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Reduction of Azo Dye from Aqueous Solution using Acid Treated Aquatic Macrophytes

R. Sivashankar, A. B. Sathya, K. Vasantharaj, V. Sivasubramanian*

Department of Chemical Engineering, National Institute of Technology Calicut, Kerala.

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Abstract

Azo compounds constitute the largest and the most diverse group of synthetic dyes and are widely used in a number of industries such as textile, food, cosmetics and paper printing. They are generally recalcitrant to biodegradation due to their xenobiotic nature. However, aquatic macrophytes are highly versatile in reduction of azo dyes due to their porous nature. In this study, adsorption of an industrial azo dye Metanil Yellow onto acid treated and non-treated biosorbent is investigated. In addition, the study emphasize on identifying the factors exerting the strongest influence on adsorption of dye. The effect of the process parameters such as contact time, adsorbent dose, pH and agitation speed are reported. The contact time of 120 min is found to be sufficient for the adsorption to reach equilibrium. The pseudo first & second order models are used to describe the kinetic data, and the rate constant is therefore evaluated. The dye adsorption to biosorbent is characterized by monolayer isotherm and caused by adsorption with relatively strong uptake. The Langmuir and Freundlich models adsorption are applied to describe the isotherm equilibrium and to determine its constants. The Langmuir and Freundlich models agree well with the experimental data with an adsorption capacity of 91.743 & 85.179 mg of dye per gram of acid treated and non-treated biosorbent respectively. A better fixation was obtained at acidic pH.

Keywords: *Aquatic macrophytes; Dye; Desorption; Equilibrium studies; Sorption.*

1. INTRODUCTION

Most of the industries like textile, rubber, paper, leather, plastics, cosmetic, printing, etc. use dyes and discharge substantial amount of coloured effluents (Banat *et al*. 2003; Ozcan *et al.* 2004,2007). About 100,000 different commercially available dyes exist and more than $7X10^5$ tonnes per year are produced (Pearce *et al*. 2003; McMullan *et al*. 2001; Crini, 2006; Gomez *et al*. 2007). It is estimated that roughly 10-15% of the dye passes wastewater stream during the dying process (Gomez *et al*. 2007). Amongst several dyes, azo dyes constitute an important class of synthetic, colored, organic compounds, which are categorized by the presence of one or more azo bonds (–N=N–). Especially azo dyes which contribute to about 60% of all used dyes are difficult to degrade due to their complex structure and synthetic nature (Fu *et al*. 2001). They are toxic, sometimes generate aesthetic problems and have been reported for possible mutagenic and carcinogenic effects (Chang *et al*. 2001). It also affects photosynthetic activity in the water body. Further, degradation of these dyes leads to form toxic amines (Chung *et al*. 1978). Therefore, the removal of these coloured compounds from effluent turns out to be significant. Conventional methods like physical, chemical and biological processes such as adsorption (Maheria and Chudasama, 2007), coagulation (Shi *et al*. 2007), oxidation (Emmert *et al*. 2008), reduction (Shu *et al*. 2007), filtration (Capar *et al*. 2006) and biological treatment Georgious *et al*. 2006) are widely

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***V. Sivasubramanian** **Tel. no.: +919446547421**
E-mail: siva@nitc.ac.in

employed for separation of dyes from wastewater. Out of which, physical adsorption process at solid-liquid interface is identified to be a potent, efficient and economic method for declining the concentration of soluble dyes in effluents. Numerous adsorbing materials for removal of dyes have been investigated such as activated carbon (Valix *et al*. 2006), alumina (Kannan *et al*. 2008), clay (Liu *et al.* 2007), silica xerogel (Pavan *et al*. 2008), titania (Bourikas *et al.* 2005), titania–silica mesoporous materials (Messina et al. 2006), waste materials (Gupta *et al.* 2008, 2007, 2006; Karthikeyan and Sivakumar, 2012) and many other materials. However, the high costs of manufacturing and regeneration makes these adsorbents an expensive material (San *et al.* 2001). For these reasons, many approaches have been attempted in recent years to produce low-cost alternatives (Gupta *et al*. 2009). A low-cost adsorbent is defined as one which is abundant in nature, or is a by-product or waste from industry and requires little or no processing (Aksu *et al.* 2005). The use of agricultural solid wastes not only transforms the waste into useful material, but also mitigates the problem of disposal of these wastes (Low *et al.* 1995; Waranusantigul *et al.* 2003).

In this contribution, we have investigated the possibility of aquatic macrophytes, *Salviniamolesta* (SM) modified with different acids such as strong and weak acid, for the first time used and evaluated as a possible biosorbent for the removal of azo dye Metanil Yellow (MY) from aqueous solution. The objective of this study is to investigate the effect of initial MY concentration, pH, agitation speed and contact time on the adsorption process. Kinetics and mass transfer studies have been performed and the results have been analyzed by applying conventional theoretical methods.

2. MATERIALS & METHODS

2.1 Preparation of chemically modified SM

Live SM was collected from riversides and ponds in the region of Calicut, India. The collected SM was thoroughly washed with warm water and sun dried for 15 days. The dried particles was subjected to grinding and sieved for equal sizes approximately mesh size of 175. The dried and sieved macrophyte was then subjected to acid treatment at different concentration (1M, 10M) using 4 different acids such as nitric acid, hydrochloric acid, acetic acid and nitrous acid.

2.2 Dye stuff

The dye chosen for this study is a commercial grade Metanil Yellow (MY). A desired quantity of dye was dissolved in 1L of distilled water to prepare stock solution. For the batch study, an aqueous working solution of dye of desired concentrations were prepared from stock solution by successive dilutions.

2.3 Procedure for dye adsorption

Raw and chemically modified SM was added to the aqueous solution of azo dye at a known concentration.The suspension was shaken for different interval of time ranging from 5 to 150 min at room temperature. An aliquot was filtered and the dye concentration in the clear solution was determined calorimetrically using spectrophotometer at the maximum wavelength of the dye. The amount of dye adsorbed onto SM biomass at time *t*, q_t (mg/g) was calculated by the following mass balance relationship:

$$q_t = \frac{(c_o - c_t)V}{m} \qquad (1)$$

And dye removal efficiency i.e. % of adsorption was calculated as

$$\% Adsorption = \frac{C_o - C_t}{C_o} X100 \qquad (2)$$

whereC_0 is the initial dye concentration (mg/L), C_t is theconcentration of dye at any time *t*, *V* is the volume of solution(L) and *m* is the mass of SM powder (g).

Table 1. .Effect of modified SM on % removal*

Types of SM	Acid concn.	% Removal
Raw SM (A)	-	85.17
HNO_3 treated SM (B)	01M 10M	95.34 99.73
HCl treated SM (C)	01M 10M	88.34 91.45
CH_3COOH treated SM (D)	01M 10M	85.12 89.65
HNO_2 treated SM (E)	01M 10M	85.99 90.46

Concentration of dye: 10mg/L, amount of adsorbent: 1gm/ 100ml, pH: 4 at room temperature, agitation time: 120min.

3. RESULTS & DISCUSSION

3.1 Effect of acid treatment on rate of adsorption

The result obtained in Table.1 indicates that increases in acid concentration from 1M to 10M leads to increased adsorption rate. Among the raw (A) and modified SM with HNO_3 (B), HCl (C), CH_3COOH (D), HNO_2 (E), modified SM (B) showed better result than the others. In addition, it was observed, effect of strong acids found to be approximately cent percent removal than the weak acids. This may be due to the reason, degree of dissociation. The strong acids dissociates completely, whereas the weak acids doesn't. Therefore the presence of cationic group in acid treated adsorbent attracts the anionic group of dye results in effective removal of dyes from aqueous solution. Concerning the data provided in the table, it can be observed that the percent dye adsorption follow the order B>C>E> D>A for macrophytes treated with all acid concentrations. The structural configuration, size and surface area of the adsorbent and adsorbate also play a great role in percent dye adsorption.

3.2 Evaluation of equilibrium time

Fig.1 shows that the percent dye adsorption increases with time for both treated and non-treated SM biomass and achieves equilibrium after 120 min of agitation. During a regular interval of time, an aliquot was drawn and centrifuged at 10000 rpm for 15 min. The residual dye concentration was measured to determine the percentage dye removed, while the optimum contact time for equilibrium was determined from the plot.

3.3 Effect of pH

Fig. 2 shows the pH of the medium plays a dominant role in the rate of dye adsorption.The modified SM shows a better result of maximum dye removal of 99.73% than raw SM at 3 pH. The rate of dissociation of the dye as well as the ionization of the cationic substrate dominates in the acidic medium. The maximum dye removal of raw SM was 85.3% at neutral pH. It was observed that, the adsorption rate of both types of SM was found to decrease on increasing pH from its optimum. Therefore, it is an evident that the interaction between dye molecules and biosorbent is basically a combined result of charges on dye molecules and the surface of the biosorbent.

3.4 Effect of adsorbent dosage

Fig. 3 shows that the percent dye adsorption increases by increasing the amount of substrate, in the range from 0.2 to 1.5 g and then levels impede after approximately 1.0 g substrate/100 ml. Leveling off can be explained in terms of diminution of dye in solution and/or accumulation of dye molecules on the surface of substrate giving rise to hindering the rest of dye to diffuse inside the biosorbent substrate matrix.

3.5 Effect of agitation speed

Adsorption studies were carried out by varying the agitation speed from 50 to 300 rpm to find out the speed at which the liquid boundary layer played insignificant role. The results are shown in Fig. 4. The adsorption efficiency increased with increase in agitation speed up to 300 rpm and thereafter, it manage to achieve a steady state. This indicates that the thin liquid film surrounding the adsorbent plays an insignificant role disallowing the adsorbate to reach the adsorbent surface.

3.6 Desorption profile

This was carried out with adsorbate loaded adsorbents (both raw and modified SM) obtained from batch processes, in which the adsorbate solutions (10 mg/L) were treated with optimum dosage of adsorbents for optimum contact time.The equilibrium time required for desorption of azo dye from raw and modified SM was found to be 120 min.Maximum desorption of 82.25% and 74.89% was obtained at 120 min for modified and raw SM respectively.

3.7 Adsorption Isotherm

3.7.1 Langmuir isotherm

The Langmuir isotherm is based upon an assumption of monolayer adsorption onto a surface containing finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate on the plane of the surface. Langmuir isotherm is given by (Langmuir, 1918; Freundlich, 1906),

$$q_e = \frac{QbC_e}{1+bC_e} \qquad (3)$$

where, C_e is the equilibrium concentration of a dye in solution (mg/L), q_e is the amount of dye sorbed on to fungal biomass (mg/g), Q is the Langmuir constant related to sorption capacity (mg/g), b is the Langmuir constant related to sorption energy (L/mg). However, the linear form of Langmuir equation can be written as:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \qquad (4)$$

Data obtained for the sorption of dye in the concentration range of 10 to 100 mg/L of MY dye were fitted to the Langmuir isotherm (Fig. 5). The computed correlation coefficients and the Langmuir constants of raw modified SM for MY dye were represented in Table 2. The R^2 values were above 0.989 & 0.996 for type A & B adsorbent respectively. Further, the maximum sorption capacity of raw and modified SM for MY dye were found to be 85.17 and 91.74mg/g respectively.

3.7.2 Freundlich isotherm

It is another approach for adsorption on amorphous surface. It assumes the heterogeneity of surface and the exponential distribution of active sites and their energies (Freudlich, 1906). The Freundlich isotherm was tested in the linear form

$$\log q_e = \log k_f + \frac{1}{n}\log C_e \qquad (5)$$

where, C_e is the equilibrium concentration of a dye in solution (mg/L), q_e is the amount of dye sorbed on to adsorbent (mg/g) and K_f & *1/n* are Freundlich constants. When log q_e was plotted against log C_e, a linear plot was obtained. Freundlich plot obtained for MY dye is shown in fig. 6. Freundlich constants 1/n (Intensity of adsorption) and K_f (Adsorption capacity) were computed and presented in Table. 2.

3.7.3. Evaluation of seperation factor

Another dimensionless equilibrium parameter (R_L) can be estimated using the following relation. The equilibrium parameter, R_L, is used to predict if an adsorption system is ‘‘favorable’’ or ‘‘unfavorable’’. $R_L>1.0$ (Unfavourable), $R_L=1.0$(Linear), $0<R_L<1.0$ (Favorable) and $R_L=0$(Irreversible).

$$R_L = \frac{1}{1+bC_0} \qquad (6)$$

where b is the Langmuir constant and C is the initial dye concentration in the solution (mg/L). R_L factor

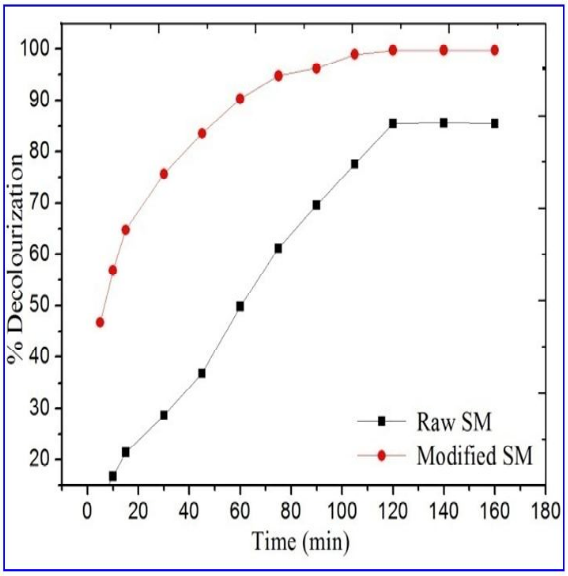

Fig. 1: Evaluation of equilibrium time

*Condition: concentration of dye: 10mg/L, amount of adsorbent: 1gm/100ml, pH: 4 at room temperature.

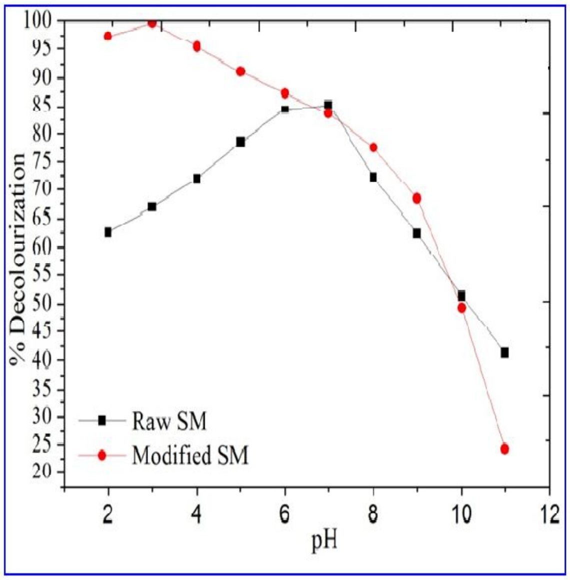

Fig. 2: Effect of pH

*Condition: concentration of dye: 10mg/L, amount of adsorbent: 1gm/100ml, agitation: 200rpm at room temperature

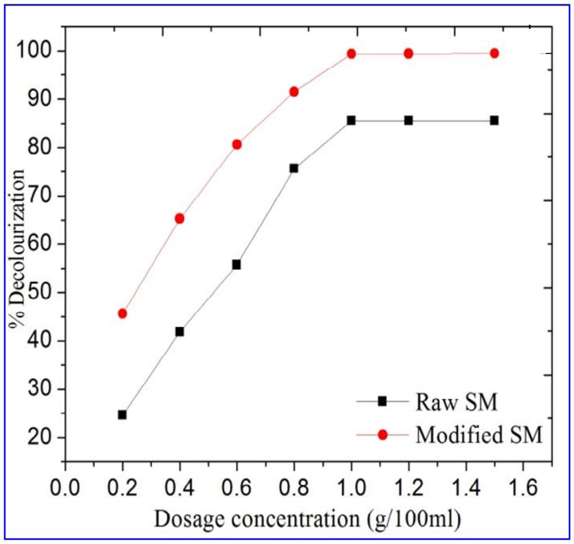

Fig. 3: Effect of adsorbent dosage concentration

*Condition: concentration of dye: 10 mg/L, agitation speed: 200 rpm at optimum pH and at room temperature

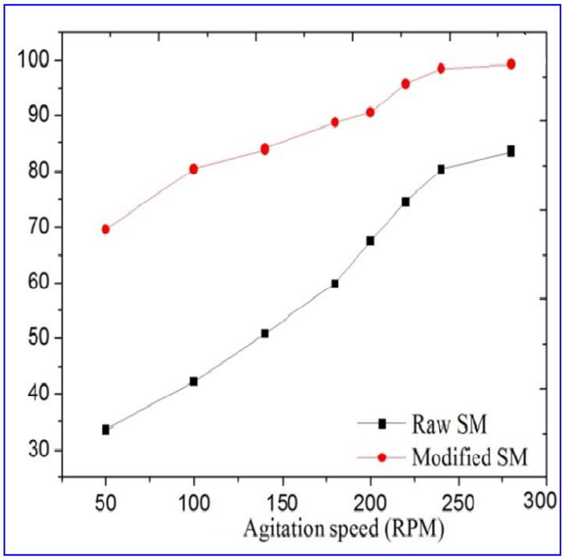

Fig. 4: Evaluation of equilibrium time

*Condition: concentration of dye: 10mg/L, amount of adsorbent: 1gm/100ml, at optimized pH and at room temperature provides an indication of type of isotherm. The adsorbent surface is proportional to the amount of dye values of R_L were between 0 and 1 for selected dyes which indicate the applicability of the Langmuir isotherm.R_L was calculated for 10mg/L dye concentration as 0.88 for both raw and modified SM (Table. 3), which indicates that this adsorption system of MY dye and SM is favourable.

3.8 Adsorption kinetics

3.8.1 Lagergrens first order model

The adsorption kinetics of batch contact time process is well described by popularly and frequently used Lagergren's first order rate equation (Baskaralingam *et al*. 2006). The specific rate constants for both the systems (raw &modified SM) were calculated using following mathematical form:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}t}{2.303} \qquad (7)$$

whereq_e and $q_t$denote the amount adsorbed at equilibrium and at any time *t*, respectively. The linear graph of log (q_e-q_t) versus time suggests involvement of first order kinetics fig. 7 in both the cases. The values of rate constant (k_{ad}) for both the adsorbents were calculated using the values of slopes of these straight lines.

3.8.2 Ho's pseudo second order model

The pseudo-second order model proposed by Ho and McKay can be represented in the following linear form

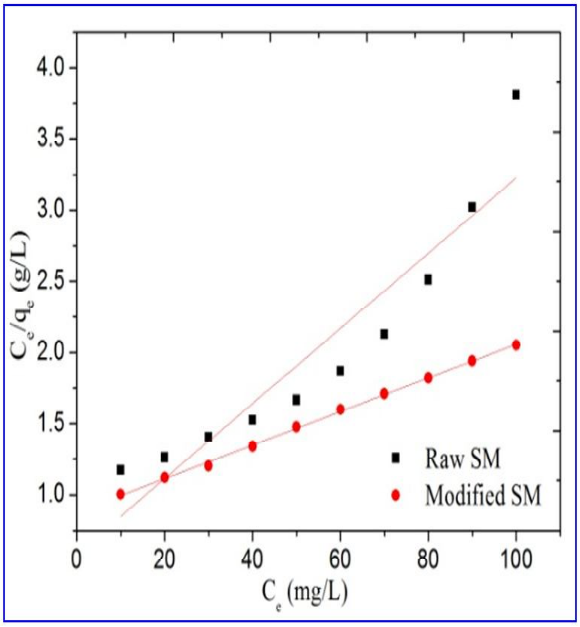

Fig. 5:Langmuir plot

*Condition: concentration of dye: 10 -100mg/L, amount of adsorbent: 1gm/100ml, agitation speed: 250rpm, pH: 7(raw SM) & 3(Modified SM) at room temperature.

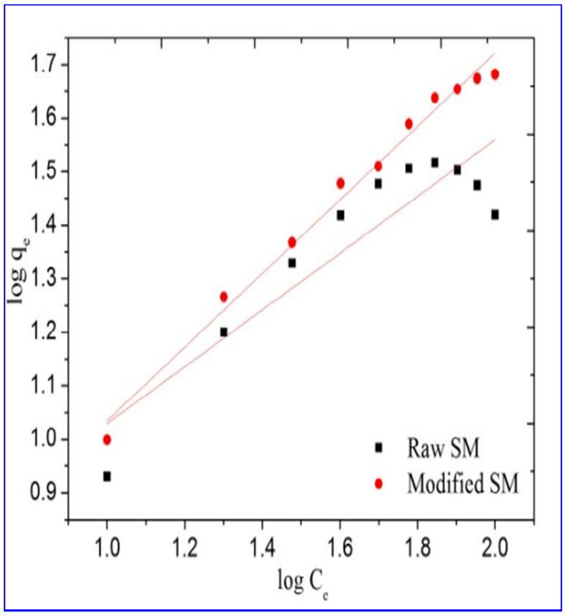

Fig. 6: Freundlich plot

*Condition: concentration of dye: 10 -100mg/L, amount of adsorbent: 1gm/100ml, agitation speed: 250rpm, pH: 7(raw SM) & 3(modified SM) at room temperature

Table 2. Adsorption Isotherm

Type of adsorbent	Langmuir Constants		R^2	Freundlich Constants		R^2
	Q(mg/g)	b(L/mg)		K	1/n	
Raw SM (A)	85.17	0.0125	0.9899	2.225	1.4547	0.8097
Modified SM (B)	91.74	0.0134	0.9960	3.160	1.887	0.9857

*Condition: concentration of dye: 10-100mg/L, adsorbent dosage: 1g/100ml, agitation speed: 200rpm, pH: optimum value, temperature: room temperature.

Table 3. Adsorption kinetics*

Type of adsorbent	R_L	Initial dye Conc. (mg/L)	q_e(exp) (mg/g)	Pseudo I order kinetic model		R^2	Pseudo II order kinetic model		R^2
				K_{adl} (1/min)	q_e (mg/g)		K (gm/mg/min)	q_e(Cal) (mg/g)	
Raw SM (A)	0.88	10	7.2	0.0219	3.712	0.7829	$5.71X10^{-3}$	7.8	0.8541
Modified SM (B)	0.88	10	9.3	0.0115	1.124	0.9548	$2.21X10^{-3}$	10.6	0.9951

*Condition: optimized experimental parameters

Table 4. .Intraparticle diffusion*

Type of adsorbent	Initial dye concentration (mg/L)	Weber-Morris model	R^2	Dumwald Wagner model	R^2
		K_{int}		K	
Raw SM (A)	10	0.9082	0.9819	0.3943	0.9518
Modified SM (B)	10	0.5766	0.9518	0.2504	0.9819

*Condition: optimized experimental parameters

$$\frac{t}{q_t}=\frac{1}{k_2 q_e^2}+\frac{t}{q_e} \qquad (8)$$

whereq_t and q_e are the amount adsorbed at time t and at equilibrium (mg/g), respectively.

k_2 is the pseudo-second order rate constant for the adsorption process (g/mg/min). The rate parameters k_2 and q_e can be directly obtained from the intercept and slope of the plot of t/q_t versus t (Fig. 8). The plot of pseudo-second order kinetics gives a linear relationship which allows computation of k_2 and q_e without having known any parameter beforehand. The results showed that the adsorption system followed the Eq. (8) for the entire adsorption period, with regression coefficients higher than 0.995 for the concentration range used in this study. Comparison of results with the correlation coefficients for the first-order kinetic and second-order kinetic models is shown in Table 3. For both raw and modified SM, the second order model is the best fit model for experimental kinetic data, this is because of the value of the calculated $q_e$approve very well with the experimental data and R^2 value is higher for all adsorbents. These results also indicated that the applicability of this kinetic equation and the second-order nature of the adsorption process of MY on SM particles.

3.9 Intraparticle diffusion

3.9.1 Weber-Morris model

Intraparticle diffusion model assumes that the film diffusion is negligible and intraparticle diffusion is the only rate controlling step, which is usually true for well-mixed solutions. Weber-Morris found that in many adsorption cases, solute uptake varies almost

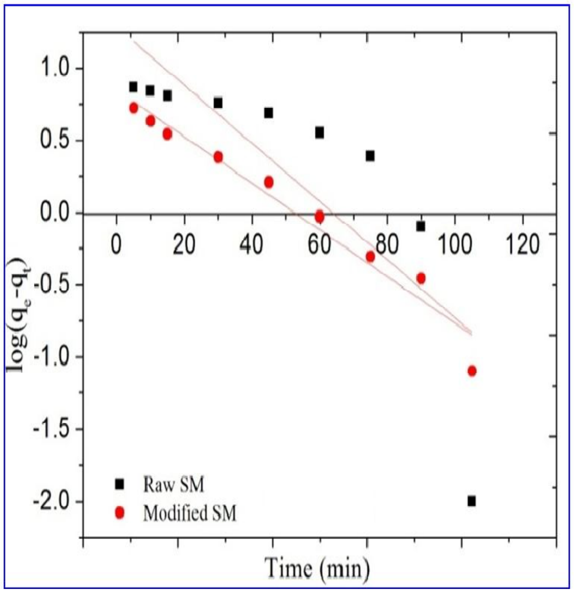

Fig. 7: Pseudo Ist order plot

*****Condition: concentration of dye: 100mg/L, amount of adsorbent: 1gm/100ml, agitation speed: 250rpm, pH: 7(raw SM) & 3(modified SM) at room temperature.

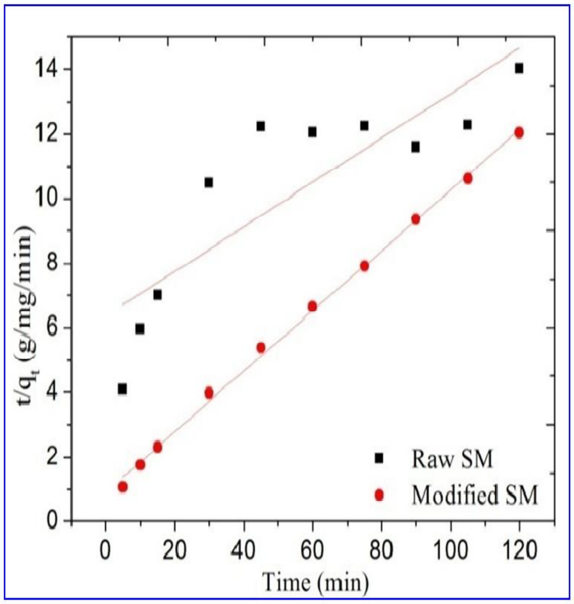

Fig. 8: Pseudo IInd order plot

*Condition: concentration of dye: 10mg/L, amount of adsorbent: 1gm/100ml, agitation speed: 250rpm, pH: 7(raw SM) & 3(modified SM) at room temperature.

proportionally with $t^{1/2}$ rather than with the contact time t,

$$q_t = k_{\text{int}} t^{1/2} \qquad (9)$$

where, k_{int} is the intraparticle diffusion rate constant. According to Eq. (9), a plot of q_t Vs $t^{1/2}$ should be a straight line with a slope k_{int} when the intraparticle diffusion is a rate-limiting step. For Weber-Morris model, it is essential for the q_t Vs $t^{1/2}$ plot to go through the origin if the intraparticle diffusion is the sole rate-limiting step. However, it is not always the case and adsorption kinetics may be controlled by film diffusion and intraparticle diffusion simultaneously. Thus, the slope is not equal to zero. Fig. 9 shows the correlation between solute uptake and time with linear fitting. The value of k_{int} was found to be higher for modified SM than other. The intraparticle diffusion rate constant was calculated with effect to its regression coefficient for both adsorbents are presented in Table 4.

3.9.2 *Dumwald-Wagner model*

Dumwald-Wagner proposed another intraparticle diffusion model (Wang *et al.* 2004). The simplified form of equation is

$$\log(1 - Q^2) = -\frac{K}{2.303} t \qquad (10)$$

Where,

$$Q = \frac{q_t}{q_e}$$

A plot of log $(1-Q^2)$ Vs t should be linear and the rate constant K can be obtained from the slope. The model fit was shown in fig. 10.

This model proved to be reasonable to model different kinds of adsorption systems. Comparing the

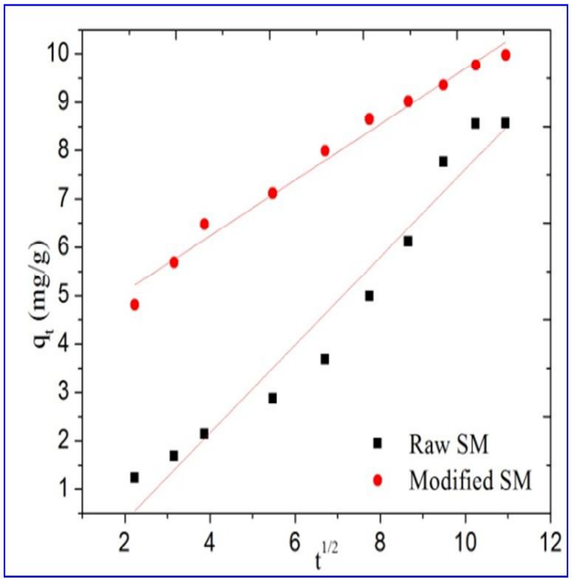

Fig. 9: Weber Morris plot
*Condition: optimum experimental parameters

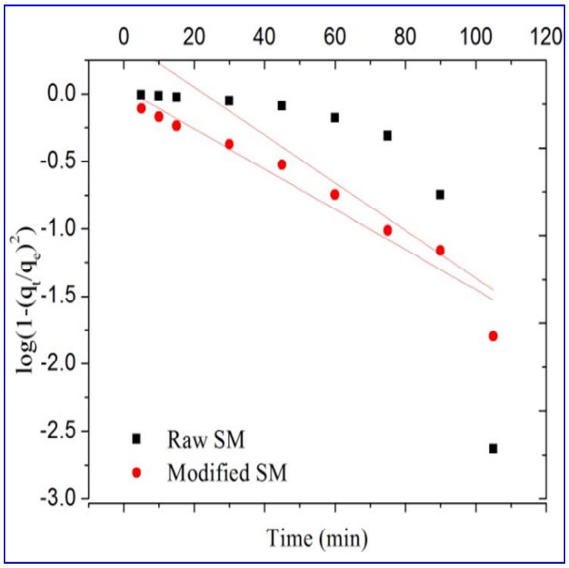

Fig. 10: Dumwald-Wagner plot
*Condition: optimum experimental parameters

results Table 4 of Weber Morris and Dumwald-Wagner intraparticle diffusion models with correlation coefficient, Weber-Morris found to be best fit for the experimental diffusion data according to the diffusions constant which approve very well with the experimental data and R^2. Therefore, it is understood that this experiment fit to intraparticle diffusion between MY and SM.

4. CONCLUSION

The present study shows that nitric-acid treated aquatic macrophyte (*Salviniamolesta)* can be used as an adsorbent effectively for the removal of MY dye from aqueous solutions. The adsorption capacity was strongly dependent on the pH. The uptake of MB increased with increase in pH. The maximum sorption was achieved at the pH of 3.0. The pseudo-second-order kinetics could explain the observed data, which suggested that chemisorption significantly contributed to the adsorption process. The adsorption isotherm followed Langmuir isotherm model. The separation factor R_L was used for the prediction, that adsorption of MY on to modified SM is favorable and spontaneous in nature. Further, rate limiting step, diffusion was explained using intraparticle diffusion models. The overall rate of dye uptake was found to be controlled by external mass transfer at the beginning of adsorption, then gradually changes to intraparticle diffusion controlled at a later stage.

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