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Biosorption Studies of Methylene Blue Using Modified Chicken Feather

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Modified chicken feather has been used as a low cost biosorbent for the studies of isotherm and kinetics of methylene blue dye adsorption from aqueous solution. Modified chicken feather was characterized by XRD and FTIR. Effects of pH, initial concentration of the dye, biosorbent dosage and contact time have been studied. Equilibrium studies showed that data fits better with Freundlich isotherm. The kinetics of adsorption has been best described by pseudo-first-order model.

Keywords: Chicken feather, Biosorption, Methylene blue.

INTRODUCTION

Industrial effluents contain a lot of organic dyes, heavy metals and other toxic chemicals which are discharged into water bodies. They contaminate water, disturb the aquatic ecosystem and finally reach us through food chain by bio accumulation and biomagnification.

Dyes may be natural or synthetic aromatic and heterocyclic conjugated systems with attached chromophores [1]. Effluents of dyeing industries create serious environmental issues because even in very minute doses their colour becomes visible and affects the aesthetic beauty of water body. It prevents light penetration into the water, adversely affect the bacterial growth and disturb aquatic ecosystem. Not only they have poor biodegradability but also many of them are carcinogenic and mutagenic.

Methylene blue is a phenothiazine based organic dye (m.f. $C_{16}H_{18}N_3SCl$), used in textile, paper, plastic and pharmaceutical industries for dyeing purposes [2]. It is extensively used as a redox indicator in laboratories and for staining in biological specimens. It is water soluble and shows absorption maximum around 670 nm. In spite of its versatile applications, its continous exposure may cause nausea, increased heart rate, hypertension and methemoglobenemia. Methylene blue can cause burning sensation to eyes of human beings and animals.

Preferential removal of dyes can be accomplished by methods such as precipitation, reverse osmosis, flocculation, ultrafiltration, *etc*. Now a days adsorption [3,4], electrochemical coagulation [5] and photo cataltytic degradation [6] are commonly used for waste water treatment. Biosorption using low cost biomass has become an attractive technique for removal of toxic chemicals from water. Consequently, various potential biosorbents like peat [7], eucaliptus bark [8], dried activated sludge [9], seaweeds [10], hen feathers [11,12] are used as biosorbents.

Present paper is an attempt to remove methylene blue using hen feathers as biosorbent. Chicken feather (CF) is such a biomass which can be economically and conveniently converted into a biosorbent for the removal of organic dyes. Poultry farms produce huge amounts of chicken feather as waste side product and usually removed by burning or landfilling. Chicken feather consists of 90 % of keratin protein fibres with $-NH_2$ and -COOH substituents which can be suitably modified [12,13]. On account of its large surface area and reactive functional groups chicken feather finds application as a potential biosorbent [12,13].

In present study, we report the optimization of parameters, kinetic and isotherm modeling for the biosorption of methylene blue on modified chicken feather.

EXPERIMENTAL

The reagents used were ethanol, methanol and HCl and were of analytical grade. The instruments used were UV-visible spectrophotometer (Shimadzu-1800), Mechanical shaker (Rotek, Model number REC27255A2), pH meter, XRD (Rigaku Miniflex X-ray Diffractometer with CuK_α radiation)

Preparation of biosorbent: The chicken feathers collected from poultry farms were cleaned, washed in water and ethanol and cut into pieces of size 5 mm. Chicken feather was modified by dipping in equimolar mixture of methanol and HCl for 2 h. 5 g chicken feather was mixed with 6 % (v/v) CH_3OH and

2 % (v/v) HCl in a 250 mL double necked flask and placed on a hot plate at 80 °C with constant stirring for 3 h. The reaction mixture was filtered, washed with distilled water and kept for drying. Modified chicken feather biosorbent was characterized by XRD and FTIR [13].

Preparation of adsorbate: The stock solution of methylene blue dye was prepared in the range 1×10^{-5} to 10×10^{-5} M.

Batch adsorption experiments: The adsorption studies were carried out to investigate the influence of initial concentration, contact time, biosorbent dose and pH on the adsorption of methylene blue by modified chicken feather. In each 100 mL conical flasks, 25 mL of methylene blue solution of known concentration was taken and 100 mg of biosorbent added and shaken for 2 h in an orbital shaker kept for 24 h for saturation. Thereafter supernatant liquid was filtered through Whatmann filter paper No. 42 and the amount of methylene blue adsorbed was determined spectrophotometrically at λ_{max} 663 nm. The amount of dye adsorbed per unit biosorbent (mg dye/g of biosorbent) was calculated using eqns. 1 and 2:

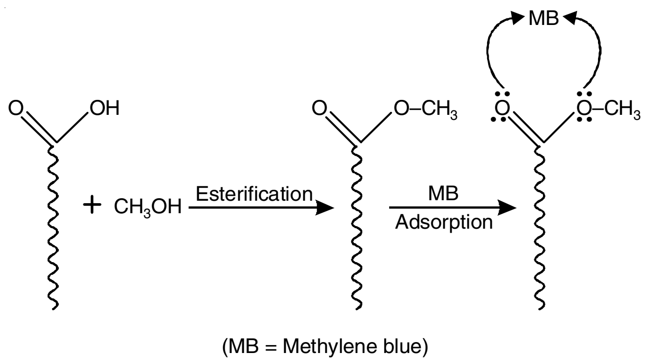
$$q_e = (C_o - C_e)V/W \quad (1)$$

$$\text{Removal (\%)} = (C_o - C_e) \times 100/C_o \quad (2)$$

where C_o and C_e represent initial and final equilibrium concentrations (mg/L), V is the volume of adsorbate taken, W is the weight of the biosorbent and q_e is the amount of dye adsorbed at equilibrium.

RESULTS AND DISCUSSION

Characterization of the biosorbent: Chemical modification of chicken feather was carried out with methanol as shown in **Scheme-I**. Modified chicken feather was characterized using XRD and FTIR. IR peaks in the range 1700-1600 cm^{-1} is due to –NH and C=O stretching vibration of the amide group. In case of modified chicken feather, this peak becomes sharp at 1653 cm^{-1} suggesting the formation of random coils at the expense of α-helix and β-pleated sheets present in the native feathers. The appearance of intense peak at 1740 cm^{-1} is due to the -C=O stretching absorption peak of the aliphatic ester of the modified chicken feather [13].



Scheme-I: Modification of chicken feather

XRD patterns of untreated chicken feather and modified chicken feather are shown in Fig. 1. Prominent peak at 9.9 corresponds to α-helix configuration and intense band at 19 is due to strand secondary structure. The modified chicken feather peaks with reduced intensity and mild shift in 2θ values indicate

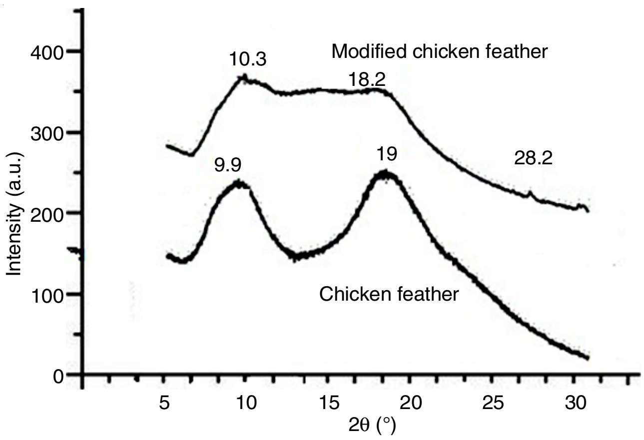


Fig. 1. XRD of chicken feather and modified chicken feather

the decrease in the β-sheet content and partial fracture of α-helix network [13].

Adsorption studies

Effect of biomass dosage: The effect of biomass dosage on biosorption of methylene blue is shown in Fig. 2. It can be seen that the biosorption efficiency increases with increase in biomass dosage. This can be expected because the higher the dose of biosorbents in the solution, the greater the availability of exchangeable sites for the ions. With increase in the biomass dosage partial aggregation occurs which reduces the effective surface area for sorption. Hence the optimum dosage was selected as 100 mg for further experiments.

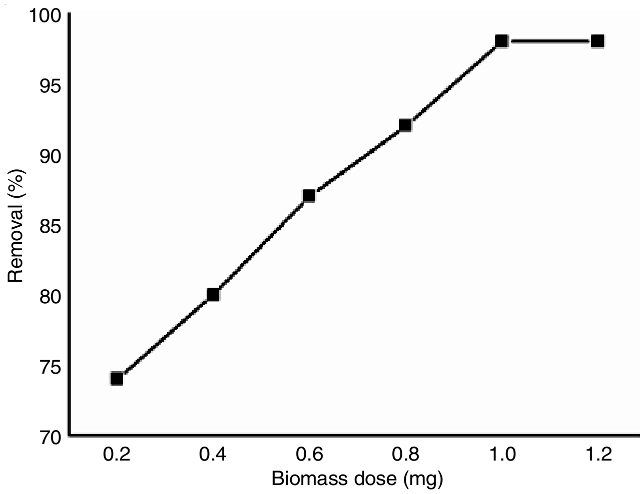


Fig. 2. Effect of biomass dose

Effect of initial dye concentration: The variation of adsorption efficiency with change in initial dye concentration is shown in Fig. 3. The biosorption efficiency significantly enhanced by increasing the initial concentration. The adsorption increases with increase in the initial concentration and maximum adsorption is attained at the highest initial concentration (100 mg/L).

Effect of pH: The effect of pH on adsorption capacity of modified chicken feather was studied ranging from 3-8. Fig. 4 shows that the sorption of methylene blue was minimum at the initial pH 3.5 and increased up to 6.0 and then remained steady over the pH 6-8. The observed low adsorption rate of

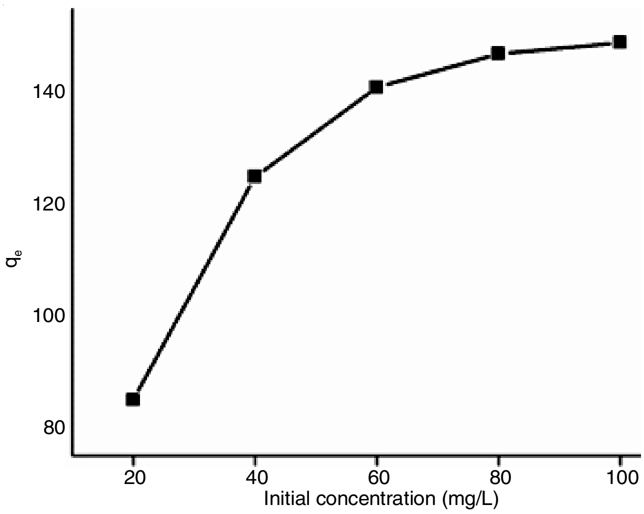


Fig. 3. Effect of initial concentration

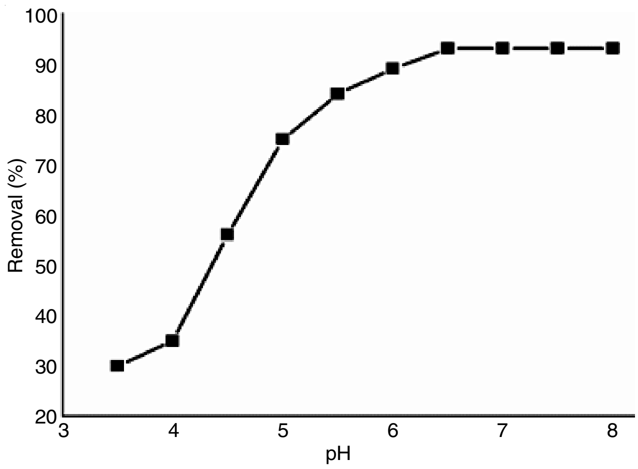


Fig. 4. Effect of pH

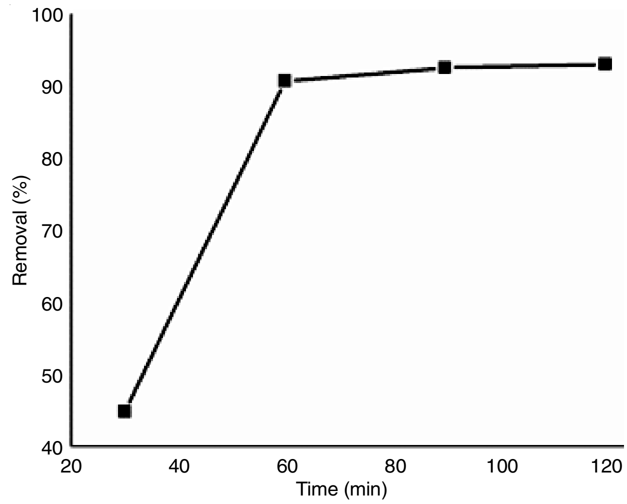


Fig. 5. Effect of contact time

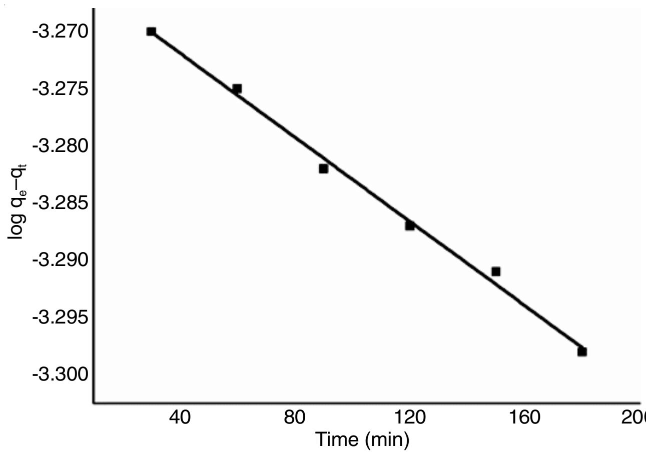


Fig. 6. Pseudo first-order kinetic plot for modified chicken feather-methylene blue system

methylene blue on the modified chicken feather at low pH may be due to the positively charged surface which makes (H^+) ions to compete effectively with dye cations.

Effect of contact time: The effect of contact time on the biosorption of methylene blue onto modified chicken feather is shown in Fig. 5. The dye binding capacity is assumed to be proportional to the number of active sites occupied on the sorbent [10]. 92.5 % of dye was found to be adsorbed within 2 h.

Adsorption kinetics: Fig. 6 shows the effect of contact time on adsorption of methylene blue onto modified chicken feather at 100 mg/L. To predict sorption kinetics, two kinetic models (i) Lagergren's pseudo-first order model (eqn. 4), (ii) Ho's pseudo-second order model (eqn. 3) were used.

$$\log (q_e - q_t) = \log q_e - k_1 t/2.303 \quad (3)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (4)$$

where k_1 (1/min) is the rate constant of pseudo-first-order adsorption, k_2 (g/mg min) is the rate constant of pseudo-second-order adsorption. The pseudo-first order kinetic model was evaluated by plotting log (q_e-q_t) against t for initial methylene blue concentration, a straight line was obtained and the first-order rate constant (k_1) and q_e values were determined from the plots. The values of correlation coefficient were very high (R^2 = 0.9949). The theoretical q_e, cal (5.43 mg/g) value and experimental q_e, exp (5.04 mg/g) value are close. The pseudo second order plot does not fall under straight line. Therefore, it can be concluded that pseudo first order model provides a better correlation compared to the pseudo-second order model for the adsorption of methylene blue on modified chicken feather.

Equilibrium studies: Adsorption data for adsorbate concentration are most commonly described by adsorption isotherms, such as the Langmuir or Freundlich isotherms. The Freundlich adsorption isotherm was applied for the adsorption of dye on modified chicken feather. Freundlich equation is represented as:

$$q_e = K_f C \ 1/n \quad (5)$$

$$\log q_e = \log K_f + 1/n \log C \quad 6)$$

So, by plotting of log q_e *vs.* log C_e, the constant K_f and exponent (n) can be determined. From Fig. 7 Freundlich constant K_f and heterogeneity factor 1/n is calculated as 0.0147 and 0.557 respectively (R^2 = 0.9936). K_f is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process.

Conclusion

We investigated the biosorption of methylene blue from aqueous solution using modified chicken feather. The para-

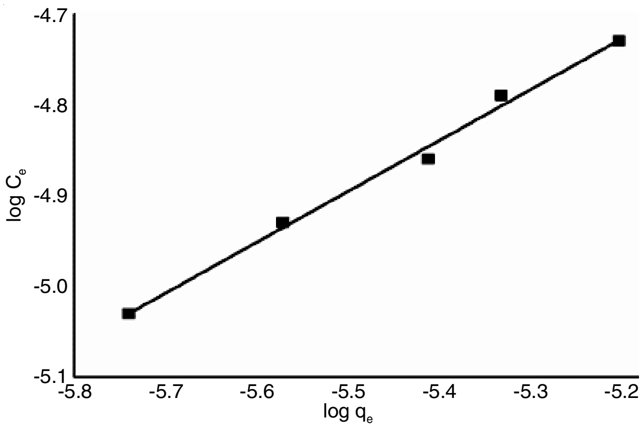


Fig. 7. Freundlich plot for modified chicken feather-methylene blue system

meters such as initial concentration of dye, contact time, pH and biosorbent dose were optimized as 100 mg/L, 2 h, 6 and 100 mg respectively. Freundlich isotherm model was found to be the most suitable in describing the equilibrium of the biosorption process. The kinetic study revealed that the adsorption process follows pseudo-first order model.

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