3. RESULTS AND DISCUSSION

3.1 Characterization by XRD & FTIR

XRD of SR and FM are given in Fig.1 (a) & (b) and are found to be almost amorphous in nature.

The FTIR spectra of SR and FM before and after biosorption are shown in Fig. 2 (a) –(d). The data indicates broad bands at 3427-3400cm^{-1} due to hydroxyl groups. The bands observed at 2925–2919 cm^{-1} might be due to stretching of C-H bond of methyl and methylene groups.[16] The peak at 1637-1624cm^{-1} could be attributed to C=O stretching peak of amide group. The figures 2 (b) & (d) show substantial decrease in the adsorption intensity of -OH group from 3427 cm^{-1} to 3411 cm^{-1} for SR and 3425 cm^{-1} to 3400 cm^{-1} for FM respectively, which indicated that the hydroxyl group played the important role in binding MB. The FT-IR spectra gives information about the exchanging sites and functional groups involved in biosorption.[17]

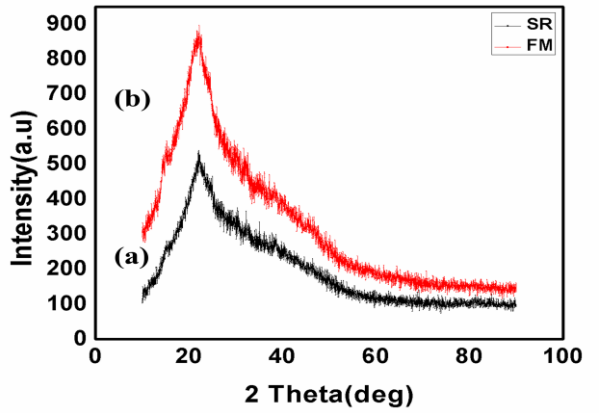

Fig.1 XRD of **(a)** SR & **(b)** FM

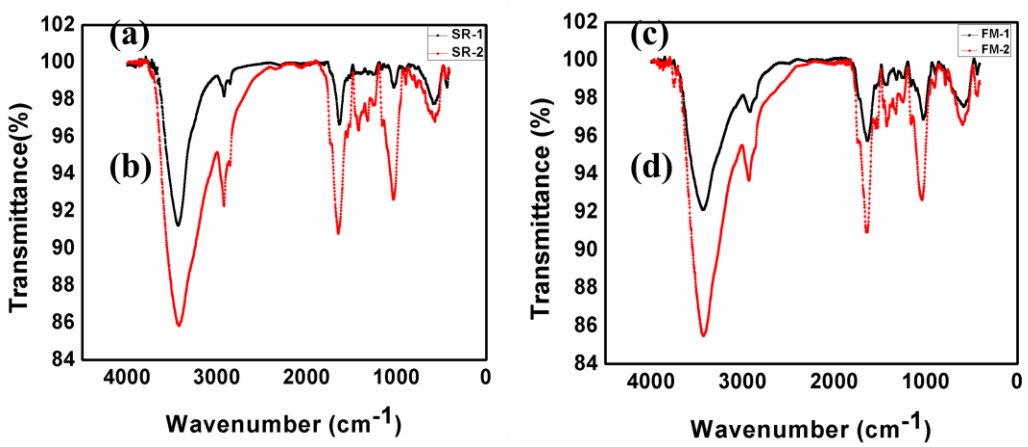

Fig.2 FT-IR (a) unloaded SR (b) SR loaded with MB
(c) unloaded FM (d) FM loaded with MB

3.2 Effect of modifiers

Table 1 shows the biosorption efficiency of various modifiers on MB removal. It can be seen that fenton reagent shows the maximum percentage removal and hence was selected for further studies.

Table 1: Effect of modifiers for removal of MB

Modifiers	**% Removal**
0.1N HCl	41
0.1N HNO_3	87
0.1 N H_2SO_4	79
1 N KOH	87
1 N NaOH	84
25% Acetone	79
25% Acetone+1N HCl	65
25% Acetone +1NHCl+0.1N NaOH	92
25% $CHCl_3$	91
25% DEE	82
Activated Charcoal	49
50% H_2O_2	83
Fenton reagent	94

3.3 Effect of fenton concentration

The varying ratios of Fe^{2+}/H_2O_2 (0.01–0.1w/w) were used for fenton modification[18] of SR and biosorption efficiency experiments showed that the ratio of 0.02 is the opitmum fenton concentration (Fig.3).

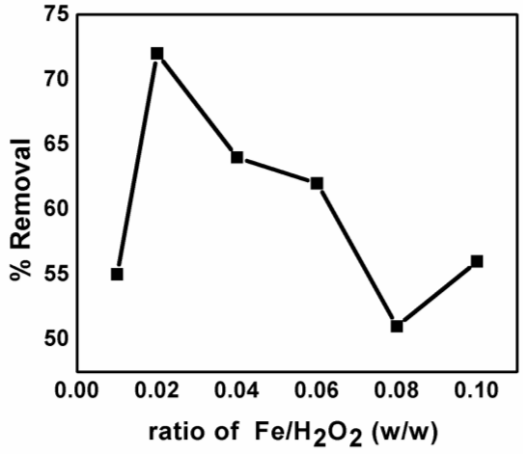

Fig. 3 Optimization of fenton concentration for MB removal

3.4 Effect of pH

The effect of pH on the amount of MB adsorption was investigated and is shown in Fig. 4 (a) SR showed maximum MB removal efficiency at pH 12. As the pH increases, the surface becomes negatively charged, which increases the adsorption of the positively charged dye particles through electrostatic forces of attraction.[19] FM showed maximum efficiency in the neutral range.

3.5 Effect of contact time

Fig. 4 (b) shows variation of adsorption efficiency with stirring time for SR and FM. It was found that equilibrium is achieved within 60 min in both cases and may be due to saturation of the active sites which does not allow further adsorption. It was observed that dye uptake was rapid for the first 60 min, and thereafter proceeded at a slower rate.

3.6 Effect of biosorbent dose

The effect of different doses of biosorbents on the removal of MB was carried out, and the results have been presented in Fig 4 (c). Results showed that at a biosorbent dosage of 25 mg, the percent removal was maximum (89%) where as the fenton modified system exhibits maximum efficiency of 93% at 50 mg dosage. The adsorption efficiency decreases with increase in the biosorbent dose which can be due to saturation of adsorption sites. At high biosorbent dosage, partial aggregation occurs which reduces the effective surface area.[20]

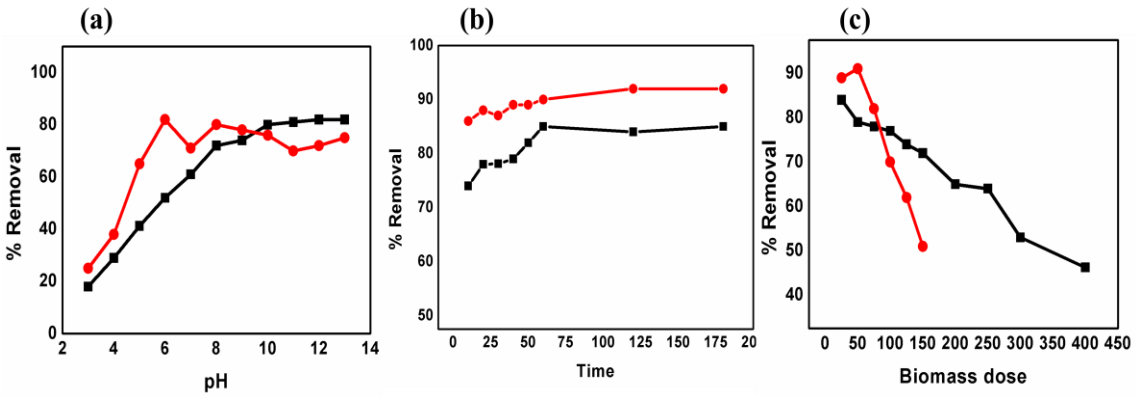

Fig. 4 Effect of **(a)** pH, **(b)** time and **(c)** biomass dosage on biosorption efficiency of SR (--) and FM (--). (Temperature = 30 ^{0}C, Volume = 75 ml, rpm = 150)

3.7 Isotherm analysis

The equilibrium study of biosorption of MB onto SR and FM were conducted at different initial dye concentrations (4-12 mg/L). The data obtained were fitted to the

Langmuir [21] and Temkin[22] isotherm models using linear methods and the fits are depicted in Fig. (5). The Langmuir isotherm model is expressed in the linear form as

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_m}\right)\left(\frac{1}{C_e}\right) + \frac{1}{q_m} \quad (4)$$

where q_m (mg/g) and K_L (L/g) are Langmuir constants related to adsorption capacity and energy. The isotherm parameters as well as the correlation coefficients were calculated and are given in Table 2. The maximum monolayer adsorption capacity (q_m) of MB onto SR and FM are 58.83 and 62.5 mg/g respectively. On further analysis of Langmuir equation, we get

$$R_L = \frac{1}{1+K_L C_0} \quad (5)$$

Where Co is initial concentration of MB (mg/L). The dimensionless parameter[23] (R_L) is considered as more reliable indicator of adsorption i.e, for favourable adsorption $0<R_L<1$.

The Temkin isotherm has generally been expressed as

$$q_e = B \ln A + B \ln C_e \quad (6)$$

where $B=RT/b$. B is the Temkin constant related to heat of sorption (J/mol); A is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol. K) and T is the absolute temperature (K). The values of A and B were calculated from the plots (Fig.5(b). The coefficient of correlation of both SR and FM was high, showing a good linearity (Table 2).

Table 2: Langmuir and Temkin Isotherm parameters.

Isotherm	**Parameters**		**Values**
		SR	**FM**
Langmuir	qm(mg/g)	51.824	62.5
	K_L(L/g)	0.0871	0.0747
	R^2	0.979	0.885
	R_L	0.43	0.46
Temkin	A (L/g)	1.059	2.035
	B (J/mol)	19.45	8.047
	R^2	0.928	0.975

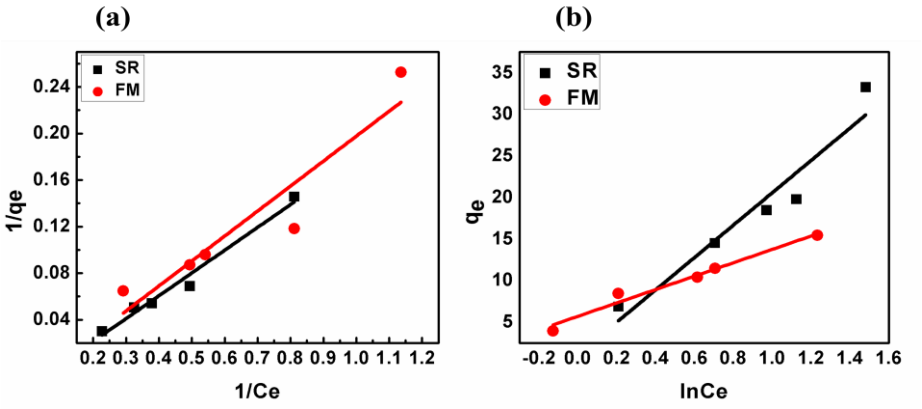

Fig. 5: Isotherms of MB onto SR and FM at 30°C: **(a).** Langmuir **(b)** Temkin

3.8 Kinetic studies

Two kinetic models (i) Lagergren's pseudo-first order model (Eq. 7), (ii) Ho's pseudo-second order model (Eq. 8) were used to predict sorption kinetics.[24,25]

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

where k_1 is the rate constant of pseudo-first-order and k_2 is the rate constant of pseudo-second-order adsorption. It can be seen that for most initial concentrations, data do not fit the pseudo-first-order model. Further analysis by using the pseudo-second-order model [Fig. 6 (a ,b,c & d)] straight lines were obtained for both SR and FM at 30°C and 40°C . The theoretical $q_{e(cal)}$ values and experimental $q_{e(exp)}$ at different initial concentrations were very close (Table 2). Therefore, it can be concluded that pseudo-second order model provides a better correlation.

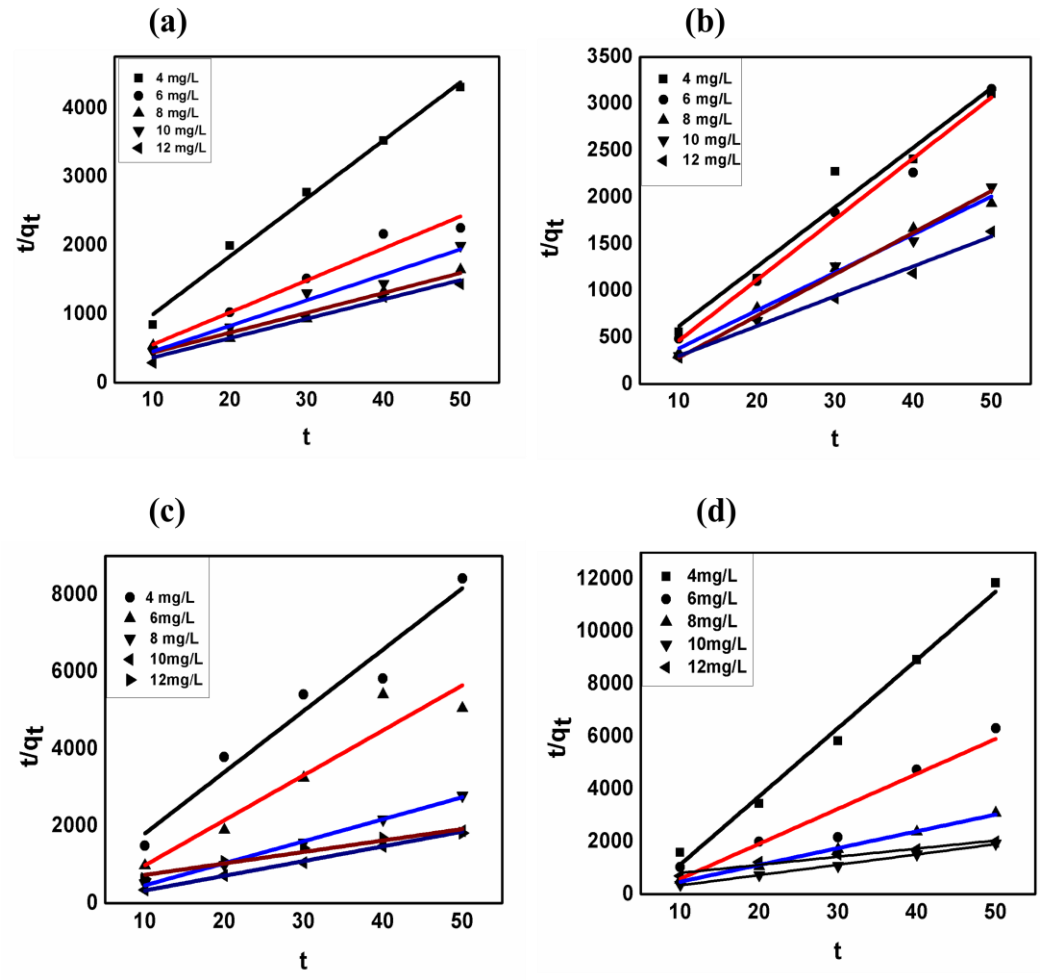

Fig. 6 (a) & (b) Pseudo second order kinetic plot of MB onto SR at 30˚C & 40˚C.

(c) & (d) Pseudo second order kinetic plot of MB onto FM at 30˚C & 40˚C

Table 3 : Pseudo-second-order kinetic parameters for MB onto **(a)** SR **(b)** FM

(a)

Initial conc.mg/L	Pseudo-second-order kinetics at 30^0C (SR)				Pseudo-second-order kinetics at 40^0C (SR)			
	K_2	$q_{e(exp)}$	$q_{e(cal)}$	R^2	K_2	$q_{e(exp)}$	$q_{e(cal)}$	R^2
4	0.047	11.5	11.8	0.991	0.024	17.0	15.7	0.956
6	0.024	22.2	21.4	0.966	0.023	15.8	15.4	0.991
8	0.032	25.2	24.4	0.957	0.06	24.3	24.6	0.990
10	0.020	27.7	26.9	0.978	0.01	23.8	22.4	0.989
12	0.027	29.5	28.4	0.995	0.012	27.0	25.7	0.986

(b)

Initial conc. mg/L	Pseudo-second-order kinetics at 30^0C (FM)				Pseudo-second-order kinetics at 40^0C (FM)			
	$q_{e(exp)}$	$q_{e(cal)}$	R^2	K_2	$q_{e(exp)}$	$q_{e(cal)}$	R^2	
4	0.118	8.1	6.289	0.959	0.046	7.1	5.849	0.990
6	0.072	9.5	8.569	0.913	0.023	6.68	7.508	0.919
8	0.029	18.48	17.50	0.997	0.024	13.9	15.645	0.997
10	0.026	29.04	26.17	0.988	0.025	27.03	25.465	0.998
12	0.020	34.68	33.61	0.961	0.019	33.736	32.352	0.963

3.9 Effect of Desorption Time and Concentration

Studies showed that HNO_3 and NaOH are the most suitable desorbing agents for SR and FM respectively. Figure 7 (a) and (b) give the variation of desorption efficiency with time at different concentrations of these agents. It was found that desorption efficiency was maximum for 0.6 N HNO_3 for SR and 0.4 N NaOH for FM. The equilibrium time is shorter (10 minutes) for desorption of SR and FM. The higher concentration of exchangable ions provides greater concentration gradient at the solid−liquid interface. The greater driving force of the concentration gradient may shorten the equilibrium time.[26]

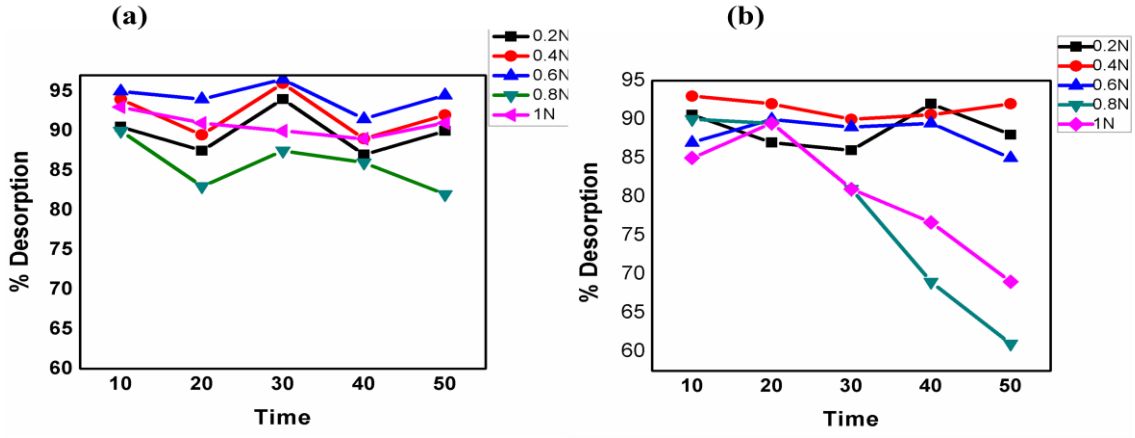

Fig. 7 Effect of time and concentration of **(a)** HNO_3 for SR & **(b)** NaOH for FM

3.10 Recycling of Biosorbent

Recycling of SR and FM have been carried out by biosorption of MB and desorption using 0.6 N HNO_3 & 0.4 N NaOH solutions. From Fig. 8 we can see that adsorption capacity is retained even after the fourth cycle.

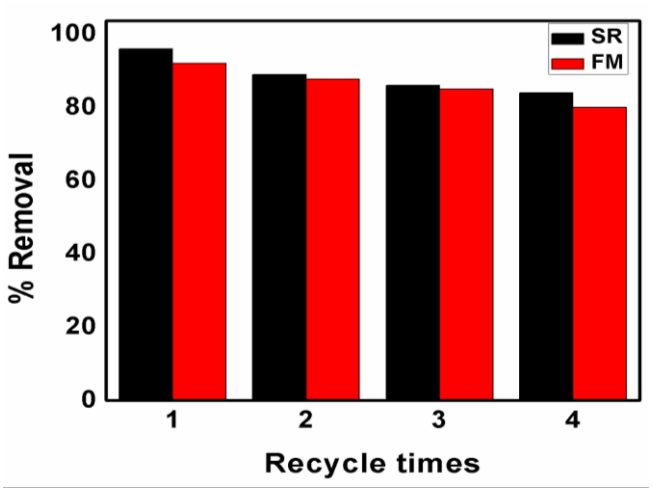

Fig. 8 The effect of recycle times on adsorption capacity of SR and FM.

CONCLUSION

We investigated the biosorption of methylene blue from aqueous solution using the weed, Sida rhombifolia and its fenton modified form. The parameters such as biosorbent dose, initial concentration of dye, stirring time and pH were optimized as 25 mg ,8 mg/L, 30 minutes & 12 for SR and 50 mg, 8 mg/L, 30 minutes & 6 for FM respectively. The Langmuir and Temkin isotherm models were found to be suitable in describing the equilibrium of the biosorption process. The kinetic study revealed that the adsorption process follows pseudo second order model. HNO_3 (0.6 N) & NaOH

(0.4 N) were found to be the most suitable desorbing agents for SR and FM respectively. The regeneration studies showed that the biosorbent is reusable. This indicates the commercial application of the biosorbent for effluent treatment. The results demonstrated that Fenton modification improves the adsorption efficiency of SR.

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