Indian Journal of Chemical Technology
Vol. 26, July 2019, pp. 321-329

Adsorption behaviour of bromophenol blue from the aqueous solution on *Labeo bata* fish scale, a bio-waste material

Abir Ghosh[1, 2], Hari Shankar Biswas[3], Sushanta Debnath[4], Palani Sasikumar[1], Krishna Biswas*[,2] & Uday Chand Ghosh*[, 1]

[1]Department of Chemistry, Presidency University, 86/1 College Street, Kolkata 700 073, India.

[2]Department of Chemistry, Maharaja Manindra Chandra College, Kolkata, 700 003 India.

[3]Department of Chemistry, Surendranath College, 24/2 Mahatma Gandhi Road, Kolkata 700 009, India.

[4]Crystallography and Molecular Biology Division, Saha Institute of Nuclear Physics, Kolkata 700 064, India.

E-mail: ucghosh@yahoo.co.in

Received 4 August 2017; accepted 22 February 2019

The processed protein-rich scales of *Labeo bata* fish have been characterized as cycloid pattern from the scanning electron and atomic force microscopic images. The scales when used for the bromophenol blue (BPB) adsorption from aqueous phases show the good BPB removal performance at *p*H 4.8 (± 0.1). The kinetic data acquired at that *p*H fits well both with the pseudo-second order and the Weber-Morris kinetic equations. Arrhenius activation energy (E_a = 4.20 kJ. mol^{-1}) as well as temperature dependent kinetic parameter (A = 75.56 g. mg^{-1}. min^{-1}) which are estimated indicate the facile BPB adsorption. The data of adsorption equilibriums describe the Freundlich model very well. Thermodynamics shows that the BPB adsorption by the fish scale is spontaneous (ΔG^0 = negative, ΔH^0 = -21.49 kJ. mol^{-1} and ΔS^0 = + 27.75 $J.mol^{-1}.K^{-1}$). The BPB adsorption by the tested fish scale has taken place with electrostatic mechanism.

Keywords: Adsorption, Breakthrough, Bio-waste material, Bromophenol blue, Kinetics, *Labeo bata* fish scale, Multilayer Thermodynamics

Restoration of our environment green is one of the major challenges and attracted much attention of present environmental research. Among the highly populated countries of Asian sub-continent, India has been suffering with serious environmental deteriorations because of the rapid industrialization. Man-made aromatic ring containing organic dyes are being extensively used in various industries including textile, paper, plastics, leather, food, cosmetics etc[1,2]. These industries generate and discharges huge volume of wastewater polluted with organic and inorganic dyes to river and oceans, consequently worsening the surface water quality and ecological balance[3,4]. These dye pollutants are not only importing the color to water bodies, and also stop the reoxygenation capacity of the water bodies (increasing BOD), cut-off sunlight by reducing water transparency, thereby reduce the photosynthetic process in aquatic organism and algae. These water-soluble aromatic ring containing synthetic dyes are highly carcinogenic, mutagenic[5] and are chromophoric[6]. Without appropriate treatment, these dyes are quite stable in the environment for a long period of time, which has not only been enhancing the cancer to the human lives but also damaging the aquatic lives.

In order to minimize this problem, an economically viable method for the treatment of liquid waste rich of dye is the most urgent demand of the present society. Several traditional physio-chemical methods have been utilized for address this problem, such as biological degradation, oxidation, flocculation, active sludge, trickling filters, coagulation with some chemicals, photodegradation, surface adsorption by different materials, membrane filtration etc had been investigated extensively for removing dyes over the years[2,7]. But, the surface adsorption method had been received a special interest worldwide owing to the requirement of small space for installation, simple operation, non-requirement of trained personnel and chemicals for the daily use, and high efficiency[8]. The adsorption of dyes using different types of porous materials has been studied in detail. These include activated carbon, silica, hardwood, hardwood sawdust, fly ashes, fibers, paddy straw, bone char, metal oxide, mixed valent metal oxides and metal sulfide nanoparticle, metal oxide nanoparticle loaded

on activated carbon. Among these activated carbon and metal oxide loaded on activated carbon is being used extensively due to its high absorption efficiency. However commercial production cost of activated carbon is quite expensive to afford for developing countries like India. Hence the current area of research looking for effective alternate adsorbents, which is affordable low-cost as well as equivalent potential of activated carbon.

Consequently, several agricultural byproducts, such as plum kernels, cassava peel, jute fiber, olive stones, nutshells, peach stones, rice husks and orange peel etc. were successfully utilized as absorbent.

Currently the surface adsorption of dye by cheap and abundantly available biomass has gained special attention. The fish source products such as the charcoal of fishbone and the fish scales had effectively been investigated[9,10] for scavenging of the water contaminants. The scales of fish had been abundantly available, often these are having little or no economic value could be used as an adsorbent material for scavenging the organic dyes and other contaminants from water. The scales of Mojarra Tilapia fish had been investigated for the removal of metallic iron[11], and zinc and ferum ion from the wastewater[12]. Bisorption of bivalent lead by the scales of Labeo rohita had also been reported[13]. Adsorption of cationic and anionic dyes and other contaminants by different types of natural adsorbents had been investigated by some researchers[10,14,15].

Bromophenol blue (BPB) is used as color marker to monitor the progress of agarose gel electrophoresis and polyacrylamide gel electrophoresis, and also for the dyeing in cotton and paper mill industries. Intake of it causes irritation of skin and respiratory tract with redness and pain[16] including cough and shortness of breath.

The removal of BPB from the contaminated water was investigated with different adsorbent materials[17,18], but the use bio-waste material (low cost) for scavenging BPB has not yet been reported in literature. Therefore, it is aimed that the scales of *Labeo bata* fish will be systematically explored for scavenging the BPB from its water solution.

Thus, this manuscript reports herein the behavior of kinetics and thermodynamics of the bromophenol blue (BPB) adsorption by the scales of *Labeo bata* fish.

Experimental Section

All chemicals and reagents used in this work were guaranteed reagent (G.R.) grade (Merck India, Mumbai).

Preparation of bromophenol blue (BPB) solution

Exactly known weight (100 mg) of BPB was transferred inside a 1000 mL volumetric flask which was dissolved in double distilled water, and the volume was made up to the mark with distilled water of adjusted *p*H to 4.8 (± 0.1). The concentration of this dye solution was 100 mg. L^{-1}. The dye solution of a required level of concentration was prepared for working as and where required.

Treatment of the scales of *Labeo bata* fish

The scales of *Labeo bata* fish was collected from a local market of Kolkata, India and washed (7-8 times) with distilled water to clean the extraneous materials. The cleaned scales were dried at 80-100°C inside an air-oven for 3 h, which were ground and sieved for separating out the scales ranged in 25-50 mesh (scale size: 0.29 – 0.71 mm) for the use in experiments.

Analytical instruments

The *p*H-meter which was used for the *p*H analysis of samples was ELICO India (Model: LI-611). The colorimetric analyses for concentration of the BPB in sample solution were conducted by UV-VIS spectrophotometer (Model: U-3210, Hitachi Japan). The surface morphology of fish scale samples was analyzed by Cambridge-360 scanning electron microscope (SEM). For taking the atomic force microscopic (AFM) image of the fish scale sample, a multimode scanning probe microscope (Agilent AFM 5500 series, U.S.A.) was used, which has multipurpose small scanner with a very low coherence laser (1 mW power, 670 nm wavelength) of coherence length (<50 μm), scan range: XY: 0-10 μm; Z: 0-2 μm, noise level: XY < 0.1 nm rms and Z < 0.02 nm rms.

Spectrophotometric analysis of bromo phenol blue (BPB) in sample solutions

The solutions of standard BPB of concentrations (C_0): 1, 2, 3, 4, 5, 6, 7 and 8 mg.L^{-1} were prepared from a stock solution of C_0 = 100 mg. L^{-1} by exact dilution method. Value of the wavelength for absorption maximum (λ_{max}) of the BPB solution was determined by auto scan mode of the spectrophotometer which was found to be at 590 nm. The absorbance value of dye solution (C_0 ranged in 1.0 and 8.0 mg. L^{-1}) was thus obtained at λ_{max} = 590 nm which was plotted against the dye C_0 for the Beer's law curve. The calibration curve drawn was used for the determination of concentration of dye samples before and after conducting each experiment.

Batch adsorption experiment

Batch adsorption experiments were conducted by mechanical agitation (speed: 600 ± 10 rpm). Here, 50 mL aliquot of BPB solution (C_0 = 10.0 to 60.0 mg. L^{-1}) was transferred into the 100 mL polyethylene (PE) bottle to which 0.2 g of *Labeo bata scale* was added and capped well. The *p*H of each of the experimental sample solution, which was taken in PE bottle was adjusted to 4.8 (± 0.1) using 0.1(M) NaOH and/ or 0.1(M) HCl as required. The reaction mixture was agitated for two hours, excepting the kinetic experiment. Once the agitation period was over, the solid scales were separated from the reaction mixture by filtration and analyzed for the dye concentration (C_f, mg. L^{-1}) in filtrate. The amount of dye left in solution after the experiment was used to evaluate the dye amount transferred from the liquid to the solid fish scale by the following mass balance relation.

$$\text{Amount of dye adsorbed (mg/g)} = \frac{\text{Amount of dye added} - \text{Amount of dye remained in filtrate}}{\text{Weight of adsorbent used}}$$

Effect of *p*H

Experimental set up described above was used separately for the determination of *p*H influence on the adsorption of BPB (C_0 = 16.0 mg. L^{-1}) by *Labeo bata* fish scale. The *p*H range of the working solution was fixed up at 2.0 to 10.0 with an increment of one unit fixing the fish scale dosage 4.0 g. L^{-1}. Here, the initial *p*H of the dye solution was adjusted at the desired level with 0. 1 M of acid/alkali solution. As this effect was estimated before determining the equilibrium time, the agitation time was fixed up to 2.0 h.

Adsorption kinetics

The reaction of kinetics of BPB adsorption by *Labeo bata* fish scale was conducted by the batch experimental program at *p*H = 4.8 (± 0.1), ionic strength = 1M (adjusted by $NaNO_3$) and temperatures (± 1.6) = 283, 303 and 323K. Here, 500.0 mL of the dye solution (C_0: 16.0 mg. L^{-1}) was taken with 2.0 g fish scale in 1000 mL glass vessel, and placed in a thermostat bath to attain the desired temperature. Thereafter, the mixture of the reactants was agitated (600 ± 10 rpm) using a speed adjustable agitator. A measured volume of the reaction mixture was withdrawn after a definite time interval- 2.0 mL at a gap of 5 minutes from the zero time up to 45 min, and then at a gap of 15 min after the 45 min till the equilibrium reached. The sample solution was taken in a 10.0 mL beaker and the *p*H of the solution was set to 4.8 (± 0.1) using 0.1(M) NaOH or 0.1(M) HCl, which was transferred in a 25.0 mL volumetric flask. The remaining volume was made up to the mark with distilled water adjusting *p*H at 4.8 (±.0.1) and analyzed for absorbance value of the solution using UV-Vis spectrophotometer for the dye concentration (C_f).

Adsorption isotherm

The studies of equilibrium isotherm of the current reaction were separately conducted at temperature (± 1.6) = 283, 303 and 323K at *p*H = 4.8 (± 0.1) by the batch adsorption procedure. Here, value of the C_0 of dye solution was taken in 10.0 to 60.0 mg. L^{-1}. The adsorbent dose used was 0.40 g for the 100 mL of dye solution. The agitation (speed: 600 ± 10 rpm) time used was 2 h. When the reaction time was over, each equilibrium mixture was filtered. The absorbance value of the filtrate was analysed after adjusting the *p*H to 4.8 (± 0.1) using UV-Vis spectrophotometer the dye concentration (C_f).

Results and Discussion

Characterisation of fish scales

The composition of scales of *Labeo bata* fish as reported by Sarower-E-Mahfuj *et al*[19] are: crude protein (66%), lipid (oil) (13%), crude ash (16%) and carbohydrate (3%). Figure 1 shows the scanning electron microscopic (SEM) image of the scales, which appeared to be cycloid type morphology. It seems to be circular thin plate of symmetrical shape (diameter: 500 μm) consisting of two segments and one crusp. The posterior portion of a scale is overlapped by the anterior portion. The cross sectional view of SEM image which appeared consists

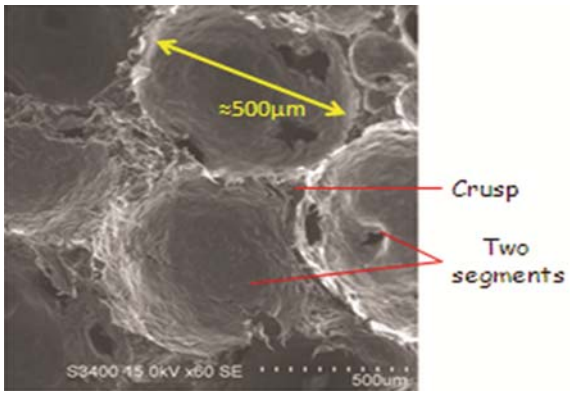

Fig. 1 — The scanning electron microscopic (SEM) image of *Labeo bata* fish scale.

of two main types of layer. The upper layer contains organic moiety impregnated with some calcium salts called 'bony' layer, and the lower layer contains collagen fiber called fibrous layer. Figure 2 shows the image of atomic force microscopy (AFM) which reflected clearly the undulated surface. The bright portions of AFM image indicates the presence of protein, which should take part an important role for the adsorption of BPB from the aqueous solution.

Effect of dose

The influence of fish scale (*Labeo bata*) dose was studied for the BPB adsorption from aqueous solution varying from 1.0 to 5.0 g. L^{-1} at *p*H 5.0 and room temperature. Figure S_1 (supporting information,SI) represents the results, indicating increase of the BPB adsorption percentage with increasing dose of the fish scale from 1.0 to 4.0 g.L^{-1}. The BPB adsorption percentage left nearly same in spite of the dose increase from 4.0 g. L^{-1}, suggesting an optimum dose of the fish scale 4.0 g. L^{-1} for the BPB adsorption.

Effect of *p*H

Figure 3 shows the effect of *p*H on BPB adsorption by the fish scale. It shows that the dye adsorption amount increased with increase of *p*H from 2.41 to 5.03 and decreased with increase of *p*H above 5.03. Lesser adsorption amount at *p*H above 5.03 is due to the weakening of columbic attraction between neutral fish scale surface and deprotonated form of the BPB. The depletion of BPB adsorption amount at *p*H above 5.03 is due to the existence of the BPB as anion and lowering of positive charge density over the fish scale surfaces. In this context, it can be remembered that the protein moiety persists predominantly as a positively charged species at strong acidic *p*H region; and strong electrostatic attraction force operates well between the positive fish scale surface and the progressively deprotonated BPB species at *p*H 5.03. The result found is similar to the observation that had been noted by other researchers [20,21].

Kinetic analysis

Figure 4 demonstrates the variation of BPB adsorption capacity (q_t, mg. g^{-1}) against time (t, min) at *p*H 4.8 (± 0.1) and at temperatures 283, 303 and 323K. It is found (Fig. 4) that the time required 2 h to reach the equilibrium. Values of the q_t increased sharply up to 50 min which reduced slowly showing nearly same up to 100 min. Decrease of q_t beyond 50 min of the reaction is owing to the decrease of

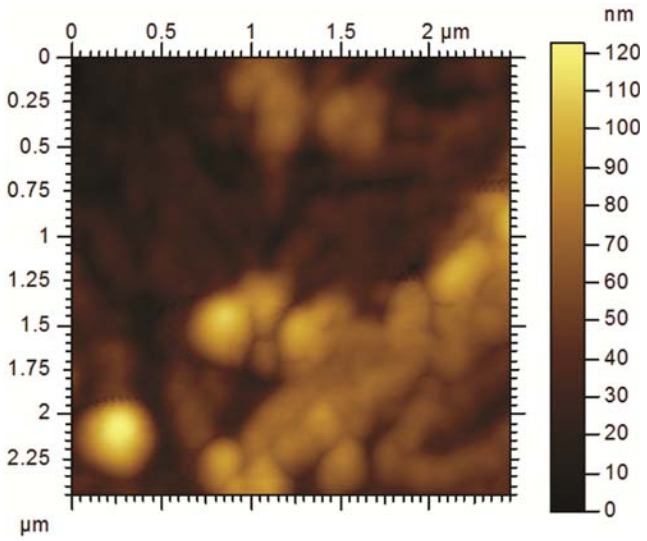

Fig. 2 — The atomic force microscopic (AFM) image of the *Labeo bata* fish scale.

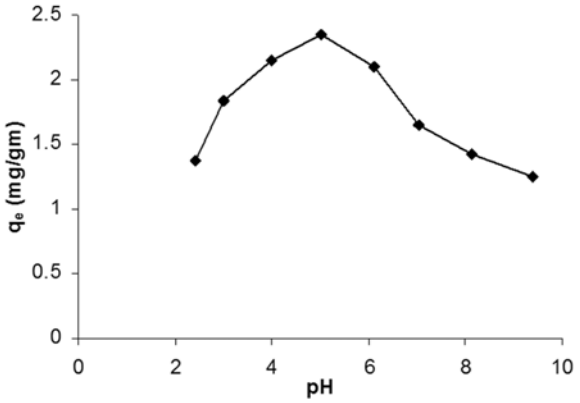

Fig. 3 — Effect of *p*H on the adsorption of BPB from the aqueous solution by *Labeo bata* fish scale.

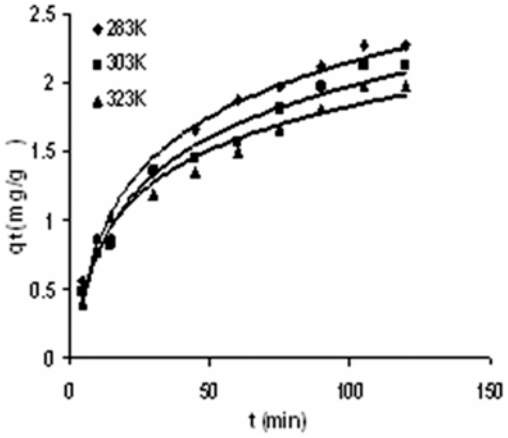

Fig. 4 — The plots of q_t vs. t of BPB adsorption kinetic data as points on *Labeo bata* fish scale at three different temperatures and the non-linear fits with pseudo-second order kinetic model. Initial concentration of BPB: 16.0 mg. L^{-1}, *p*H = 4.8 (± 0.1).

surface active sites on fish scale surfaces and decrease of BPB concentration in solution. The kinetic data (shown as points) of Fig. 4 were modelled with the linearised form of pseudo-first-order (Eq. 1) and pseudo-second order (Eq.2)[22–24] relations.

$$\log (q_e - q_t) = \log q_e - (k_1 / 2.303)t \quad \ldots (1)$$

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

where q_e and q_t are the adsorption capacities (mg. g^{-1}) at equilibrium and at any time t, respectively; and k_1 the pseudo-first order rate constant ($time^{-1}$),and k_2 is the pseudo-second order rate constant (g. mg^{-1}. $time^{-1}$).

Figs. S_2 and S_3 (S. I. section) show the pseudo-first and the pseudo-second order model equation fits, respectively. Figure 4 shows only the non-linear pseudo second order model fit. Table 1 shows the kinetic parameters calculated from the slope and intercept of the plots. Analyses of the kinetic parameters suggested that the BPB adsorption by the *Labeo bata* fish scales described the pseudo-second order equation (Eq. 2) ($0.99 < R^2 < 1.0$) better than the pseudo-first order equation ($0.89 < R^2 < 0.91$) (Table 1)**.** Thus, it can be concluded that the BPB adsorption on the fish scale takes place obeying the pseudo-second order kinetics, which is different from the result that had been reported by El-Zahhar *et al.*[21]. In general, it is noted that the values of k_2 increased while the q_e (mg. g^{-1}) decreased with increase of temperature on the adsorption reaction. This is due to the increase of the fraction of effective collisions with enhancing the temperature as the fraction of the adsorbent species takes part in the reaction with energy greater than or equal to the threshold energy (for an effective collision initiation required minimum energy) which increases rapidly[25]. Decrease of the q_e with increasing temperature indicates the exothermic nature of BPB adsorption on *Labeo bata* fish scales.

Table 1— The kinetic parameters for BPB adsorption by *Labeo bata* fish scale at three temperatures.

Model kinetic equations	Parameters	283K	303K	323K
Pseudo-second order	$k_2 \times 10^2$ (mg/g/min)	14.11	14.14	18.06
	q_e (mg/g)	2.71	2.55	2.30
	h_0	0.10	0.09	0.09
	R^2	0.99	0.99	0.98
Pseudo-first order (Lagergren)	k_1 (min^{-1})	1.39	1.44	1.52
	q_e (mg/g)	4.79	4.2	3.93
	R^2	0.90	0.89	0.88

Diffusion kinetics

The functional relationship used by many workers to predict the rate of an adsorption reactions is presented (Eq. 3)[26] below,

$$q_t = k_{id}\, t^{0.5} + C \quad \ldots (3)$$

where k_{id} is the intra-particle diffusion rate constant (mg. g^{-1}. $time^{-0.5}$) and C is the intercept which gives the idea about the film thickness. The larger the value of C the greater is the boundary layer effect. The adsorption process onto an adsorbent follows three steps viz., film diffusion, macro and micro-pore diffusions phenomena and the slowest of the three steps controls the overall rate process [27]. Generally, intra-particle (pore) diffusion is the rate-limiting step in batch process, while for a continuous flow system film (or boundary layer) diffusion is more likely to be the rate-limiting step**.**

Figure 5 shows the plots of q_t versus $t^{0.5}$ for the temperature 283, 303 and 323 K. The good linearity ($R^2 > 0.95$) of the Weber and Morris plots suggested that the rate of dye adsorption reaction is controlled solely by the boundary layer (inter particle) diffusion with very low boundary layer thickness, which is similar to the result reported by El-Zahhar *et al.*[21]. Thus, the rate limiting step of the adsorption reaction of BPB with the *Labeo bata* fish scale at any of the investigated temperatures is controlled by the boundary layer diffusion process.

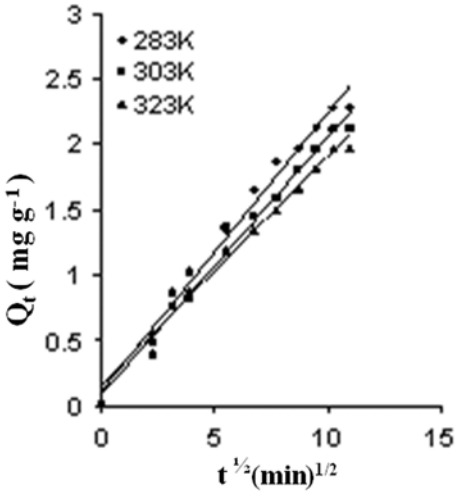

Fig. 5 — The plots of q_t versus $t^{1/2}$ for the BPB adsorption over *Labeo bata* fish scale for the diffusion kinetics at investigated three different temperatures.

Equilibrium data analysis

The plot-A of Fig. 6 shows the equilibrium data of BPB adsorption by the *Labeo bata* fish scale at *p*H 4.8 (± 0.1) and the temperatures noted therein. It is seen that the BPB adsorption amount (q_e, mg. g^{-1}) at equilibrium decreased with the rise of reaction temperature. These q_e data were analyzed by linear regression using Freundlich (Eq. 4)**,** Langmuir (Eq. 5) [28] and Redlich-Peterson (R-P) (Eq. 6) equations [29]**.**

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad \ldots (4)$$

$$\frac{C_e}{q_e} = \frac{1}{\theta_0 b} + \frac{C_e}{\theta_0} \quad \ldots (5)$$

$$\frac{C_e}{q_e} = \frac{1}{\alpha} + \left(\frac{\beta}{\alpha}\right) C_e^{\gamma} \quad \ldots (6)$$

where C_e (mg. L^{-1}) and q_e (mg. g^{-1}) are the equilibrium concentration and the capacity, respectively. K_F and n are the Freundlich constants. Θ_0 and b are the Langmuir monolayer capacity (mg. g^{-1}) and the Langmuir constants related to the equilibrium constant (g. L^{-1}), respectively. The α, β and Θ_0 are the three constants of the R-P (Eq. 6) which bears the characteristics of both Langmuir and Freundlich model isotherms. If the value of γ is unity, the R-P equation becomes the Langmuir model and, if the value of γ deviates largely from unity, the R-P equation Eq. (6) changes to the Freundlich model (4). When γ = 0, the R-P equation converts to the Henry's law.

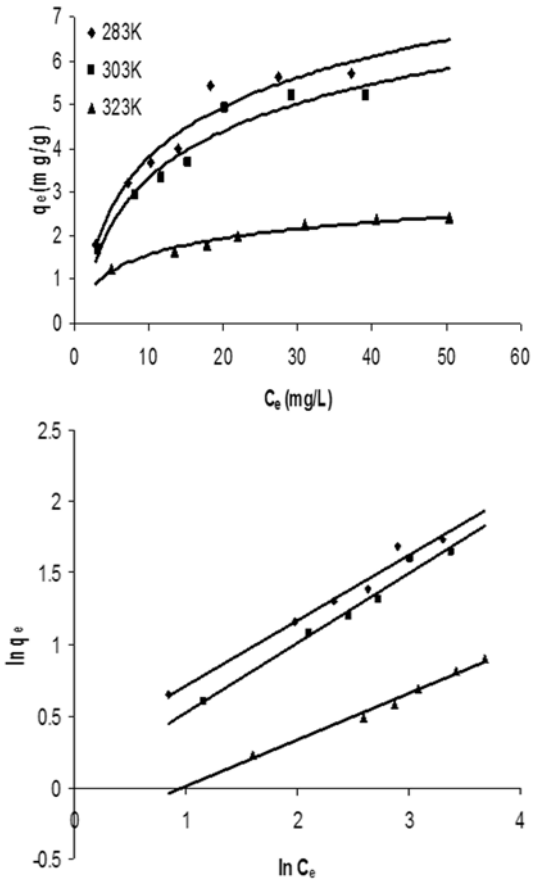

Fig. 6 — The equilibrium data as points of BPB adsorption by *Labeo bata* fish scale at *p*H 4.8 (± 0.1) and Freundlich isotherm fits of the data: (A) non-linear and (B) linear.

Figure 6 shows the equilibrium data as points which were modeled by the isotherm equations (Eq. 4-6). It is seen (Figure 6) that the data fit is very well with the Freundlich isotherm (Eq. 4) which is better than the Langmuir (Figure S_4, SI) and the R-P (Figure S_5, SI) isotherm [21]. Table 2 shows the model parameters estimated for the each model equation including the correlation coefficient (R^2). Goodness of the data fit order [Freundlich (R^2 = 0.97-0.98) >Redlich-Peterson (R^2=0.95-0.978) ≈ Langmuir (R^2 = 0.95-0.98)] indicated the BPB adsorption has taken place with multilayer surface coverage, and the surface coverage theoretically increased without limitation with increasing adsorbate concentration[30]. The Freundlich constant "n" is ranged in 2.19 to 3.08, suggesting a high adsorption capacity. The "γ" value of the Redlich-Peterson model is 0.91 (much less than unity), indicating the BPB adsorption inclines to multilayer phenomenon than monolayer. Despite the fitness of present data with the Langmuir isotherm model is rather poor (R^2 = 0.95) than the Freundlich isotherm, the q_e (mg. g^{-1}) values for the monolayer coverage are ranged in 6.95 to 7.39. That is, the *Labeo bata* fish scale may be used as a cheap

Table 2 — The estimated isotherm parameters for the BPB adsorption on *Labeo bata* fish scale at three temperatures

Isotherm Models	Parameters	283K	303K	323K
Freundlich	K_F	1.29	1.03	0.72
	n	2.19	2.04	3.08
	R^2	0.97	0.97	0.98
Langmuir	θ (mg/g)	7.39	7.17	6.95
	b (L/mg)	0.11	0.086	0.10
	R^2	0.94	0.94	0.97
Redlich-Peterson	α	1.05	1.44	2.61
	β	0.18	0.19	0.48
	R^2	0.95	0.95	0.98

bio-waste adsorbent for scavenging the BPB profitably from water at *p*H ~ 5.0.

Activation energy

Arrhenius equation (Eq. 7) was used for the activation energy (E_a) of the reaction. The value of k_2 inserted here was the pseudo-second order rate constant as the kinetic data for the present case described the pseudo-second order kinetic equation Eq. (2) better than the pseudo-first Eq. (1).

$$k_2 = A \exp(-E_a / RT) \quad \ldots (7)$$

where A (g. mg^{-1}. min^{-1}) is considered as a temperature independent factor and E_a (kJ. mol^{-1}) the activation energy of a particular reaction. R and T are universal gas constant (8.314×10^7 erg. mol^{-1}) and temperature (K), respectively.

Logarithmic form of the Arrhenius equation (7) can be illustrated as a linear form which can be written as below [Eq. 8],

$$\ln k_2 = \ln A + (-Ea/R)1/T \quad \ldots (8)$$

Figure 7A shows the linear plot of $\ln k_2$ versus T^{-1}. The activation energy (E_a) and the temperature dependent parameter (A) of this reaction as calculated from the slope and the intercept of plot are found to be 4.20 kJ. mol^{-1} and 75.56 g. mg^{-1}. min^{-1}, respectively. The activation energy barrier of this adsorption reaction is sufficiently small which can be provided easily from the mechanical agitation of reaction mixture at room temperature for the transfer of BPB species from solution over the surface of fish scale for adsorption.

Temperature effect and thermodynamic parameters

Thermodynamic parameters for the adsorption reaction can be calculated using the following standard relations (Eq. 9, 10) [15].

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \ldots (9)$$

and

$$\Delta G^0 = -2.303RT \log K_c \quad \ldots (10)$$

where ΔG^0, ΔH^0 and ΔS^0 are the standard changes of free energy, enthalpy and entropy, respectively; K_c (=1000 q_e/c_e) is the equilibrium constant

The adsorption of BPB onto the fish scale as a function of temperature was investigated and the changes of Gibbs free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were calculated for the present process from the intercept and the slope from the ΔG^0 versus T plot (Fig. 7B). Table 3 shows the relevant data for adsorption of BPB by the fish scale. The obtained negative ΔG^0 values at three temperatures indicate the spontaneous nature under the applied conditions [31]. Inspection of the data

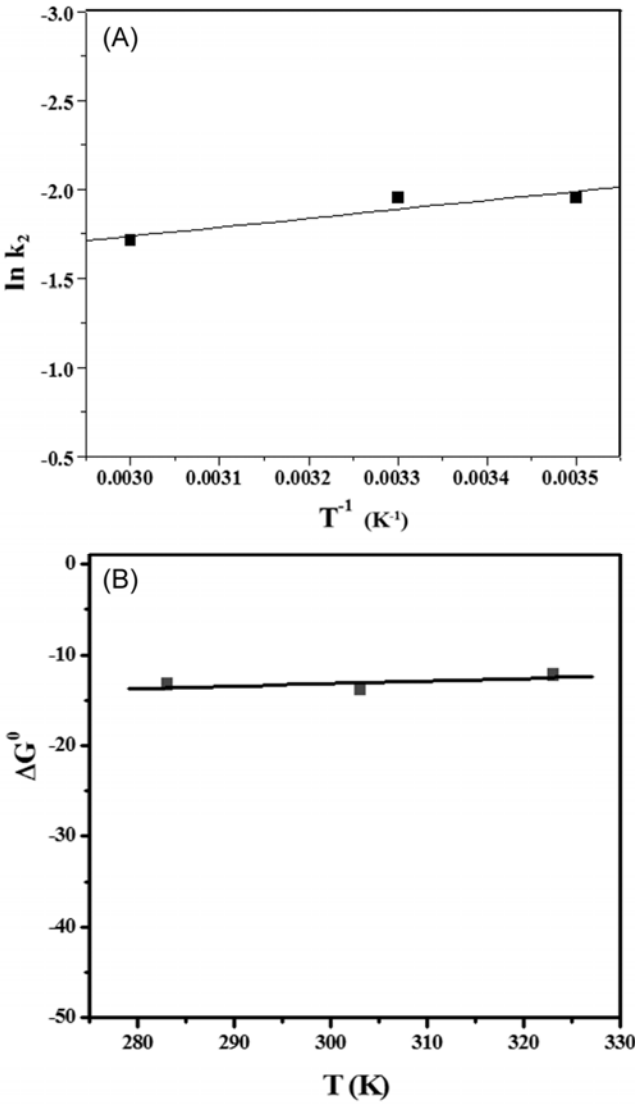

Fig. 7 — (A) The plots of $\ln k_2$ versus T^{-1} for activation energy and (B) the plots ΔG^0 versus T for thermodynamic parameters for the adsorption of BPB by *Labeo bata* fish scale.

Table 3 — Thermodynamic parameters for adsorption of the BPB on *Labeo bata* fish scale *p*H 4.8(±0.1)

Temperature (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol/K)
283	-13.3		
303	-13.78	-21.49	27.75
323	-12.19		

of Table 3 reveals that the ΔG^0 values are found to be nearly same with increasing temperature indicating the adsorption process becomes equally favorable at all three studied temperatures. The negative enthalpy change (ΔH^0) for the adsorption indicates the exothermic nature of the process and the adsorption is unfavored according to the La Chattelier principle. The positive value of entropy change (ΔS^0) reflects the affinity of fish scale toward BPB. This is due to the increase of randomness at the solid-liquid interface with transfer of BPB for the release of water molecules from the hydrated dye.

Adsorption mechanism

Labeo bata fish scale is rich with protein and lignin which contain carboxyl and quaternary amino functionalities for the adsorption of BPB. The protein exists predominantly as a positively charged species in the strongly acid *p*H. In acid *p*H range, presence of H^+ ions assists to stabilize the C terminal of the protein unlikely the N terminal. Cationic N terminal involves in the electrostatic interaction with the oxygen and negative sulfur center of BPB. Figure 8 depicts the proposed adsorption mechanism. The exothermic and multilayer adsorption reaction is driven by an electrostatic interaction between fish scale and BPB occurring through the inter particle diffusion.

Conclusion

Removal of BPB from the aqueous solutions by *Labeo bata* fish scale through adsorption process has been experimentally investigated aiming to use the bio-waste material for cleaning of waste water. The percentage of BPB removal increases with increasing the *p*H of solution and attains a maximum at *p*H ~ 5.0, and that decreases with increasing the *p*H above 5.0. Increase of dosage of the fish scales and also the contact time increases the capacity of BPB removal by the employed fish scale. The pseudo-second model describes the kinetic data fairly well. The low activation energy (4.20 kJ. mol^{-1}) and temperature dependent parameter (75.56 g. mg^{-1}. min^{-1}) have supported the use of the present bio-waste material for scavenging the BPB from solutions. The adsorption equilibrium reaction of BPB with fish scale takes place obeying the assumption of Freundlich isotherm. Thermodynamics shows exothermic and spontaneous nature under the conditions of experiment. Thus, the *Labeo bata* fish scale is a useful cost effective bio-waste which can be recycled as a suitable BPB scavenging material from the contaminated water.

Acknowledgement

Authors are thankful to the Head, Department of Chemistry, Presidency University, Kolkata-700073, India for providing laboratory facilities. P.S. kindly acknowledge to DST and UGC start up grant0 for their financial support.

References

1 Ayad M M & El-Nasr A A, *J Phys Chem C*, 114 (2010) 14377.
2 Wong Y C, Szeto Y S, Cheung W H & McKay G, *Langmuir*, 19 (2003) 7888.
3 Khattri S D & Singh M K, *J Hazard Mater*, 167 (2009) 1089.
4 Kumari K & Abraham T E, *Bioresour Technol*, 98 (2007) 1704.
5 Peralta-Zamora P, Kunz A, Gomes de Moraes S, Pelegrini R, De Campos Moleiro P, Reyes J & Durán N, *Chemosphere*, 38 (1999) 835.
6 Daneshvar N, Ayazloo M, Khataee A R & Pourhassan M, *Bioresour Technol*, 98 (2007) 1176.
7 Gomes A C, Gonçalves I C & De Pinho M N, *J Memb Sci*, 255 (2005) 157.
8 Sivakumar P & Palanisamy P N, *Int J ChemTech Res*, 1 (2009) 502.
9 Bhargava D S & Killedar D J, *Water Res*, 26 (1992) 781.
10 Kongsri S, Janpradit K, Buapa K, Techawongstien S & Chanthai S, *Chem Eng J*, 215 (2013) 522.
11 Villanueva-Espinosa J F, Hernández-Esparza M & Ruiz-Treviño F A, *Ind Eng Chem Res*, 40 (2001) 3563.
12 Othman N, Abd-Kadir A & Zayadi N, *ARPN J Eng Appl Sci*, 11 (2016) 1584.
13 Srividya K & Mohanty K, *Chem Eng J*, 155 (2009) 666.
14 Begum H A & Kabir H, *Dhaka Univ J Sci*, 61 (2013) 7.
15 Saha I, Kanrar S, Gupta K, Show B, Nandi D, Biswas K, Manna B, Chatterjee D & Chand Ghosh U, *RSC Adv*, 6 (2016) 93842.
16 R S, Githin J M, Abhishek V & Chetan D, *Curr Sci*, 94 (2008) 765.
17 Salem I A, *Appl Catal B Environ*, 28 (2000) 153.
18 Nezamzadeh-Ejhieh A & Zabihi-Mobarakeh H, *J Ind Eng Chem*, 20 (2014) 1421.
19 Sarower-E-Mahfuj M, Hossain M B & Minar M H, *Am J Food Technol*, 7 (2012) 633.
20 Dhananasekaran S, Palanivel R & Pappu S, *J Adv Res*, 7 (2016) 113.
21 El-Zahhar A A, Awwad N S & El-Katori E E, *J Mol Liq*, 199 (2014) 454.
22 Kameda T, Oba J & Yoshioka T, *J Hazard Mater*, 300 (2015) 475.
23 Canzano S, Iovino P, Salvestrini S & Capasso S, *Water Res*, 46 (2012) 4314.
24 Tang D & Zhang G, *Chem Eng J*, 283 (2016) 721.

25 Saha I, Ghosh A, Nandi D, Gupta K, Chatterjee D & Ghosh U C, *Chem Eng J*, 263 (2015) 220.

26 Weber W J J & Morris J C, *J Sanit Eng Div Am Soc Civ Eng*, 89 (1963) 31.

27 Biswas K, Gupta K & Ghosh U C, *Chem Eng J*, 149 (2009) 196.

28 Belala Z, Jeguirim M, Belhachemi M, Addoun F & Trouvé G, *Desalination*, 271 (2011) 80.

29 S.E. S, & N. T, *Process Saf Environ Prot*, 106 (2017) 1.

30 Tomar V, Prasad S & Kumar D, *Microchem J*, 111 (2013) 116.

31 Roy A, Chakraborty S, Kundu S P, Adhikari B & Majumder S B, *Ind Eng Chem Res*, 51 (2012) 12095.