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# Removal of Brilliant Red from Aqueous Solutions by Adsorption on Fish Scales

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**Abstract**

Removal of brilliant red (C. I. Reactive Red 2) from aqueous solutions by adsorption on fish scales of *Labeo rohita* was investigated. Batch adsorption experiments were carried out under different experimental conditions such as contact time, initial concentration of dye solutions, temperature and pH of the solution. The optimum pH for the adsorption experiment was found to be 7.2. The equilibrium time for the adsorption of brilliant red (BR) on fish scales was estimated and found to be three hours. The amount of brilliant red adsorbed on fish scale surface decreased with increasing pH and temperature of the solution. The negative value of differential heat of adsorption suggests that the adsorption process is exothermic. Langmuir adsorption isotherm was found to fit the experimental data better than that of the Freundlich adsorption isotherm.

**Keywords:** Fish scales, brilliant red, adsorption, isotherms.

## I. Introduction

In recent years, increasing awareness of the environment has prompted a demand for the purification of industrial wastewater prior to discharge into natural water. The industrial effluents of textile dying and finishing factories are coloured because of the presence of dyes in them. Many of the dyes are not easily biodegradable under aerobic condition. Some of these dyes are considered carcinogenic. They can travel long distance in the surface water and cause environmental concern. Therefore, dyes from the wastewater of these factories must be removed before discharging into water body.

A variety of physical, chemical and biological methods are presently available for treatment of dye-containing wastewater discharged from various industries[1]. However, each method has advantages and disadvantages. Some of these processes are very expensive and cannot effectively be used to treat wide range of dyes.

Adsorption has received considerable attention for colour removal from waste waters as it offers the most economical and effective treatment methods[2-4]. Adsorbents like activated carbon, diatomite, silica, dolomite, Fuller's earth, bentonite, zeolite, peat, lignite, fly ash, clay, mud, coal etc. have received considerable interest because of their local availability and effectiveness[2]. Use of biosorbent like baggase[5], banana pith[6], water hyacinth root[7], sawdust[8], leaf powder[9], chitin[10] and chitosan[11] etc. have been found to be highly effective, cheap and eco-friendly for removal of organic pollutants from wastewater.

In the present study, the feasibility of using fish scales of *Labeo rohita* (Rui) was investigated as a non-conventional and low-cost adsorbent for dye adsorption from wastewater. The fish scales have an orthogonal plywood structure of stratified lamellae consisting of closely packed collagen fibers. The mineral phase in the scale is calcium-deficient hydroxyapatite containing a small amount of sodium and magnesium ions, as well as carbonate anions in phosphate sites of the apatite lattice[12]. Organic compounds comprise 40–90% in scales and most of them are collagen, regardless of fish species[13]. The functional groups in the fish scale structure, such as phosphate, carboxyl, amine and carbonyl, are supposed to be involved in the sorption process[14]. At present, large quantities of fish scales are produced in fish shops and fish-processing factories. However, the effective use of these scales is minimal.

Application of fish scales to remove heavy metals is a recent innovation. The experimental study of the adsorptive properties for the removal of copper, lead, cobalt, and nickel ions from water by thermally pretreated fish scales from *Oreachromis niloticus* (Mojarra Tilapia) was reported[15]. A study on the application of Atlantic code scales in removing the heavy metals such as lead, arsenic and chromium from energy-produced waste streams was also reported[16]. Removal of lead and cobalt ions from both industrial and municipal water using fish scales of the *Gadus morhua* (Atlantic cod) and *Lethrinus nebulosus* (Spangled emperor) as adsorbents were investigated[17]. Bisorption of bivalent lead by *Labeo rohita* scales[18] and hexavalent chromium by *Catla catla* scales[14] from aqueous solutions were studied.

A little information is available related to the adsorption of dye onto fish scales. The chemical and physical principles of astaxanthin sorption to fish scales towards applicability in fisheries waste management was investigated[19]. A study on dye-binding interaction of chitosan obtained from the fish scale of Tilapia (*Tilapia nilotica*) was reported [20]. Recently, a report on adsorption of acid yellow dye on chitosan flakes, extracted from *Labeo rohita* scales, has been published[21].

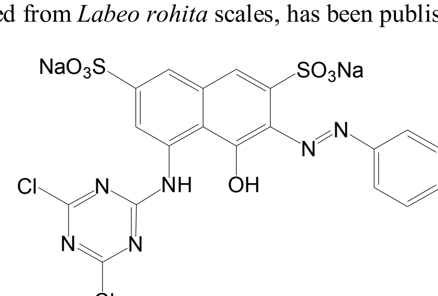


**Fig. 1.** Molecular structure of brilliant red (BR)

The reactive dye, BR (Fig. 1) (C. I. Reactive Red 2), is extensively used in the textile industry. Degradation of this dye by various physical and chemical methods has been

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reported[22-23]. The adsorption efficiency of organic aerogels and carbon aerogels towards reactive BR was investigated[24]. To the best of our knowledge, no systematic investigation appears to have been done on the adsorption of this dye using fish scales as adsorbent.

The present study was undertaken to investigate the efficiency of fish scales (*Labeo rohita*) as a low cost biosorbent for the removal of brilliant red (BR) from aqueous solution. Batch adsorption experiments were carried out at different experimental conditions to evaluate optimum pH and equilibrium time for the adsorption, to study the effect of pH and temperature on adsorption. Adsorption isotherms were also calculated and discussed.

## II. Experimental

### Materials

The raw fish scales (*Labeo rohita*) were collected from a local fish market in Dhaka city. The material was washed repeatedly with deionized distilled water to remove soluble impurities from their surface. The fish scales were allowed to dry in the sun for a day. The scales were then kept in an oven at 60°C for 24 hours, grounded and sieved through a set of metallic sieves ranging from 0.144 mm to 0.355 mm. The sieved fish scales particles were stored in air-tight containers for further use.

A stock solution of BR ($1.0\times10^{-3}$ M) was prepared using de-ionized double distilled water. The experimental solutions (within the range of 1–15 $\times10^{-5}$ M at pH 7.0) were prepared by diluting the stock solution with de-ionized double distilled water when necessary.

### Determination of optimum pH for adsorption study

For the determination of optimum pH, 0.1 g of fish scales was taken in each of the eight bottles. 25.0 mL BR solution of different pH's (ranging from 3.0 to 10.0) was taken in each bottle. The bottles were placed in a thermostatic mechanical shaker (HAKKE, SW B-2, Fisons Ltd. Germany), maintained at 30°C. The reagent bottles were successively withdrawn after shaking for 6 hours and the solutions were centrifuged. After centrifuge the pHs of the solutions were measured using a pH-meter (HANNA instrument, Romania). These pHs were different from the initial value. The difference of pH from the initial values was estimated as ΔpH. The plot of ΔpH vs. initial pH produces a curve which intersects the X-axis at a point as shown in Fig. 2.

### Estimation of equilibrium time for adsorption of brilliant red on fish scale

The equilibrium time of adsorption of BR on fish scale was estimated at pH 7.0 and 30°C. 0.1 g of fish scales and 25 mL of $7\times10^{-5}$ M brilliant red solution were used in each of the 11 bottles. The bottles were shaken in a thermostatic shaker at 30°C. After a definite interval of time each bottle was withdraw from the shaker. The supernatant of the bottle was transferred and centrifuged repeatedly until a clear liquid was obtained. The absorbance of the clear solution was measured at $\lambda_{max}$ 534.0 nm using a double beam UV-visible spectrophotometer (UV-160A, Shimadzu, Japan). For blank 0.1 g of fish scale and 25 mL of water (pH 7.0) was added in a bottle and after shaking for two hours at 30°C, a clear solution was obtained after centrifuge the supernatant. This clear solution was used as reference solution for measuring absorbance. Following the same procedure, the equilibrium time of adsorption of $14\times10^{-5}$ M BR solution on fish scales was also estimated at pH 7.0 and 30°C. The amount adsorbed per g *vs* adsorption time plot is shown in Fig. 3.

### Adsorption isotherm of brilliant red on fish scale at different temperatures and pH

For the determination of adsorption isotherm, 0.1 g of fish scales was taken in each of the eight bottles. 25.0 mL BR solution of different concentration (ranging from 2 to $14\times10^{-5}$ M) was taken in each bottle and the pH was adjusted to 7.0. The bottles were placed in a thermostatic shaker maintained at 30°C and were shaken continuously for three hours, which was the estimated equilibrium time. After three hours, the solution of each bottle was centrifuged and analysed by UV-visible spectrophotometer. Similar experiments were performed at 40°C and 50°C to obtain the adsorption isotherms at different temperatures (Fig. 4). Again, the adsorption experiments were repeated at 30°C using the solutions pH 3.0 and pH 10.0. A plot of amount adsorbed per g versus equilibrium concentration at different pH is shown in Fig. 5.

### Effect of pH on adsorption

In order to study the effect of pH on dye adsorption, the pH of the solutions was varied from 3.0 to 10.0 by adding a small amount of NaOH or HCl solution without affecting the volume. After adjusting the pH of the solutions, the initial absorbance of the solutions was measured at $\lambda_{max}$ 534.0 nm. 25.0 mL BR solution ($15\times10^{-5}$ M) of different pH's (ranging from 3.0 to 10.0) was taken in each of the eight bottles. Now, 0.1 g of fish scales was taken in 25.0 mL BR solution ($15\times10^{-5}$ M) in each of the eight bottles and placed in a thermostatic shaker for shaking continuously for three hours at 30°C. The reagent bottles were successively withdrawn after three hours and the solution was centrifuged. After centrifuge, the pHs of the solutions were readjusted to the initial pH of the BR solutions and the absorbance of the solutions were measured using the $\lambda_{max}$ as before. The plot of amount adsorbed per g versus initial pH of solution is shown in Fig. 9.

## III. Results and Discussion

### Determination of optimum pH

The optimum pH for the adsorption of BR on fish scales was found to be around 7.2 (Fig.2). At the optimum pH, minimum variation of solution pH during adsorption was observed.

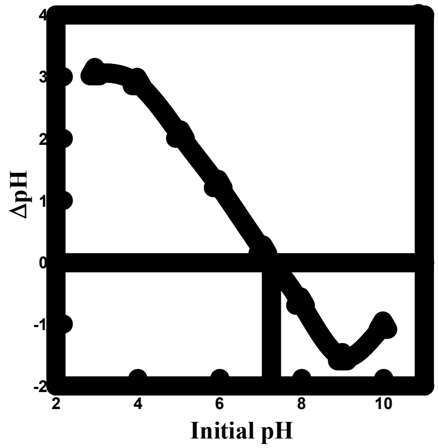


**Fig. 2.** Determination of optimum pH of fish scale for adsorption of BR.

**Estimation of equilibrium time**

The adsorption equilibrium was determined at pH 7.0 and at 30°C using the initial BR concentrations of $7\times10^{-5}$ M and $14\times10^{-5}$ M. The amount of BR adsorbed on fish scales at various intervals of time is presented in Fig. 3. The figure indicates that the removal of BR initially increases with time but attains almost equilibrium within three hours. The absorption process was found to be very rapid initially and a large fraction of total concentration of BR was removed in the first 30 minutes. The adsorption of BR increased with an increase in initial BR concentration of the solution.

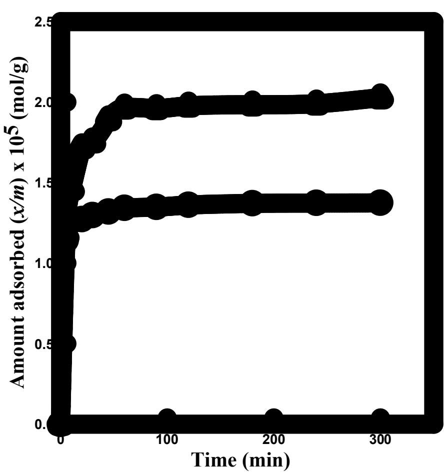


**Fig. 3.** Estimation of equilibrium time for the adsorption of BR on fish scale at pH 7.0 and 30°C using different initial concentration. (● = $7\times10^{-5}$ M and ▲ = $14\times10^{-5}$ M)

***Adsorption isotherms at different temperatures and pHs***

Adsorption isotherm is an important parameter for the characterization of adsorption process. In this study, adsorption isotherms of BR solution on fish scales were determined at temperatures, 30, 40 and 50°C, at pH 7.0. The adsorption isotherms were obtained by plotting the amount adsorbed per g against equilibrium concentration ($C_e$) and the results are shown in Fig. 4. Under all conditions amount adsorbed of BR increased with the increase of equilibrium concentration. It was observed that the amount of adsorption decreased slightly with the increase of temperature from 30 to 40°C. A significant decrease of the amount adsorbed was observed with the increase of temperature from 40 to 50°C. The effect of pH on adsorption of BR on fish scales was studied at pH 3.0, 7.0 and 10.0 and at 30°C (Fig. 5). The adsorption isotherm shows that the amount adsorbed increases with the increase of initial concentration of BR solution. It is observed that the amount adsorbed decreases when pH increases.

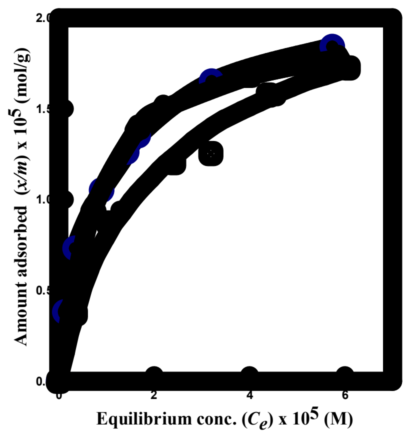


**Fig. 4.** Adsorption isotherms of BR on fish scale at pH 7.0. (●= 30°C, ▲= 40°C and ■= 50°C)

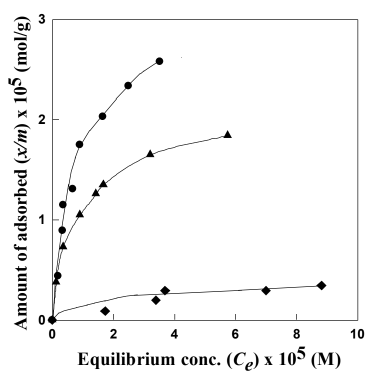


**Fig. 5.** Effect of pH on adsorption isotherms of BR on fish scale at 30°C. (●=pH 3.0, ▲= pH 7.0 and ■ = pH 10.0)

The experimental equilibrium adsorption data were analysed using the linear form of Langmuir[25] and Freundlich[26] isotherm models (Eqn. 1 and 2). Here, $C_e$ is the equilibrium concentration of BR in solution, $x$ is the amount of BR adsorbed on fish scale, m is the amount of fish scale used for adsorption experiment, $b$ is a constant related to the affinity of binding sites with the adsorbate and $q_m$ is the maximum value of sorption capacity (corresponding to complete mono-layer coverage), $k_F$ is Freundlich constant and $n$ is a measure of sorption intensity.

$$C_e/(x/m) = 1/q_m b + C_e/q_m \quad (1)$$

$$\log (x/m) = \log k_F + 1/n \log C_e \quad (2)$$

The Langmuir parameters for adsorption of BR on fish scales at different temperatures and pHs were determined by the linear plot of $C_e/(x/m)$ vs $C_e$ (Fig. 6 and 7) and the results and regression value ($R^2$) are presented in Table-1.

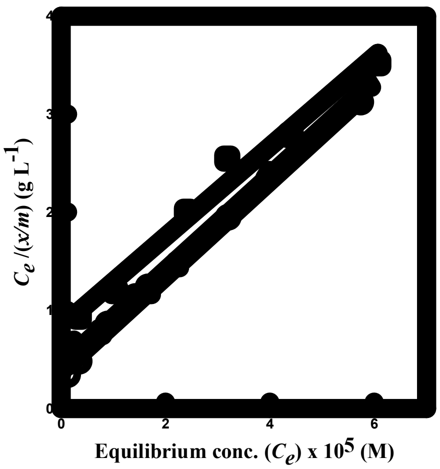


**Fig. 6.** Plot of Langmuir isotherms of BR on fish scale at different temperatures and pH 7.0. (● = 30°C, ▲ = 40°C and ■ = 50°C)

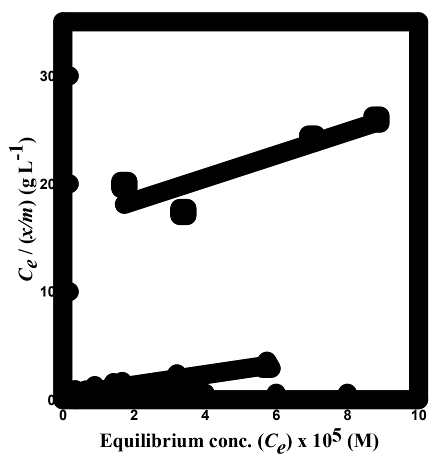


**Fig. 7.** Plot of Langmuir isotherms of BR on fish scale different pHs and 30°C. (● = pH 3.0, ▲ = pH 7.0 and ■ = pH 10.0)

**Table 1. Langmuir parameters for adsorption of BR on fish scales at different temperatures and pHs**

| Temp. (°C) | pH | $q_m$ (mol/g) | $b$ | $R^2$ |
|---|---|---|---|---|
| 30 | 3.0 | 3.199 | 1.121 | 0.987 |
| 30 | 7.0 | 2.053 | 1.324 | 0.996 |
| 40 | | 2.066 | 1.008 | 0.998 |
| 50 | | 2.179 | 0.553 | 0.980 |
| 30 | 10.0 | 0.974 | 0.062 | 0.898 |

The experimental data of the isotherms are found to fit better into Langmuir isotherm than Freundlich isotherm. Table-1 shows that the maximum mono-layer adsorption capacity ($q_m$) decreases with increase in solution pH and was found to be highest at pH 3.0.

### Heat of adsorption

From the adsorption isosteres, the value of differential heat of adsorption for a definite surface coverage ($0.70\times10^{-5}$ mol g$^{-1}$) has been obtained from the slope of a linear plot of –ln $C_e$ vs 1/T (Fig. 8). The value of heat of adsorption is found to be –34.92 kJ/mol at pH 7.0. The negative values of differential heat of adsorption, suggests that the adsorption is exothermic.

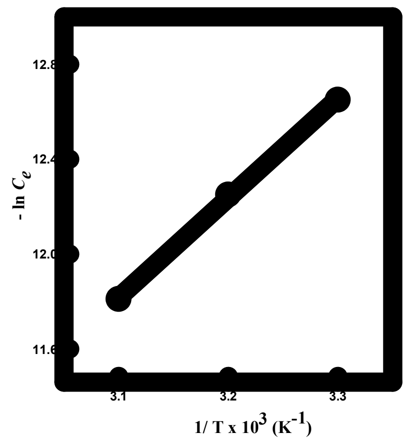


**Fig. 8.** A plot of -ln $C_e$ vs 1/T for the adsorption of BR on fish scale at pH 7.0

### Effect of pH and adsorption mechanism

The chemical constituents of fish scales consist mainly of collagen fibers and hydroxyapatite[12]. So, the active functional groups on the fish scale surface which involve in the sorption process are carboxyl (–COOH), amine (–$NH_2$) and phosphate ($PO_4^{3-}$) groups[14]. The results of studies on adsorption isotherms at different pHs show that the adsorption of BR on fish scale surface is decreased with increasing pH of the solution (Fig. 9).

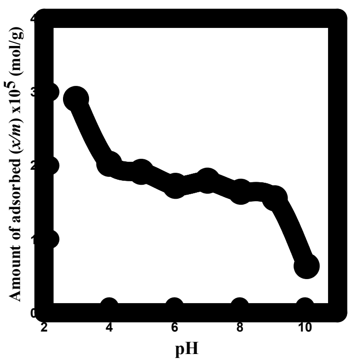


**Fig. 9.** Effect of initial pH on adsorption of BR on fish scale at 30°C.

The results suggest that at low pH, i.e. at pH 3.0, the amount adsorbed is very high. The positively charged amine groups ($-NH_3^+$) of fish scales are mainly responsible for adsorption of BR onto fish scales surface as BR is negatively charged in aqueous solution. These negatively charged dye anions exhibit electrostatic attraction toward the positively charged amine groups of fish scales. This is the reason for the maximum adsorption occurred at acidic pH. A sharp reduction in dye uptake is observed from pH 3.0 to pH 4.0. After that the gradual reduction in the BR uptake with increasing pH is observed upto pH 9.0. A sharp reduction of BR uptake is observed again from pH 9.0 to pH 10.0. The gradual reduction in the dye BR uptake with increasing pH suggests that the electrostatic repulsion between the sulfonate groups (dye–$SO_3^-$) of the BR and carboxyl ($-COO^-$) and phosphate ($PO_4^{3-}$) groups of the fish scale surface is involved in the process. This electrostatic repulsion gradually increased with increase of surface negativity. At pH 10.0, surface of absorbent is highly negative and interaction between negative surface of adsorbent and negatively charged adsorbate is the minimum.

## IV. Conclusion

The present study has shown that inexpensive fish scales can be used as an effective adsorbent for removal of BR from water. The optimum pH for favourable adsorption of BR was 7.0. The equilibrium time for the adsorption of BR on fish scales was found to be three hours. The adsorption decreased with increasing pH and temperature of the solution. The values of differential heat of adsorption suggest that the adsorption of BR on fish scales is an exothermic process. The experimental data agreed well with Langmuir isotherm model.

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