | % age of Dye removed | | | | |
|-------|-----------|--------|------------|--------|---------|---------|---------|----------------------|--------|-------|--------|-------|
| | 30 | 40 | 50 | 60 | 30 | 40 | 50 | 60 | 30 | 40 | 50 | 60 |
| Sorel | 's Cement | x | Carrent I. | 210.00 | | 10.000 | 00000 | and the | Tabler | | 000005 | 2000 |
| 25 | 7.421 | 6.219 | 5.061 | 4.23 | 87.85 | 93.9 | 99.7 | 103.85 | 70.32 | 75.13 | 79.26 | 83.08 |
| 50 | 16.944 | 14.631 | 12.9 | 10.093 | 165.28 | 176.85 | 185.5 | 199.54 | 66.11 | 70.74 | 74.2 | 79.8 |
| 75 | 36.144 | 30.208 | 26.419 | 23.074 | 194.28 | 223.96 | 242.92 | 259.14 | 51.81 | 59.23 | 64.77 | 69.1 |
| 100 | 53.56 | 47.409 | 39.17 | 34.644 | 232.7 | 263 | 304.1 | 329.2 | 46.54 | 52.6 | 60.83 | 65.86 |
| Sorel | 's Cement | A | | | | | | | | | | |
| 25 | 7.780 | 6.513 | 5.641 | 4.816 | 86.1 | 92.435 | 96.795 | 100.92 | 68.9 | 73.9 | 77.4 | 80.7 |
| 50 | 17.190 | 16.431 | 14.810 | 12.009 | 164.05 | 167.845 | 175.95 | 189.955 | 65.6 | 67.1 | 70.4 | 76.0 |
| 75 | 38.941 | 33.110 | 28.194 | 25.431 | 180.295 | 209.45 | 234.03 | 247.845 | 48.1 | 55.9 | 62.4 | 66.1 |
| 100 | 55.400 | 49.071 | 43.147 | 37.920 | 223.0 | 254.645 | 284.265 | 310.4 | 44.6 | 51.0 | 56.8 | 62.1 |
| Sorel | 's Cement | В | | | | | | | | | | |
| 25 | 7.271 | 6.102 | 4.911 | 4.10 | 88.64 | 94.49 | 100.44 | 104.50 | 70.91 | 75.59 | 80.35 | 83.6 |
| 50 | 15.726 | 13.071 | 11.24 | 9.67 | 171.37 | 184.64 | 193.80 | 201.65 | 68.54 | 73.85 | 77.52 | 80.66 |
| 75 | 349 | 29.22 | 25.12 | 22.02 | 200.2 | 228.92 | 249.42 | 264.94 | 53.46 | 61.04 | 66.51 | 70.65 |
| 100 | 51.47 | 45.33 | 37.15 | 32.6 | 242.64 | 273.33 | 314.25 | 337.00 | 48.52 | 54.66 | 62.85 | 67.40 |

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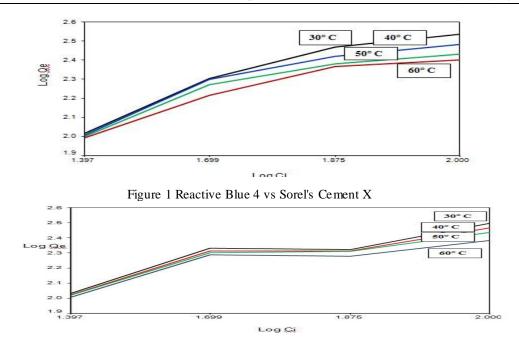
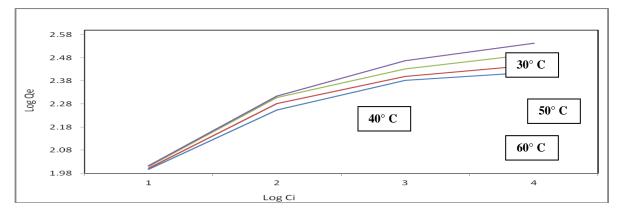


Figure 2 Reactive Blue 4 vs Sorel's Cement A

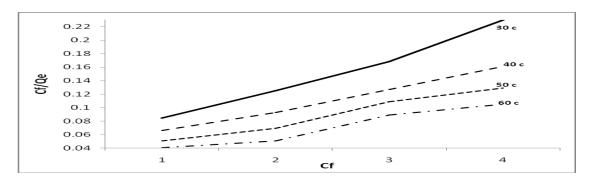


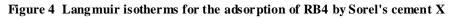




$$C_f/Q_e = 1/Q_m b + C_f/Q_m$$

| Sorel's cement | °C | 25 mg/l | | 50 mg/1 | | 75 mg/l | | 100 mg/1 | |
|-------------------|----|---------|-------------|---------|--------|---------|--------|----------|--------|
| | | Cf | Cf/Qa | Çf | Cf/Qa | Cf | Cf/Qa | Cf | Cf/Qa |
| X | 30 | 7.421 | 0.0845 | 16.944 | 0.0801 | 36.144 | 0.1221 | 53.36 | 0.1985 |
| | 40 | 6.219 | 0.0664 | 14.631 | 0.0631 | 30.208 | 0.1072 | 45.712 | 0.1684 |
| | 50 | 5.061 | 0.0508 | 12.900 | 0.0509 | 26.419 | 0.0845 | 39.416 | 0.1301 |
| | 60 | 4.230 | 0.0405 | 10.093 | 0.0495 | 23.074 | 0.0602 | 31.441 | 0.0917 |
| A | 30 | 7.780 | 0.0904 | 17.190 | 0.1048 | 38.941 | 0.2169 | 55.400 | 0.2484 |
| | 40 | 6.513 | 0.0705 | 16.431 | 0.0979 | 33.110 | 0.1581 | 49.071 | 0.1927 |
| | 50 | 5.641 | 0.0583 | 14.810 | 0.0842 | 28.194 | 0.1204 | 43.147 | 0.1517 |
| | 60 | 4.816 | 0.0477 | 12.009 | 0.0632 | 25.431 | 0.1086 | 37.920 | 0.1221 |
| В | 30 | 7.271 | 0.0820 | 15.726 | 0.092 | 349 | 0.1743 | 51.47 | 0.1743 |
| | 40 | 6.102 | 0.0646 | 13.071 | 0.0708 | 29.22 | 0.1276 | 45.33 | 0.1658 |
| | 50 | 4.911 | 0.0497 | 13.071 | 0.0609 | 25.12 | 0.1007 | 37.15 | 0.1182 |
| | 60 | 4.10 | .0.039 2 | 9.670 | 0.0479 | 22.02 | 0.083 | 32.60 | 0.0967 |





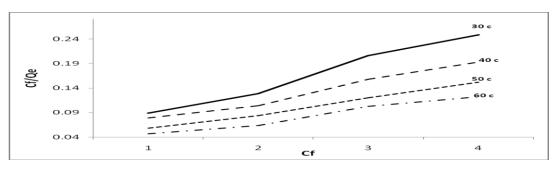
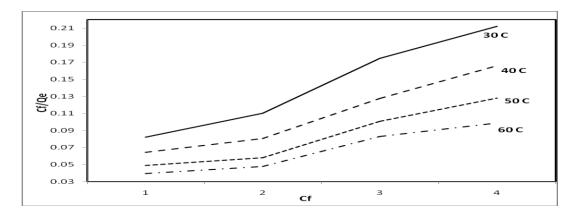
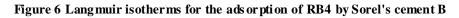
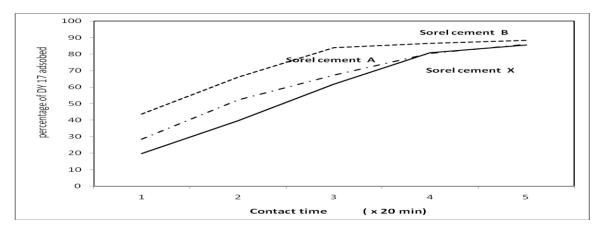
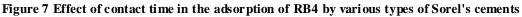


Figure 5 Langmuir isotherms for the adsorption of RB4 by Sorel's cement A









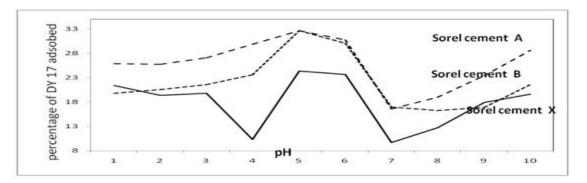


Figure 8 Effect of pH in the adsorption of RB4 by various types of Sorel's cements

| Table 4 | Langmuir Isotherm results for Reactive Blue 4 |
|---------|---|
| | $C_f/Q_e = 1/Q_mb + C_f/Q_m$ |

| Dyes | Temperature | Statistical parameters/ constants | | | | |
|------------------|-------------|-----------------------------------|--------|-------|--|--|
| | °C | r | Qm | b | | |
| Sorel's Cement X | 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 | | |
| Sorel's Cement A | 30 | 0.937 | 9.3377 | 0.038 | | |
| | 40 | 0.939 | 9.5661 | 0.034 | | |
| | 50 | 0.947 | 9.5911 | 0.029 | | |
| | 60 | 0.950 | 9.6953 | 0.022 | | |
| Sorel's Cement B | 30 | 0.940 | 9.3997 | 0.048 | | |
| | 40 | 0.941 | 9.6360 | 0.043 | | |
| | 50 | 0.947 | 9.6939 | 0.039 | | |
| | 60 | 0.959 | 9.7353 | 0.033 | | |

Table 5 Dimensionless separation factor (R_L) for Reactive Blue 4 $R_L = 1/(1\!+\!bC_o)$

| Temperature | | | | | | |
|------------------|--------|--------|--------|--------|--|--|
| Do (mg/L) | 30 °C | 40 °C | 50 °C | 60 °C | | |
| Sorel's Cement X | | | • | | | |
| 25 | 0.4646 | 0.5063 | 0.5714 | 0.6349 | | |
| 50 | 0.3076 | 0.3389 | 0.4000 | 0.4651 | | |
| 75 | 0.2285 | 0.2547 | 0.3076 | 0.3664 | | |
| 100 | 0.1818 | 0.2042 | 0.2500 | 0.3030 | | |
| Sorel's Cement A | | | | · | | |
| 25 | 0.5128 | 0.5405 | 0.5797 | 0.6451 | | |
| 50 | 0.3448 | 0.3703 | 0.4081 | 0.4761 | | |
| 75 | 0.2597 | 0.2816 | 0.1410 | 0.3773 | | |
| 100 | 0.2083 | 0.2272 | 0.2564 | 0.3125 | | |
| Sorel's Cement B | | | | | | |
| 25 | 0.4545 | 0.4819 | 0.5063 | 0.5479 | | |
| 50 | 0.2941 | 0.3174 | 0.3389 | 0.3802 | | |
| 75 | 0.2173 | 0.2366 | 0.2547 | 0.2877 | | |
| 100 | 0.1724 | 0.1886 | 0.2040 | 0.2325 | | |