Fish (*Labeo rohita*) scales as a new biosorbent for removal of textile dyes from aqueous solutions

Sagnik Chakraborty, Shamik Chowdhury and Papita Das Saha

ABSTRACT

The feasibility of utilizing fish scales as a new biosorbent for removal of textile dyes, namely crystal violet (CV) and methylene blue (MB), from their aqueous solutions was investigated in a batch system. Experiments were conducted as a function of initial solution pH (2–10), contact time (0–180 min), biosorbent dose (0.5–5 g) and temperature (293–313 K). The Langmuir isotherm model showed excellent fit to the equilibrium biosorption data of both CV and MB. The maximum dye biosorption capacity of fish scale was calculated as 74.39 and 58.67 mg g^{-1} for CV and MB, respectively, at 313 K. Biosorption phenomena of CV and MB by fish scales followed pseudo-second-order kinetics. Activation energy calculated by using the Arrhenius equation suggested the chemisorption nature of the biosorption processes. A thermodynamic assessment indicated the spontaneous and endothermic nature of biosorption of the textile dyes. It could be concluded that fish scales may be used as an inexpensive and effective biosorbent for removal of dyes from aqueous solutions.

Key words | biosorption, dyes, fish scales, isotherm, kinetics, thermodynamics

Sagnik Chakraborty
Shamik Chowdhury (corresponding author)
Papita Das Saha
Department of Biotechnology,
National Institute of Technology-Durgapur,
Mahatma Gandhi Avenue,
Durgapur (WB) 713209,
India
E-mail: *chowdhuryshamik@gmail.com*

NOMENCLATURE

C_a equilibrium dye concentration on the biosorbent (mg L^{-1})

C_e equilibrium dye concentration in solution (mg L^{-1})

C_i initial dye concentration (mg L^{-1})

E mean free energy (kJ mol^{-1})

ΔG^0 Gibbs free energy change (kJ mol^{-1})

ΔH^0 enthalpy of reaction (kJ mol^{-1})

K_C distribution coefficient for adsorption

K_F Freundlich constant (mg g^{-1}) (L g^{-1})$^{1/n}$

K_L Langmuir constant (L mg^{-1})

k rate constant

k_i intraparticle diffusion rate constant (mg g^{-1} min$^{-0.5}$)

k_1 pseudo-first-order rate constant (min^{-1})

k_2 pseudo-second-order rate constant (g mg^{-1} min^{-1})

m mass of biosorbent (g)

n Freundlich isotherm constant

q_e equilibrium dye concentration on biosorbent (mg g^{-1})

q_m maximum biosorption capacity (mg g^{-1})

q_t amount of dye adsorbed at time t (mg g^{-1})

R universal gas constant (8.314 J mol^{-1} K^{-1})

R^2 correlation coefficient

ΔS^0 entropy of reaction (J mol^{-1} K^{-1})

T temperature (K)

V volume of the solution (L)

β D–R isotherm constant (mmol^2 J^{-2})

ε Polanyi potential (J mmol^{-1}) = $RT \ln(1 + 1/C_e)$

INTRODUCTION

In today's society, an increasing number of hazardous organic compounds are being discharged into the environment as a result of rapid industrialization. In this context, the contamination of water bodies by discharge of highly coloured synthetic dye effluents, particularly from textile industries, needs special mention (Chowdhury *et al.* 2011a; Silveira *et al.* 2011). The release of coloured effluent waste-waters into the aquatic ecosystem presents both environmental and public health risks because of their

negative ecotoxicological effects and bioaccumulation in wildlife (Saha et al. 2010). Therefore, removal of dyes from effluents is essential not only to protect human health but also for the protection of the natural environment.

Present techniques for removal of dyes from wastewater include oxidative degradation, photochemical degradation, coagulation, electrokinetic coagulation, flocculation, hydrogen peroxide catalysis, membrane separation, reverse osmosis, ozonation and ultrachemical filtration (Chowdhury & Saha 2012). However, practical application of these technologies is restricted because of technical or economic constraints. In recent years, biosorption has been extensively studied by researchers worldwide as an efficient and economically sustainable technology for the treatment of dye-stuff effluents (Chowdhury et al. 2011b; Saha et al. 2012a). Biosorption has been found to be superior to other techniques for removal of dyes from wastewater in terms of its simplicity and flexibility of design, its high selectivity and efficiency, low operating cost and the high quality of the treated effluent (Aksu 2005). A number of low-cost sorbent materials including waste/by-products from industries and agricultural operations, natural materials and microbial and non-microbial biomass have been identified and documented as effective dye-removing agents (Gupta & Suhas 2009; Rafatullah et al. 2010; Srinivasan & Virarghavan 2010). Unfortunately, although wastes from animal sources are abundant in nature, they still need to be explored for their dye sorption ability.

India is a land of exotic fishes. A huge variety of fish are available in the coastal waters of India, harvested by local fishermen. There is a great demand for Indian fish and fishery products on the world market. Fish scale is a significant solid waste from the fishing and fishery industries. Traditionally, most of the fish scale waste is disposed in landfills without any pre-treatment because it has no practical utility. However, such waste management is not a desirable practice in view of the environmental odour from biodegradation. Utilization of this waste material as a biosorbent for the treatment of dye bearing effluents is a win–win strategy because it not only converts the waste into a useful material but also helps solve the disposal problem. Therefore, the primary aim of this study was to investigate the biosorption potential of fish scales for the removal of textile dyes, namely crystal violet (CV) and methylene blue (MB), from their aqueous solutions in a batch experimental set-up. CV is a well-known textile colourant (Chakraborty et al. 2011). The dye is non-biodegradable and environmentally persistent, and has been found to have cytotoxic and carcinogenic effects on mammalian cells (Chakraborty et al. 2011). MB is commonly used for the dyeing of silk, leather, plastics, paper, cotton mordanted with tannin, and also in the manufacturing of paints and printing inks (Nasuha et al. 2010). Exposure to MB can cause hypertension, precordial pain, dizziness, headache, fever, faecal discolouration, profuse sweating, mental confusion, methaemoglobinaemia and haemolytic anaemia (Saha 2010). Both CV and MB, due to their wide presence in dye-stuff effluents and reported toxicological effects, were chosen as model pollutants during the current investigation. The study includes an evaluation of the effects of various operational parameters such as initial solution pH, biosorbent dose, contact time and temperature on the biosorption processes with special focus on biosorption isotherms, kinetics and thermodynamics.

MATERIALS AND METHODS

Biosorbent

Fish (*Labeo rohita*) scales were collected from the Fishermen's Market located in Benachity, Durgapur, India, and washed repeatedly with distilled water to remove adhering dust, dirt and soluble impurities from their surfaces. The fish scales were then sun dried for about 2 days and subsequently oven dried at 343 K until the scales became crispy. The dried scales were ground to fine powder using a grinder and sieved to a constant size (100–125 μm), and then used as a biosorbent without any pretreatment.

Dyes

CV (colour index: 42555; molecular formula: $C_{25}H_{30}N_3Cl$; molecular weight: 408, λ_{max}: 580 nm) and MB (colour index: 52015; molecular formula: $C_{16}H_{18}N_3SCl$; molecular weight: 319.86, λ_{max}: 663 nm) used in this study were of commercial quality and were used without further purification. Stock solutions (1,000 mg L^{-1}) were prepared by dissolving accurately weighed quantities of the dye in double-distilled water. Experimental working solutions were prepared by diluting the stock solutions with a suitable volume of double-distilled water.

Batch experiments

All biosorption experiments were performed in 250 mL glass-stoppered Erlenmeyer flasks with 100 mL (50 mg L^{-1}) of dye solution. A weighed amount of biosorbent was added to the solution. The flasks were agitated at a constant speed of 150 rpm for 3 h in an incubator shaker (Innova 42, New Brunswick Scientific, Canada) at 303 ± 1 K. The influence of pH (2.0–10.0), biosorbent dose (0.5–5 g), contact time (0–180 min) and temperature (293–313 K) was evaluated. Samples were collected from the flasks at regular time intervals until equilibrium was reached. The residual dye concentration in each flask was analysed using a UV/VIS spectrophotometer (U–2800, Hitachi, Japan). The amount of dye adsorbed per unit fish scales (mg dye per g biosorbent) was calculated according to a mass balance on the dye concentration using Equation (1):

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

The percentage removal of dye was calculated using the following equation:

$$Removal\ (\%) = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

Statistical analysis

To ensure the accuracy, reliability and reproducibility of the collected data, all biosorption experiments were performed in triplicate, and the mean values were used in data analysis. Relative standard deviations were found to be within ±3%. Data were processed using Microsoft Excel 2007. Linear regression analysis was used to determine the model parameters and constants.

Biosorbent characterization

The surface structure of the biosorbent, before and after biosorption of the dyes, was analysed by a scanning electron microscope (SEM) (S-3000N, Hitachi, Japan) at an electron acceleration voltage of 15 kV. Prior to scanning, the unloaded and dye-loaded fish scale samples were mounted on a stainless steel stub with double-sided tape and coated with a thin layer of gold in a high vacuum condition.

The BET (Brunauer-Emmett-Teller) surface area, pore volume and pore size of the biosorbent were measured by a surface area and porosity analyser (NOVA 2200, Quantachrome Corporation, USA). A gas mixture of 22.9 mol% nitrogen and 77.1 mol% helium was used for this purpose.

RESULTS AND DISCUSSION

Biosorbent characterization

The BET surface area of the biosorbent was found to be 85.7 m^2 g^{-1}. The relatively large surface area suggests that there was a good possibility for the dye molecules to be trapped and adsorbed onto the surface of the biosorbent. In order to examine the surface morphology of the biosorbent, SEM micrographs were taken before and after biosorption of the dyes (Figure 1(a)–1(c)). Before dye uptake, the biosorbent is characterized by a rough and uneven surface with wide ridges (Figure 1(a)). Following dye biosorption there is a considerable change in the surface morphology of the biosorbent, suggesting the biosorption of dyes by fish scales (Figure 1(b) and 1(c)).

Effect of pH

Solution pH is an important governing parameter in biosorption processes. Therefore, in the present investigation, the effect of pH on the removal efficiency of CV and MB by fish scales was studied at different solution pH (2.0 to 10.0). As expected, pH significantly affects the extent of biosorption of both CV and MB (Figure 2). The percentage removal of the dyes increases appreciably with the increase in solution pH up to pH 6.0. Further increase in pH does not significantly change the biosorption yield. Maximum removal of CV and MB was noted at pH 9.0 and pH 8.0, respectively. Therefore, all further studies pertaining to CV and MB were carried out at pH 9.0 and pH 8.0, respectively. These findings suggest that, as both CV and MB are cationic dyes, the degree of their biosorption onto the biosorbent surface is primarily influenced by the surface charge of the biosorbent, which in turn is influenced by the solution pH
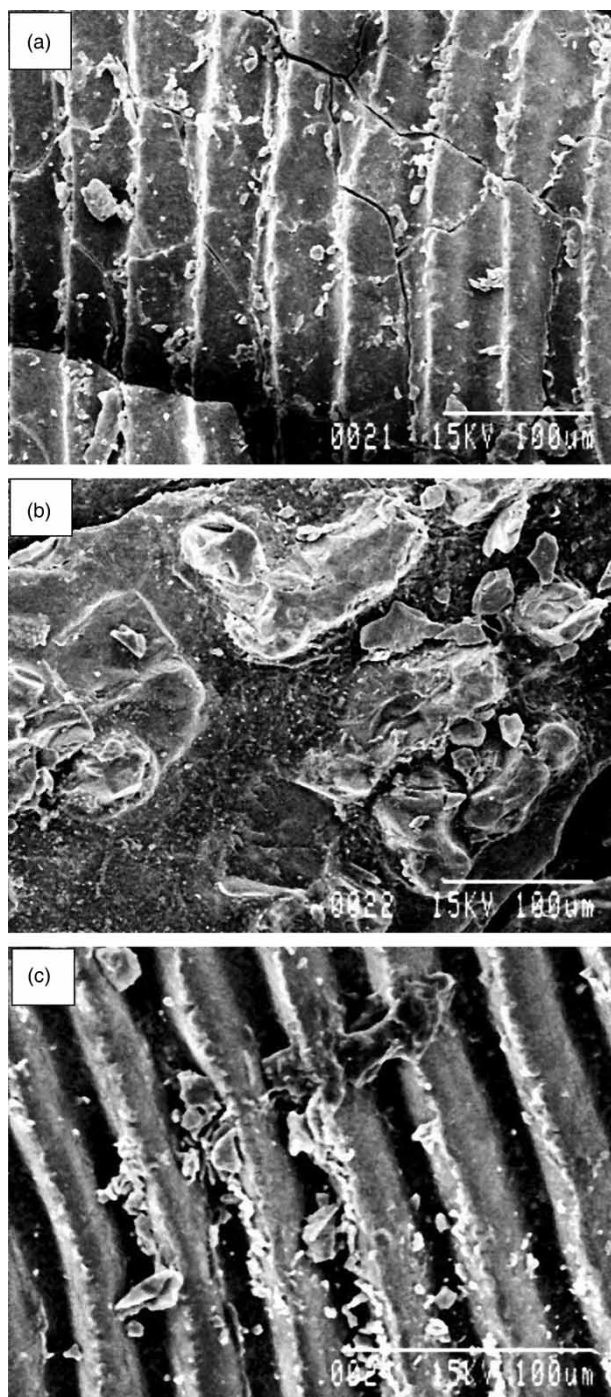
Figure 1 │ Scanning electron micrographs of fish scales (a) before biosorption (b) after biosorption of CV, and (c) after biosorption of MB.

Figure 2 │ Effect of solution pH on biosorption of textile dyes by fish scales (experimental conditions: $C_0 = 50$ mg L^{-1}, $m_{CV} = 1$ g/0.1 L, $m_{MB} = 2$ g/0.1 L, agitation speed = 150 rpm, $T = 303$ K, contact time = 3 h).

positively charged, thereby decreasing the biosorption of the positively charged dye ions through electrostatic repulsion. With increase in solution pH, deprotonation of the positively charged groups on the biosorbent surface leads to an increase in the biosorption of the dyes due to electrostatic attraction between negatively charged sites on the biosorbent and dye cations (Saha *et al.* 2012b). The present findings are in accordance with those previously reported for biosorption of CV by coniferous pinus bark powder (Ahmad 2009) and of MB by garlic peels (Hameed & Ahmad 2009).

Effect of biosorbent dose

Biosorbent dose is an important parameter influencing the sorption processes since it determines the sorption capacity of a biosorbent for a given initial concentration of the adsorbate under the operating conditions. The effect of biosorbent dose in the range of 0.5–5.0 g on the biosorption removal of the textile dyes by fish scales is illustrated in Figure 3. Dye removal efficiency increased with increasing biosorbent dose, reaching a maximum at around 1.0 g for CV and 2.0 g for MB. Such behaviour is a result of an increase in biosorbent surface area and the availability of more biosorption sites with increasing biosorbent dose (Nasuha *et al.* 2010). However, further increase in biosorbent dose reduced the maximum dye removal efficiencies, which can be explained by the saturation of dye binding sites due to particulate interaction such as aggregation (Aksakal & Ucun 2010). Since the optimum biosorbent dose was found to be 1.0 and 2.0 g,

(Saha *et al.* 2012a). At low pH values, protonation of the functional groups present on the biosorbent surface easily takes place. The surface of the biosorbent becomes
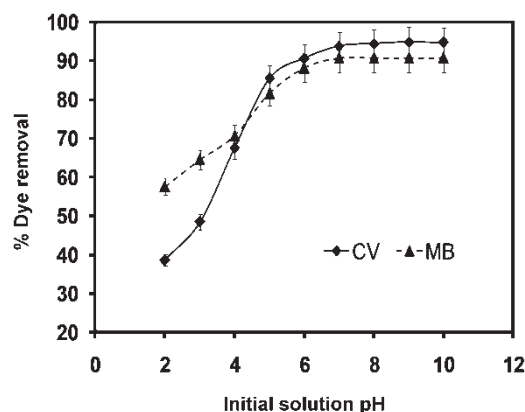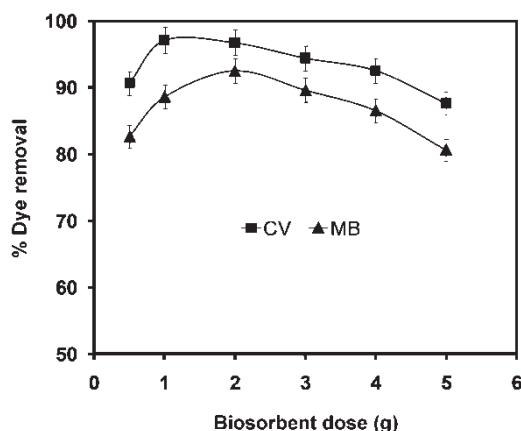
Figure 3 | Effect of biosorbent dose on removal of textile dyes by fish scales (experimental conditions: $C_0 = 50$ mg L^{-1}, agitation speed = 150 rpm, $T = 303$ K, contact time = 3 h).

respectively, for CV and MB, these biosorbent doses were used in the successive experiments. Similar results have been reported previously by other researchers for the sorption of dyes by different biological materials (Crini *et al.* 2007; Aksakal & Ucun 2010).

Effect of temperature and contact time

Figure 4 presents the CV biosorption capacity of fish scales at different temperatures as a function of contact time. The biosorption capacity of fish scale for CV and MB increases with increase in temperature, suggesting an endothermic nature for the biosorption processes. An increase in temperature increases the mobility of the dye molecules and a decrease in the retarding forces acting on the molecules, resulting in the enhancement in the dye binding capacity of the biosorbent (Chowdhury & Das 2011). It is also interesting to note that the removal takes place in two phases. The first phase involves rapid dye uptake within 30 min of the dye-biosorbent contact which is followed by a subsequently slower uptake phase gradually leading to equilibrium. The initial faster biosorption rate is due to the large amount of surface area available for biosorption of the dye molecules.

Biosorption isotherms

In the present study, the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models were used to describe the equilibrium biosorption data obtained at
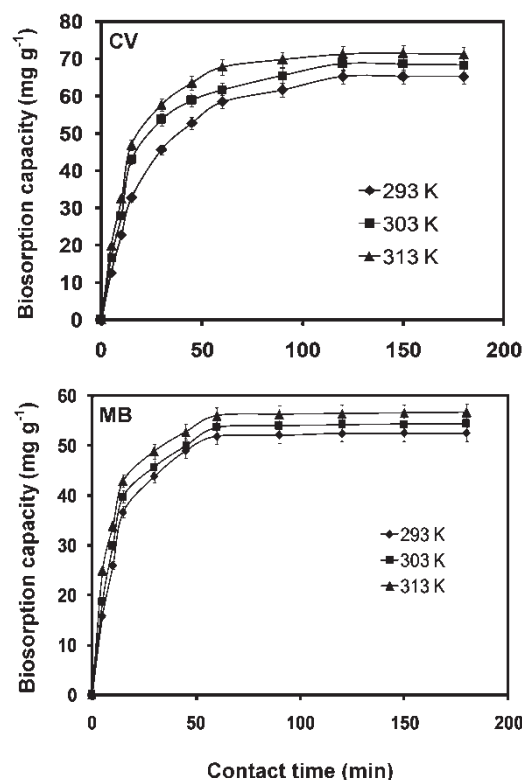

Figure 4 | Time profiles for biosorption of textile dyes by fish scales at different temperatures (experimental conditions: $C_0 = 50$ mg L^{-1}, $m_{CV} = 1$ g/0.1 L, $m_{MB} = 2$ g/0.1 L, agitation speed = 150 rpm).

different temperatures (Chowdhury & Saha 2010).

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \qquad (3)$$

$$\text{Freundlich: } \log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \qquad (4)$$

$$\text{Dubinin–Radushkevich (D–R): } \ln q_e = \ln q_m - \beta \varepsilon^2 \qquad (5)$$

The parameters and correlation coefficients obtained from the plots of Langmuir (C_e/q_e vs C_e), Freundlich ($\log q_e$ vs $\log C_e$) and D–R ($\ln q_e$ vs ε^2) for CV and MB are listed in Table 1. Based on the correlation coefficients, the applicabilities of the isotherms were compared (Table 1).

From Table 1, it is clearly evident that the Langmuir isotherm model shows better fit to the equilibrium biosorption data of both CV and MB than the Freundlich and D–R isotherms. It can thus be said that the biosorption of the dyes is

Table 1 | Isotherm constants for biosorption of textile dyes by fish scales at different temperatures

Dye	T (K)	Langmuir			Freundlich			Dubinin–Radushkevich			
		q_m (mg g^{-1})	K_L (l mg^{-1})	R^2	K_F (mg g^{-1})(l mg^{-1})$^{1/n}$	n	R^2	q_m (mg g^{-1})	β (mmol^2 J^{-2})	E (kJ mol^{-1})	R^2
CV	293	67.241	0.287	0.999	12.476	2.268	0.953	55.287	3.689×10^{-9}	11.642	0.902
	303	70.816	0.413	0.996	17.298	2.621	0.951	58.712	3.284×10^{-9}	12.339	0.903
	313	74.397	0.629	0.998	20.725	3.017	0.957	61.493	2.963×10^{-9}	12.990	0.907
MB	293	54.162	0.455	0.997	2.934	1.279	0.946	43.188	5.461×10^{-9}	9.569	0.913
	303	56.243	0.589	0.999	6.625	1.782	0.955	45.936	4.986×10^{-9}	10.014	0.917
	313	58.678	0.670	0.999	10.289	2.437	0.951	48.671	4.532×10^{-9}	10.503	0.911

by a monolayer; biosorption of each molecule has equal activation energy and sorbate-sorbate interaction is negligible. The maximum biosorption capacity of (q_m) increases from 67.24 mg g^{-1} at 293 K to 74.39 mg g^{-1} at 313 K for CV while it increases from 54.16 mg g^{-1} at 293 K to 58.67 mg g^{-1} at 313 K for MB.

The Freundlich constant n gives a measure of favourability of biosorption with values of n between 1 and 10 (i.e. $1/n$ less than 1) representing a favourable biosorption process (Chowdhury et al. 2011b). For the present study, the value of n also presented the same trend suggesting the favourable nature of biosorption of CV and MB by fish scales.

The D–R isotherm model constant β is commonly used to calculate the mean free energy E (kJ mol^{-1}) of biosorption, which in turn gives valuable information on the nature of the biosorption process as chemical ion exchange ($E = 8$–16 kJ mol^{-1}), or physical sorption ($E < 8$ kJ mol^{-1}). E is calculated using the relationship (Chakraborty et al. 2011):

$$E = \frac{1}{\sqrt{2\beta}} \tag{6}$$

In this study, the E values were found to be >8 kJ mol^{-1} for both dyes (Table 1), implying that biosorption of CV and MB by fish scales proceeds via a chemical ion exchange mechanism.

Biosorption kinetics

The pseudo-first-order and pseudo-second-order kinetic models were used to study the biosorption kinetics of CV and MB onto fish scales (Chowdhury & Saha 2010).

$$\text{Pseudo-first-order:} \log (q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{7}$$

$$\text{Pseudo-second-order:} \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{8}$$

The values of pseudo-first-order rate constants k_1 and q_e were calculated from the slope and intercept of the plots of $\log (q_e - q_t)$ versus t. The k_1 values, the correlation coefficients and theoretical and experimental equilibrium biosorption capacity q_e for both the adsorbates are listed in Table 2. The low correlation coefficient values at all temperatures for both CV and MB suggest that the pseudo-first-order kinetic model is not suitable for describing the kinetics of the biosorption processes. Also, the theoretical and experimental equilibrium biosorption capacities (q_e) differ widely for both CV and MB, confirming that biosorption of CV and MB by fish scales does not follow pseudo-first-order kinetics. On the other hand, the pseudo-second-order kinetic model shows excellent fit to the experimental biosorption kinetic data of CV and MB at all temperatures studied (Figure 5). The pseudo-second-order rate constants k_2 and q_e for biosorption of CV and MB at different temperatures as calculated from the plots of t/q_t versus t and the corresponding correlation coefficients values are given in Table 2. All the correlation coefficients at different temperatures for both the dyes are considerably high ($R^2 > 0.99$). In addition, the theoretical q_e values show good agreement with the experimental q_e values for both CV and MB, confirming that the ongoing biosorption processes proceed via a pseudo-second-order mechanism involving sharing or exchange of electrons between the adsorbate ions and the biosorbent.

In a well-agitated batch sorption system, there is a possibility of intraparticle pore diffusion of adsorbate ions, which can be the rate-limiting step. Therefore, the possibility of intra particle diffusion resistance affecting the biosorption

Table 2 | Kinetic parameters for biosorption of textile dyes by fish scales

Dye	T (K)	$q_{e,exp}$ (mg g^{-1})	Pseudo-first-order			Pseudo-second-order		
			$q_{e,cal}$ (mg g^{-1})	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
CV	293	65.296	48.267	0.656	0.926	65.935	1.353×10^{-3}	0.997
	303	68.674	51.729	0.813	0.918	69.271	4.341×10^{-3}	0.999
	313	71.253	54.583	0.987	0.916	72.036	7.896×10^{-3}	0.999
MB	293	52.524	35.188	0.352	0.922	53.108	1.615×10^{-2}	0.999
	303	54.315	37.024	0.469	0.920	54.882	5.263×10^{-2}	0.998
	313	56.763	40.348	0.578	0.927	57.457	9.622×10^{-2}	0.999
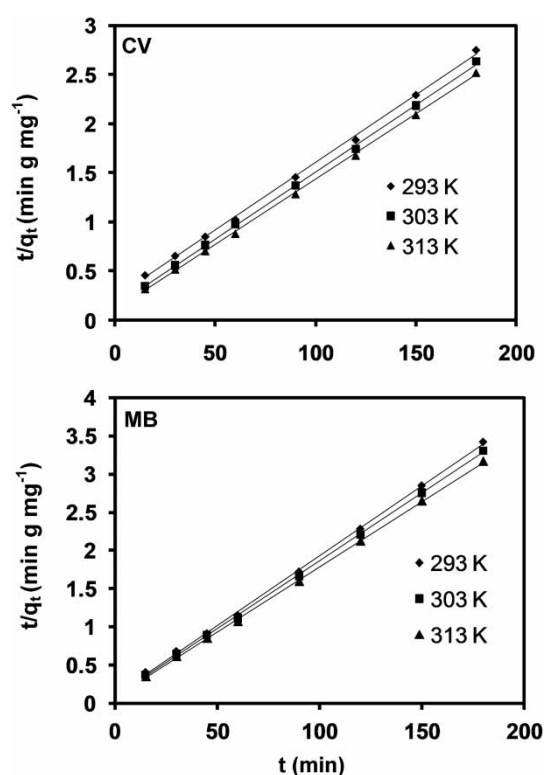
Figure 5 | Pseudo-second-order kinetic plots for biosorption of textile dyes by fish scales at different temperatures (experimental conditions: $C_0 = 50$ mg L^{-1}, $m_{CV} = 1$ g/0.1 L, $m_{MB} = 2$ g/0.1 L, agitation speed = 150 rpm, $T = 303$ K, contact time = 3 h).

process was explored by using an intra particle diffusion model (Chakraborty et al. 2011).

Intraparticle diffusion: $q_t = k_i t^{0.5}$ (9)

According to Equation (9), if a plot of q_t versus $t^{0.5}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. In the present study, the plots of q_t versus $t^{0.5}$ were linear at all temperatures for both CV and MB, but the plots did not pass through the origin, implying that although intraparticle diffusion is involved in the biosorption processes, it is not the sole rate-controlling step and some other mechanisms also play an important role.

Activation energy

The activation energy (E_a) for the biosorption processes of CV and MB by fish scales was determined using the Arrhenius equation (Chowdhury & Saha 2010):

$$\ln k = \ln A - \frac{E_a}{RT} \tag{10}$$

E_a was obtained from the slope of the linear plots of $\ln k_2$ versus $1/T$ and were calculated as 67.35 and 68.17 kJ mol^{-1} for CV and MB, respectively. According to the literature, these E_a values suggest that biosorption of both CV and MB onto fish scales proceeds via a chemical ion exchange mechanism as already inferred from the D–R isotherm (Chowdhury & Saha 2010).

Biosorption thermodynamics

Thermodynamic parameters, namely Gibbs free energy change (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0), were calculated using the following equations for the temperature range 293–313 K (Chowdhury & Saha 2010):

$$\Delta G^0 = -RT \ln K_C \tag{11}$$

$$K_C = \frac{C_a}{C_e} \tag{12}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{13}$$

The calculated ΔG^0 values for biosorption of CV and MB by fish scales at all temperatures are listed in Table 3. The values of ΔH^0 and ΔS^0 as determined from the slope and intercept of the plots of ΔG^0 versus T (Figure 6) are also listed in Table 3. Negative values of ΔG^0 indicate the thermodynamically feasible and spontaneous nature of the dye biosorption processes. Positive ΔH^0 values, 47.23 and 50.21 kJ mol^{-1} for CV and MB respectively, imply that the biosorption phenomena are endothermic. In addition, positive ΔS^0 values for both the dye-biosorbent systems reflect the affinity of fish scale towards the dyes. It also suggests increased randomness at the solid/solution interface.

Table 3 │ Thermodynamic parameters for biosorption of textile dyes by fish scales

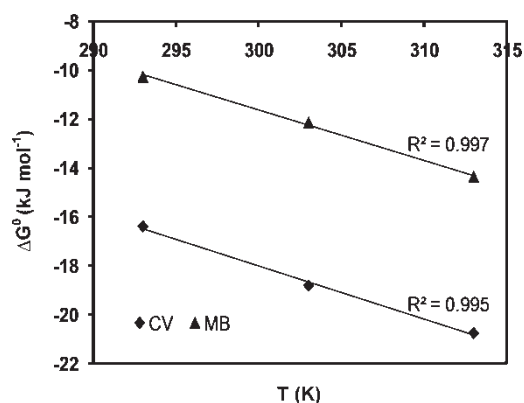| Dye	T (K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
CV	293	−16.39	47.23	180.41
	303	−18.82		
	313	−20.74		
MB	293	−10.23	50.21	171.26
	303	−12.12		
	313	−14.35		

Figure 6 │ Plots of Gibbs free energy change versus temperature for biosorption of CV and MB by fish scales.

Comparison of fish scale with other sorbents

A comparative study of the maximum dye uptake capacity of fish scale has been carried out with other reported low-cost sorbents and is presented in Table 4. It is to be noted that the maximum amount of dye uptake by various sorbents varies as a function of experimental conditions. In particular, the pH, temperature and sorbent dose have a very important effect on the estimation of the maximum amount of dye uptake per unit sorbent (Chowdhury & Saha 2011). Therefore, for a direct and meaningful comparison, the maximum amount of dye sorbed by fish scales has been compared to the maximum dye sorption capacity of other reported sorbents under different experimental conditions. From Table 4, it is evident that the maximum biosorption capacity of fish scale for both CV and MB is comparable and moderately higher than that of many corresponding sorbent materials. Differences in the uptake capacity are due to the properties of each sorbent material such as structure, functional groups and surface area. Easy availability and low cost are some additional advantages, suggesting that fish scales are a better biosorbent for the treatment of textile effluents.

CONCLUSIONS

The following conclusions are made based on the results of the present study:

1. The dye removal efficiency of fish scale varies significantly with initial solution pH up to a certain level. The biosorption capacity increases considerably with increasing temperature for both CV and MB.
2. The Langmuir isotherm model shows better fit to the equilibrium biosorption data of both CV and MB than the Freundlich and D–R isotherms, thus indicating monolayer sorption on a homogenous surface.
3. Biosorption phenomena of CV and MB by fish scales follow pseudo-second-order kinetics. Intraparticle diffusion model studies indicate that both boundary layer and pore diffusion might affect the biosorption rate of the dyes.
4. Activation energy calculated using the Arrhenius equation confirms that the biosorption processes involved chemical ion exchange.

Table 4 | Comparison of CV and MB biosorption capacity of fish scales with other reported low-cost adsorbents

Sorbent	pH	Bisorbent dose (g L^{-1})	Temp. (K)	Maximum sorption capacity (mg g^{-1})	Reference
CV					
Agaricus bisporous	4.0	4	303	19.18	Pandey et al. (2012)
Jute fibre carbon	8.00	1	303	27.99	Porkodi & Kumar (2007)
Coniferous pinus bark powder	8.0	–	303	32.78	Ahmad (2009)
Rice bran	10.0	5	313	42.25	Wang et al. (2008)
NaOH-modified rice husk	8.0	10	293	44.87	Chakraborty et al. (2011)
Jackfruit leaf powder	7.0	10	293	43.39	Saha et al. (2012b)
Pineapple leaf powder	8.0	20	293	78.22	Chakraborty et al. (2012)
Wheat bran	10.0	5	313	80.37	Wang et al. (2008)
Fish scales	9.0	10	313	74.39	This study
MB					
Brazil nut shells	6.50	100	303	7.81	de Oliveira Brito et al. (2010)
Spent coffee grounds	5.0	10	298	18.7	Franca et al. (2009)
Rice husk	8.0	1.2	305	40.59	Vadivelan & Kumar (2005)
Olive pomace	–	5	298	42.3	Banat et al. (2007)
Yellow passion fruit waste	8.0	10	298	44.70	Pavan et al. (2008)
Luffa cylindrical fibres	–	0.8	303	47	Demir et al. (2008)
Walnut sawdust	–	10	293	59.17	Ferrero (2007)
Garlic peel	–	3	303	82.64	Hameed & Ahmad (2009)
Fish scales	8.0	20	313	56.76	This study

5. An assessment of the process thermodynamics suggests the spontaneous and endothermic nature of biosorption of both CV and MB by fish scales.

6. The maximum CV and MB biosorption capacity of fish scale is comparable and moderately higher than that of many corresponding sorbent materials.

The results suggest that fish scale is a suitable biosorbent for the treatment of textile effluents.

REFERENCES

Ahmad, R. 2009 Studies on adsorption of crystal violet dye from aqueous solution onto coniferous pinus bark powder (CPBP). *J. Hazard. Mater.* **171**, 767–773.

Aksakal, O. & Ucun, H. 2010 Equilibrium, kinetic and thermodynamic studies of the adsorption of textile dye (Reactive Red 195) onto *Pinus sylvestris* L. *J. Hazard. Mater.* **181**, 666–672.

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

Banat, F., Al-Asheh, S., Al-Ahmad, R. & Bni-Khalid, F. 2007 Bench-scale and packed bed sorption of methylene blue using treated olive pomace and charcoal. *Bioresour. Technol.* **98**, 3017–3025.

Chakraborty, S., Chowdhury, S. & Saha, P. 2011 Adsorption of Crystal Violet from aqueous solution onto NaOH-modified rice husk. *Carbohydr. Polym.* **86**, 1533–1541.

Chakraborty, S., Chowdhury, S. & Saha, P. D. 2012 Insight into biosorption equilibrium, kinetics and thermodynamics of crystal violet onto *Ananus comosus* (pineapple) leaf powder. *Appl. Water. Sci.* **2**, 135–141.

Chowdhury, S. & Saha, P. 2010 Sea shell powder as a new adsorbent to remove to Basic Green 4 (Malachite Green) from aqueous solutions: equilibrium, kinetic and thermodynamic studies. *Chem. Eng. J.* **164**, 168–177.

Chowdhury, S. & Das, P. 2011 Utilization of a domestic waste – Eggshells for removal of hazardous malachite green from aqueous solutions. *Environ. Prog. Sust. Energy*, in press.

Chowdhury, S. & Saha, P. D. 2011 Biosorption kinetics, thermodynamics and isosteric heat of sorption of Cu(II) onto *Tamarindus indica* seed powder. *Colloids Surf. B.* **88**, 697–705.

Chowdhury, S. & Saha, P. D. 2012 Artificial neural network (ANN) modeling of adsorption of Methylene blue by NaOH-modified rice husk in a fixed-bed column system. *Environ. Sci. Pollut. Res.*, in press.

Chowdhury, S., Mishra, R., Saha, P. & Kushwaha, P. 2011a Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk. *Desalination* **265**, 159–168.

Chowdhury, S., Chakraborty, S. & Saha, P. 2011b Biosorption of Basic Green 4 from aqueous aqueous solution by *Anannus comosus* (pineapple) leaf powder. *Colloids Surf. B.* **84**, 520–527.

Crini, G., Peindy, H. N., Gimbert, F. & Robert, C. 2007 Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solution by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies. *Sep. Purif. Technol.* **53**, 97–110.

Demir, H., Top, A., Balkose, D. & Ulku, S. 2008 Dye adsorption behavior of *Luffa cylindrica* fibers. *J. Hazard. Mater.* **153**, 389–394.

Ferrero, F. 2007 Dye removal by low cost adsorbents: hazelnut shells in comparison with wood sawdust. *J. Hazard. Mater.* **142**, 144–152.

Franca, A. S., Oliveira, L. S. & Ferreira, M. E. 2009 Kinetics and equilibrium studies of methylene blue adsorption by spent coffee grounds. *Desalination* **249**, 267–272.

Gupta, V. K. & Suhas 2009 Application of low-cost adsorbents for dye removal – a review. *J. Environ. Manage.* **90**, 2313–2342.

Hameed, B. H. & Ahmad, A. 2009 Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass. *J. Hazard. Mater.* **164**, 870–875.

Nasuha, N., Hameed, B. H. & Din, A. T. M. 2010 Rejected tea as a potential low-cost adsorbent for the removal of methylene blue. *J. Hazard. Mater.* **175**, 126–132.

de Oliveira Brito, S. M., Andrade, H. M. C., Saores, L. F. & de Azevedo, R. P. 2010 Brazil nut shells as new biosorbent to remove methylene blue and indigo carmine from aqueous solutions. *J. Hazard. Mater.* **174**, 84–82.

Pandey, P., Singh, R. M., Singh, K. N. & Manisankar, P. 2012 Evaluation of the individuality of white rot macro fungus for the decolorization of synthetic dye. *Environ. Sci. Pollut. Res.*, in press.

Pavan, F. A., Lima, E. C., Dias, S. L. P. & Mazzocato, A. C. 2008 Methylene blue biosorption from aqueous solutions by yellow passion fruit waste. *J. Hazard. Mater.* **150**, 703–712.

Porkodi, K. & Kumar, K. V. 2007 Equilibrium, kinetics and mechanism modelling and simulation of basic and acid dyes sorption onto jute fiber carbon: Eosin yellow, malachite green and crystal violet single component systems. *J. Hazard. Mater.* **143**, 311–327.

Rafatullah, M., Sulaiman, O., Hashim, R. & Ahmad, A. 2010 Adsorption of methylene blue on low-cost adsorbents: A review. *J. Hazard. Mater.* **177**, 70–80.

Saha, P. 2010 Assessment on the removal of methylene blue dye using tamarind fruit shell as biosorbent. *Water Air Soil Pollut.* **213**, 287–299.

Saha, P., Chowdhury, S., Gupta, S. & Kumar, I. 2010 Insight into adsorption equilibrium, kinetics and thermodynamics of Malachite Green onto clayey soil of Indian origin. *Chem. Eng. J.* **165**, 874–882.

Saha, P. D., Chowdhury, S., Mondal, M. & Sinha, K. 2012a Biosorption of Direct Red 28 (Congo Red) from aqueous solutions by eggshells: batch and column studies. *Sep. Sci. Technol.* **47**, 112–123.

Saha, P. D., Chakraborty, S. & Chowdhury, S. 2012b Batch and continuous (fixed-bed column) biosorption of crystal violet by Artocarpus heterophyllus (jackfruit) leaf powder. *Colloids. Surf. B.* **92**, 262–270.

Silveira, E., Marques, P. P., Macedo, A. C., Mazzola, P. G., Porto, A. L. F. & Tambourgi, E. B. 2011 Decolorization of industrial azo dye in an anoxic reactor by PUF immobilized *Pseudomonas oleovorans*. *J. Water Reuse Desalin.* **1**, 18–26.

Srinivasan, A. & Virarghavan, T. 2010 Decolorization of dye wastewaters by biosorbents: a review. *J. Environ. Manage.* **91**, 1915–1929.

Vadivelan, V. & Kumar, K. V. 2005 Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *J. Colloid Interface Sci.* **286**, 90–100.

Wang, X. S., Liu, X., Wen, L., Zhou, Y. & Li, Z. 2008 Comparison of basic dye crystal violet from aqueous solution by low-cost biosorbents. *Sep. Sci. Technol.* **43**, 3712–3731.