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Biosorption of Hazardous Azo Dye Metanil Yellow using Immobilized Aquatic weed

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Abstract: ***Release of coloured textile effluent in to aquatic environment is detrimental as they prevent penetration of light in to water, thereby affecting aquatic life and creates harmful water. Biosorption is an alternative treatment available other than physicochemical and biological methods to treat these toxic effluents. This study investigates the potential of water hyacinths to adsorb hazardous azo dye metanil yellow from aqueous solution. Metanil Yellow, is a widely used toxic dye containing one or more azo bonds (-N=N-). Metanil Yellow is used in number of industries such as textile, dyeing, food, cosmetics, paper printing industries and with textile industries as large consumers. Biosorption process was carried out using immobilized dead aquatic weeds. The influences of adsorption parameters such as initial dye concentration, pH, contact time, adsorbent dosage, agitation speed, and temperature were evaluated and optimized. Further the mechanism of biosorption earned good fits for Langmuir isotherm model. The pseudo first order and second order kinetic model described well the experimental data. The batch studies clearly suggest that the maximum adsorption capacity for the removal of Matanil Yellow dye were obtained at 6 pH and up to 98.8 % color removal is achieved with contact time of 240mins. Further desorption techniques were employed to recover the loaded pollutants and it is found to be the reusability of the immobilized aquatic weeds after storage may be a potential advantage in wastewater treatment.***

Keywords: ***Biosorption, Immobilized waterhyacinth, Metanil Yellow dye, Desorption, Wastewater treatment.***

Introduction

The utilization of synthetic chemical dyes in diverse industrial processes has increased significantly over the last decade, which results in release of dye-containing industrial effluents into the land and aquatic systems [1]. Most of these dyes are found to be toxic in nature and are xenobiotic [2]. The dye solution discharged sometimes undergoes anaerobic degradation to form carcinogenic compounds [3].

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The survival of various aquatic lives is put to risk since the discharge of highly coloured wastewaters in to aquatic system can block the penetration of sunlight and oxygen, thereby arresting photosynthesis of aquatic plants and also the dyes becomes carcinogenic [4]. These dyes linger in aquatic system to longer period if discharged with-out adequate treatment. The Azo dyes are toxic when it is absorbed through skin, respiratory and intestinal tract and may act as a skin, eye or respiratory irritant. These dyes are harmful if swallowed or inhaled and act as a carcinogen for chronic exposure. It may even cause genetic mutations on continuous exposure [5]. Metanil Yellow (3-(4-Anilinophenylazo) benzene sulfonic acid sodium salt) is an organic compound which constitutes one or more azo bonds (–N=N–), used in number of industries such dyeing industry, food industry, cosmetics, paper printing industries and with textile industries as large consumers [6]. Therefore, it is vital responsibility of the industries to remove dyes from the effluent before discharged in to the environment. This study investigates the removal of Acid dye 36 (metanil yellow) due to its colossal application and known for its strong adsorption on to solids. Though there are several methods of dye removal, such as membrane separation process, membrane filtration, microbial degradation, coagulation, electrochemical, chemical oxidation, reverse osmosis, none of them were completely successful in removing the color from wastewater [7, 8].

Adsorption is a surface phenomenon wherein substance adheres to the surface of the other (on an atomic or molecular scale) has been applied for color removal using immobilized aquatic weeds [9]. Report suggests that the water hyacinth has a potential adsorbing capacity due to their porous nature [10]. In this study, the potential of water hyacinth in adsorbing the Acid Yellow 36 is investigated in batch studies. The influence of adsorption parameters such as initial dye concentration, pH, contact time, adsorbent dosage, agitation speed, and temperature were evaluated and optimized. Further the mechanism of biosorption was studied using Langmuir and Freundlich isotherm model. The kinetics of the process was evaluated using pseudo first order and second order reaction kinetic models.

Materials and methods

Adsorbents (Aquatic Weed)

Aquatic weeds, water hyacinth were collected from ponds and river sides in the region of Calicut, India. The roots and leaves of the certain water hyacinth were washed with warm water several times and followed by soaking in 0.1M HCl for 20 min and again washed with double distilled water. Further, the biomaterials were dried in Hot air oven at 75°C for 12 hours. After drying, the biomaterials were crushed and powdered in Ball mill and then passed through sieve trays until the weeds are separated on different meshes. The desired size of sample was then immobilized using alginate immobilization method, which serves as immobilized adsorbents [10].

Adsorbate (Dye stuff)

The Acid dye 36 [Metanil Yellow (MY)] was procured from Sigma Aldrich was used as adsorbate without any purification. 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. NaOH and HCl solutions were used to adjust pH.

Measurement of decolourization

The Experiments were carried out in batch mode operation to investigate the effect of pH, agitation time, agitation speed, initial dye concentration, dosage of adsorbent with respect to percentage decolorization of MY dye. The absorbance of MY dye solution was measured using uv-vis spectrophotometer at maximum wavelenngth of λ_{max} = 660nm []. The initial and final absorbance obtained was used to determine the percentage decolorization with calibration curve.

$$\% \text{ Removal} = \frac{\text{Initial absorbance} - \text{Final absorbance}}{\text{Initial absorbance}} \times 100$$

Results and Discussion

Investigation of sorption parameters

A. Effect of pH

The effect of pH was studies by varying the pH of dye solution. The dye solution was prepared at various pH (2-10) using NaOH and HCl. The maximum percent removal of MY dye was 98.9% for the minimal test concentration of 10mg/L and 69.6% for the maximum concentration of 100mg/L at pH value of 6.0. Biosorption of dye on to immobilized adsorbents at extreme acidic and alkaline condition decreases the percent decolourization of MY dye (10-100mg/L) (Figure 1).

B. Effect of adsorbent dosage

The dosage concentration was varied (0.1 -1.2gm/100ml) to study the effect of dosage on colour removal from aqueous solution. Considering the dead aquatic immobilized weed, an optimum dye removal of 63.5 – 98.9% was observed at 1gm/100ml of adsorbent dosage (Figure 2). The availability of surface active sites determines the maximum decolourization for an optimized dosage.

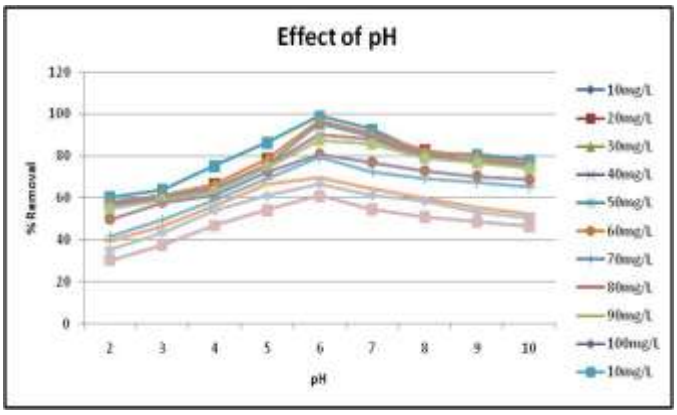

Figure 1. Effcet of pH on the removal of MY dye

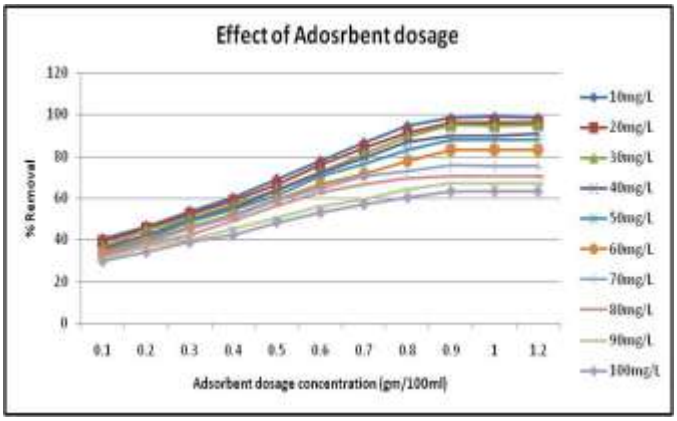

Figure 2. Effcet of adsorbent dosage on the removal of MY dye

C. Effect of agitation time and initial dye concentration

Equilibrium time required for maximum adsorption was determined for different initial dye concentration (10mg/L-100mg/L). The adsorption data of dye concentration versus agitation time on dye removal by immobilized biosorbent (Figure 3) indicated that the uptake of dye increased with increase in agitation time, but remained constant after the equilibrium time period whereas the percent dye removal decreased with an increase in the initial dye concentration in the solution. The equilibrium time required for the maximum removal of MY dye by immobilized biosorbent was 240 min at all the dye concentrations studied. The percent dye removal at equilibrium time was found to be 98.1% and 51.2% for the dye concentrations of 10 and 100 mg/L respectively.

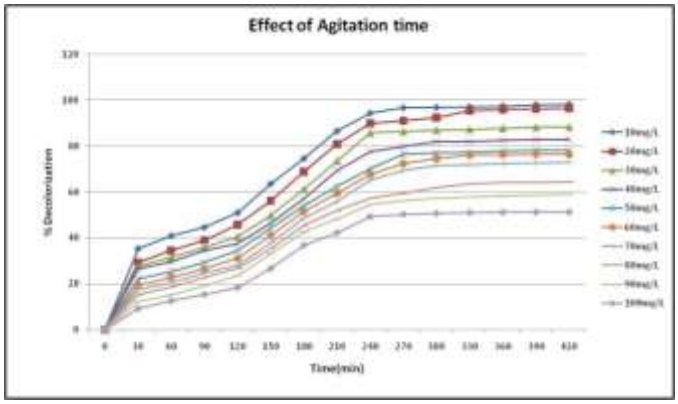

Figure 3. Effcet of agitation time and initial dye concentration

Desorption profile

Desorption of dye from used adsorbent was carried out (dye concentration:10-100mg/L) by changing the pH using 0.1M NaOH. The equilibrium time required for the desorption of various MY dye concentrations from Immobilized weed was found to be 120 min. Maximum desorption of 80.9% at 10 mg/L dye concentration and 56.1% at 60 mg/L was observed at 180 mins (Figure 4).

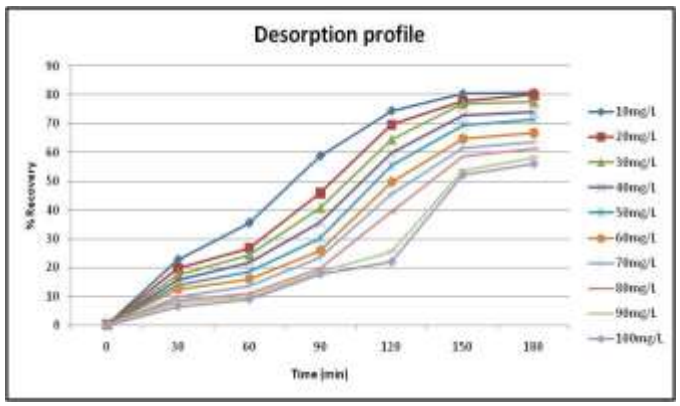

Figure 4. Effcet of agitation time and initial dye concentration

Adsorption isotherm

A. 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 [12],

$$q_e = \frac{QbC_e}{1 + bC_e}$$

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:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q}$$

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 (Figure 5). A plot of C_e / q_e versus C_e yields a straight line, the slope and intercept of which correspond to Q and b respectively. The computed correlation coefficients and the Langmuir constants for MY dye were represented in Table 1. The R^2 values were above 0.991. On analyzing the table, the maximum sorption capacity of immobilized water hyacinth for MY dye was found to be 9.9108mg/g.

B. 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 [13]. The Freundlich isotherm was tested in the linear form

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$

where, C_e is the equilibrium concentration of a dye in solution (mg/L), q_e is the amount of dye sorbed on to immobilized weed (mg/g) and K_f and 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 Figure 6. Freundlich constants 1/n (Intensity of adsorption) and K_f (Adsorption capacity) were computed from the slope and intercept of the plot. The computed correlation coefficients and Freundlich constants for the MY dye studied was presented in the Table 1.

TABLE I. LANGMUIR AND FREUNDLICH CONSTANTS

Langmuir Constants		R^2	Freundlich Constants		R^2
Q(mg/g)	b(L/mg)		K	1/n	
9.9108	0.1155	0.991	2.0137	0.741	0.969

The R^2 value was found to be 0.9690. However, the R^2 value of Langmuir equation for MY dye was higher than Freundlich equation. The constant 1/n showed the sorption intensity and its fractional value (0<1/n<1) showed the heterogenous nature of sorbent surface. The calculated

sorption capacity for immobilized water hyacinth for MY dye was 2.0137.

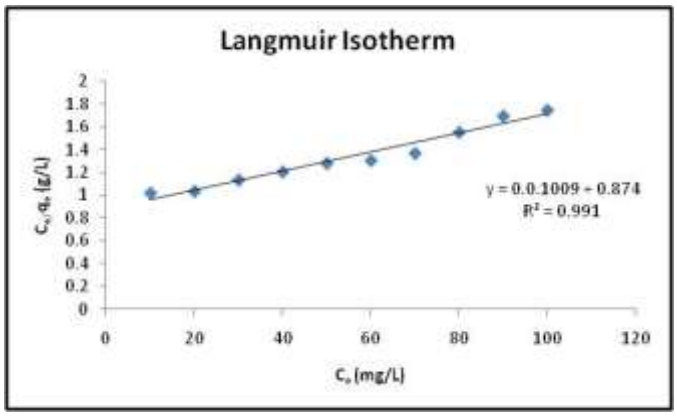

Figure 5. Langmuir plot for MY dye removal using immobilized biosorbent

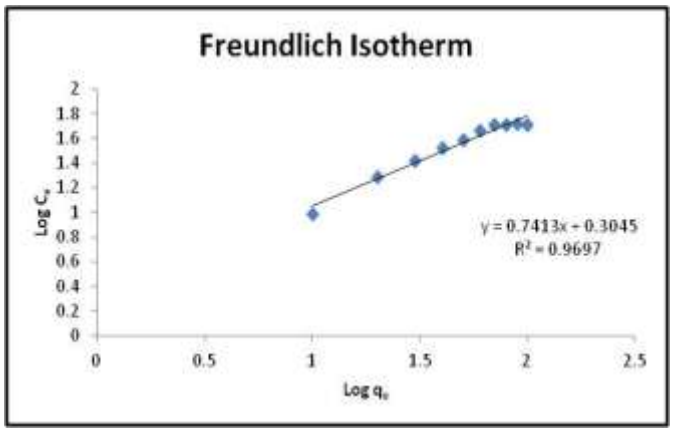

Figure 6. Freundlich plot for MY dye removal using immobilized biosorbent

Adsorption Kinetics

The study of adsorption kinetics describes the solute uptake rate and obviously this rate controls the residence time of the adsorbate at the solid solution interface. Rate of sorption plays a vital role in designing of batch system. The rate of sorption can be computed from the kinetic study. In this study the kinetics of MY dye biosorption on the adsorbent, immobilized water hyacinth were analyzed using pseudo first order, pseudo second order [14]. The confirmation between experimental data and the predicted values using different models were expressed by the correlation coefficients (R^2 value close or equal to 1).

A. Lagergrens pseudo first order model

For a batch system, the rate of sorption of dyes on to the biosorbent surface is proportional to the amount of dye adsorbed from the aqueous phase. The pseudo first order kinetic equation may be expressed as [14, 15]

where, q_e and q_t are the amount of dye adsorbed (mg/g) at time t and at equilibrium time, respectively and K is the rate constant of adsorption (1/min). On integration, we obtain a linear form first kinetic equation as

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

The slope and intercepts of plot of log (q_e-q_t) versus t were used to determine the first order constants K_{ad} and equilibrium adsorption capacity q_e (Figure 7).

B. Ho's pseudo second order model

The pseudo second order kinetic model was expressed as

where, K is the pseudo second order rate constant (g/mg/min), q and q represent the amount of dyes adsorbed (mg/g) at equilibrium and at time t [16]. The integral form of equation becomes

$$\frac{t}{q_t} = \frac{1}{K q_e^2} + \frac{t}{q_e}$$

The kinetic data were analyzed using the equation. The values of K and q_e calculated from the intercept and slope of the plots of t/q_t vs t (Figure 8). The R^2 values for the pseudo second order kinetic plots were lower than those for pseudo first order kinetic plots (Table 2). The calculated rate constants, experimental and predicted q_e with corresponding correlation coefficient values are presented in Table 2.

TABLE II. PSEUDO I AND II ORDER KINETIC CONSTANTS

Initial concen-tration (mg/L)	Pseudo I order kinetic model		R^2	Pseudo II order kinetic model		R^2
	K_{ad} (1/min)	q_e (mg/g)		K (gm/mg/ min)	q_e (mg/g)	
20	0.0063	8.26	0.985	0.0015	2.04	0.868
40	0.0096	6.24	0.964	0.0056	3.98	0.819
60	0.0013	6.79	0.959	0.0078	4.69	0.855
80	0.0016	7.15	0.903	0.0001	4.99	0.838
100	0.0100	7.26	0.808	0.0009	9.65	0.900

The correlation coefficients of pseudo second order model for all concentrations (20, 40, 60, 80 and 100mg/L) obtained were low as the predicted values deviated reasonably from the experimental values.

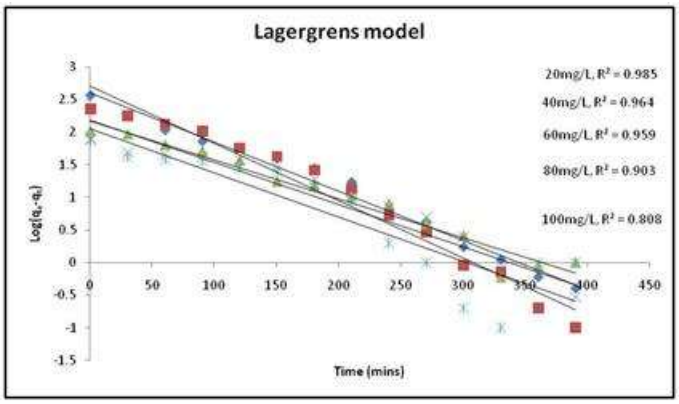

Figure 7. Pseudo first order plot for MY dye biosorption

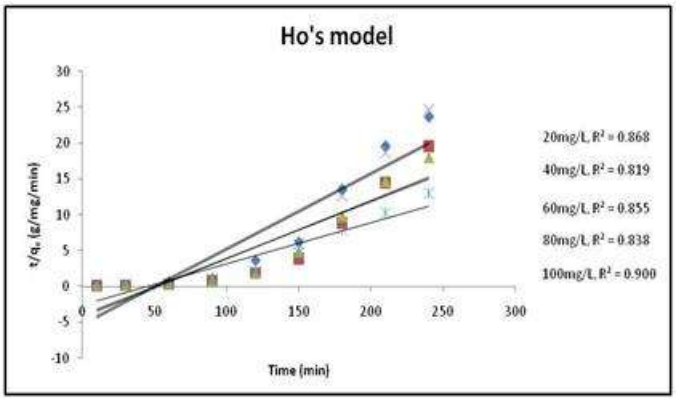

Figure 8. Pseudo second order plot for MY dye biosorption

The higher R^2 values confirm that the sorption process of dyes onto immobilized biosorbent followed a pseudo first order kinetic model and thus fitted well. The rate constants of pseudo first order increased with an increase in the initial dyes concentration.

Conclusion

The potential of using immobilized water hyacinth in the removal of azo dye metanil yellow from aqueous solution has been demonstrated. The maximum sorption was achieved at the pH of 6.0. The results of equilibrium isotherm and kinetic studies suggested that the biosorption follows a complicated multi-step processes with multilayer heterogeneous adsorption controlled by chemisorption. Further the process of biosorption is spontaneous and endothermic in nature. The randomness at the interface of solid and liquid during adsorption of dye on biosorbent has no change in entropy. Desorption efficiency was found ranged from 30 to 80%, using NaOH for regeneration. Therefore, the immobilized biosorbent of aquatic weed would be able to be repeatedly reused. The immobilized biosorbent showed highest decolorization of metanil yellow effectively during optimization but predominantly showed consistent sorption of MY dye and consequently this immobilized biosorbent can be duly used in continuous column reactors for the effective treatment of dye effluents.

References

[1] Aksu, Z. Application of biosorption for the removal of organic pollutants: A review. *Process Biochem*. 2005, *40*, 997–1026.

[2] Pagga, U, Brown, D. The degradation of dyestuffs. *Chemosphere* 1986, *15*, 479–491.

[3] Banat, I.M.; Nigam, P.; Singh, D.; Marchant, R. Microbial decolourization of textile-dye-containingeffluents. *Bioresour. Technol.* 1996, *58*, 217–227.

[4] Crini, G. Non-conventional low-cost adsorbents for dye removal. *Bioresour. Technol.* 2006, *97*, 1061–1085.

[5] R. Jain, N. Sharma and K. Radhapyari. Removal of hazardous azo dye metanil yellow from industrial wastewater using electrochemical technique. *European Water*. 2009, 27/28: 43-52.

[6] T.N. Nagaraja, T. Desiraju. Effects of chronic consumption of metanil yellow by developing and adult rats on brain regional levels of noradrenaline, dopamine and serotonin, on acetylcholine esterase activity and on operant conditioning. Food and Chemical Toxicology. 1993, 31, 41–44.

[7] Y. M. Slokar and A. Majcen Le Marechal, Methods of decoloration of textile wastewaters, Dyes and Pigments, 37 (1998) 335-356.

[8] T.Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textiles effluent: a critical review on current treatment technologies with a proposed alternative, Bioresource Technology, 77 (2001) 247-255.

[9] Rouf Ahmad Shah, D.M. Kumawat, Nihal Singh and Khursheed Ahmad Wani. Water hyacinth (eichhornia crassipes) as a remediation tool for dye-effluent pollution. International journal of science and nature. 2010: 172-178.

[10] Bao-E. Wang, Yong-You Hu, Lei Xie, Kang Peng, Biosorption behavior of azo dye by inactive CMC immobilized *Aspergillus fumigatus* beads, 99 (2008) 794–800.

[11] Langmuir, I., 1918. The adsorption of gases on surfaces of glass, mica and platinum. J. Am. Chem. Soc., 40: 1361-1368.

[12] K. Nanthakumar, K. Karthikeyan and P. Lakshmanaperumalsamy. Investigation on Biosorption of Reactive Blue 140 by Dead Biomass of *Aspergillus niger* HM11: Kinetics and Isotherm Studies. Global Journal of Biotechnology & Biochemistry. 2009, 4 (2): 169-178.

[13] Freundlich, H., Adsorption in solution. Phys. Chem. Soc., 1906. 40: 1361-1368.

[14] Ho, Y.S. and G. McKay, Pseudo second-order model for sorption process. Process Biochem., 1999. 34: 451-465.

[15] Ho, Y.S. and C.C. Chiang, Sorption studies of dye by mixed sorbents. Adsorpt. J. Int.Adsorpt. Soc. 2001. 7: 139-147.

[16] K. Vasanth Kumar., Linear and non-linear regression analysis for the sorption kinetics of methylene blue onto activated carbon., Journal of Hazardous Materials B137 (2006) 1538–1544.