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Identification of Fish Toxic and Non-Toxic Organic Dyes through Adsorption of Organic Dyes on Fish

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Abstract : Organic dyes are used for dyeing cotton, plastic, wool etc. The dye manufacturing and dyeing industries are releasing unused organic dyes as an effluent. Every year five billion tons of waste organic dyes are pumped into river, ocean and other water bodies. The dyes are stable and non – bio degradable. Many methods are adopted to remove the dyes from dye effluent. But, these methods are creating another environmental issue and also dye removal is not 100% successful. Identification of Human, animal and fish poisoning organic dyes are essential, to control their toxicity. In this present investigation, sardine fish is selected to identify the fish poisoning and non – poisoning organic dyes through adsorption method. The experimental conditions like contact time, temperature, dye concentration, fish powder dosage are optimized to find out the maximum toxic effect of organic dyes on fish. The poisoning effect has been evaluated by adsorption thermodynamics, kinetics and isotherms.
Keywords : Sardine fish, Toxicity, Adsorption, Organic dyes.

Introduction

Dyes are basically a coloured substance [1]. Heavy metal ions and dyes are playing an important role for environmental pollution. Nowadays, water pollution is a very common problem [2]. Dyes that are used by the textile industry are now mostly synthetic, aromatic, water soluble and miscible organic colorants [3]. They are more stable and more difficult to biodegradation [4]. In general, reactive dyes are most problematic among the other dyes [5]. Dyes are used in various industries such as textile, leather, paint, paper, food and cosmetics etc [6]. At present, more than 10,000 dyes with an estimated annual production of 7×10^5 metric tons are commercially available worldwide [7].

Among, the numerous dye removal techniques, adsorption is the familiar method [8], because of its cheapness and easy operation [9]. Biomaterials are available in huge amount and environmental friendly disposable [10]. The scope of the present study is to analyse the toxic effects of organic dyes on fish and it is used as an adsorbent in this adsorption study. The fish (Cyprinus carpio.L, Heteropneustes fossilis) and fish scale

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(Carp, Labeo rohita,) is used as an adsorbent for the removal of Malachite green, Teflon red, Brilliant red and Methylene blue. In the present study Sardine Fish has been used as an adsorbent for Rhodamine-B (RB) and metanil yellow (MY) [11-13].

Materials:

Dye:

Stock solution [1000 mg/l] is prepared by dissolving 1g of dyes [MY, RB] in 1 litre of distilled water. The desired concentrations are prepared by successive dilutions of stock solutions. The dye concentration is studied by UV-spectrophotometer (Perkin Elmer, Lambda 25).

Table 1: Properties of dye molecules:

S.No	Name of the dye	Molecular formula	Maximum adsorption λ_{max}
1.	Metanil yellow	$C_{18}H_{14}N_3NaO_3S$	434.76
2.	Rhodamine B	$C_{28}H_{31}ClN_2O_3$	553.65

Adsorbent:

The low cost Sardine Fish (SF) is collected from local area. The fish is cut into small pieces and washed thoroughly with water to remove the dust particles. Then it is dried under sun light for one week. The dried materials are grained well to make a fine powder. Then the powder is washed with distilled water to remove the soluble and adhered materials. Finally the powder is dried in oven at 110^0C.

Batch Adsorption Studies:

0.5g of dried adsorbent is taken in a 250ml reagent bottle.50 ml of dye solution is added into the bottle. The solutions are shaken (Remi-model-1MH) at 150rpm. After the adsorption process, dye solution is filtered off. The concentration of unabsorbed dye solution has been measured by using UV-spectrophotometer (Perkin Elmer, Lambda 25).

Results and Discussion:

Adsorption studies:

Effect of removal of different dyes on bio-adsorbent through adsorption at various parameters such as contact time, concentration, temperature, pH and dosage was analyzed for maximum adsorption.

Effect of contact time:

The study of contact time dependent process of cationic dye (RB) adsorption on SF have been carried out at different time intervals between 30 to 180 minutes. Time increases, adsorption also increases up to all the sites are occupied or to attain equilibrium adsorption (figure 1). The study of contact time dependent process of anionic dye (MY) adsorption on SF have been carried out at various time intervals between 5 to 60 minutes. Time increases, dye removal also increases and reaches the maximum and then decreases or attain equilibrium adsorption (figure 1). These two dyes are having different structure and charge. The equilibrium adsorption time depends on the structure, charge of the dyes and particle size of the adsorbent[14].

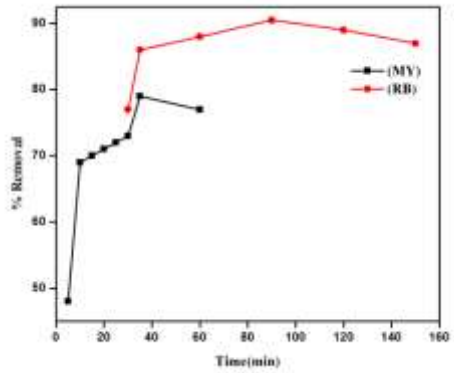

Figure 1: Effect of contact time for the adsorption of RB and MY on SF
RB –Time: 90 min, Temperature: 30°C, Adsorbent dosage: 0.5g
MY -Time: 30 min, Temperature: 30°C, Adsorbent dosage: 0.5g

Effect of concentration:

Effects of concentration on adsorption of cationic dye (RB) on SF have been performed at various concentrations between 100 ppm-1000 ppm at the room temperature. Increases of dye concentration decrease the adsorption percentage. This is may be due to the saturation of the surface of the adsorbent (figure 2). Effects of concentration on adsorption of anionic dye (MY) on SF have been performed at various concentrations between 100 ppm-250 ppm. When increase the concentration of dye solution, the surface area and active sites are saturated and hence adsorption decreases with increased of dye concentration[15].

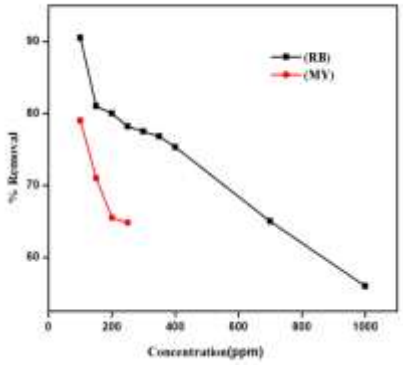

Figure 2: Effect of concentration for the adsorption of RB and MY on SF
RB -Time: 90 min, Temperature: 30°C, Adsorbent dosage: 0.5g.
MY -Time: 30 min, Temperature: 30°C, Adsorbent dosage: 0.5g.

Effect of Temperature:

The cationic dye (RB) removal is dependent on its temperature. RB adsorption increases with increased of temperature on SF (figure 3). The anionic dye (MY) removal is not dependent on the temperature. Because, when the temperature increases, dye molecule absorbs the heat energy and randomness increases too high. Hence adsorption decreases with increased of temperature[16]. This fact may be proved that the cationic RB has attractive force may be due tonegative charge present on the SF. Hence, it has more adsorption than MY.

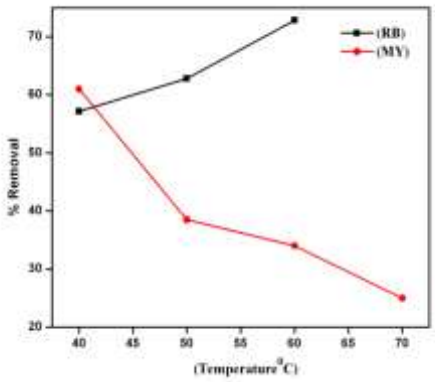

Figure 3: Effect of temperature for the adsorption of RB and MY on SF
RB -Time: 90 min, Concentration: 100 ppm, Adsorbent dosage: 0.5g.
MY -Time: 30 min, Concentration: 100 ppm, Adsorbent dosage: 0.5g.

Effect of pH:

The pH value of the dye solution plays an important role in the whole adsorption method and mainly on the adsorption capacity(figure 4). RB dye adsorption on SF increases at basic pH[17]. It is proved that, RB adsorption is pH dependent on SF due to the attraction between the cationic RB and the basic surface of SF. MY adsorption on SF is not pH dependent. At lower pH adsorption is more and further increased of pH decreases of adsorption. MY is anionic, at higher pH the adsorbent surface become basic. So adsorption of anionic dye decreases with increased of pH due to the repulsion between the negative charged MY and the basic surface of SF (figure 4).

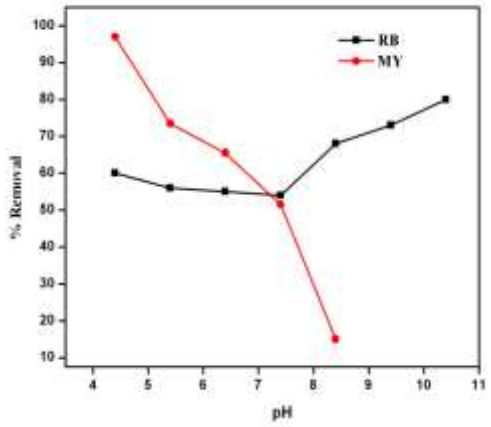

Figure 4: Effect of pH for the adsorption of RB and MY on SF
RB -Time: 90 min, Concentration: 100 ppm, Adsorbent dosage: 0.5g.
MY -Time: 30 min, Concentration: 100 ppm, Adsorbent dosage: 0.5g.

Effect of dosage:

Effects of dosage on adsorption of cationic dye (RB) on SF have been carried out between 0.5g to 2g (figure 5). Dye removal increases with increased of dosage due to the increase of surface area and active sites of the adsorbent[19].

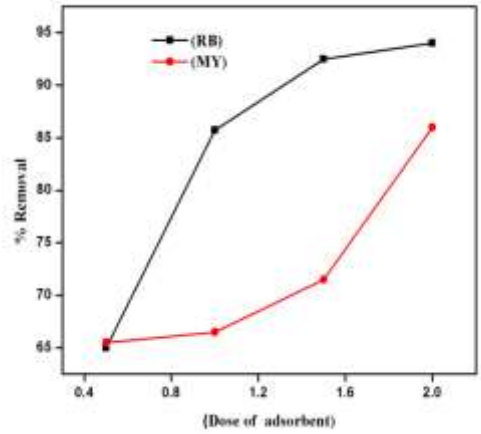

Figure 5: Effect of dosage for the adsorption of RB and MY on SF
RB -Time: 90 min, pH:4.5, Concentration: 100 ppm, Adsorbent dosage: 0.5g.
MY -Time: 30 min, pH:10.5,Concentration: 100 ppm, Adsorbent dosage: 0.5g.

Adsorption Kinetics:

The adsorption kinetics of RB and MY have been studied by using SF. The first order kinetics has been evaluated for these dyes on the adsorbent. These dyes adsorption has not followed the first order kinetics. Then the data is applied for second order kinetics and observed that these dyes are following second order kinetics (figure 6). The second order kinetics is given below, $t/Q_t = 1/k_2\ Q_e^2 + t/Q_e t$.

k_2 = Pseudo second order rate constant ($gm^{-1}\ min^{-1}$)
q_e = amount of dye adsorbed at equilibrium (mg/g)
q_t = amount of dye adsorbed at time 't' (mg/g)

The kinetics plot is shown in the Figure 6 and the kinetic parameters are shown in Table 2. The R^2 value is 0.99. It is almost equal to 1. This proved that, adsorption follows pseudo second order kinetics[20].

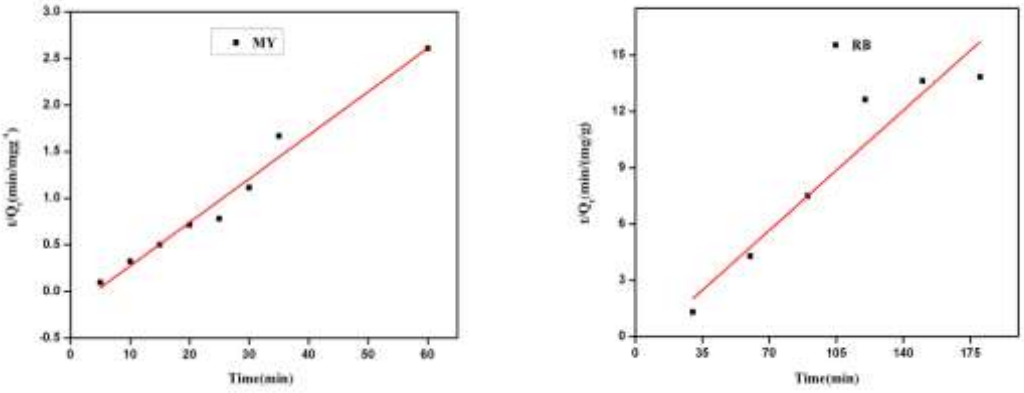

Figure 6: Second order kinetics for MY and RB adsorption on SF

Table 2: Pseudo second order kinetics parameters

S.No	Kinetic parameters	Cationic dye	Anionic dye
		RB	MY
1	K_2	0.0913	0.0467
2	R^2	0.9626	0.9743

Adsorption Isotherm:

The distribution of RB and MY between the adsorbent (SF) and the solution is determined by Langmuir and Freundlich isotherms. Langmuir adsorption isotherm data at different concentrations are calculated for the adsorption of organic dyes (RB & MY). These data are fitted with Langmuir adsorption isotherm equation. This study has been carried out for understanding the monolayer adsorption of organic dyes on SF.

The Langmuir equation is represented as $C_e/Q_e = (1/Q_{max}K_L) + (C_e/Q_{max})$

Where, Q_e is the equilibrium concentration of dyes on the adsorbent (mg/g)

C_e is the equilibrium concentration of dyes in solution (mg/L)

Q_{max} is the monolayer capacity of adsorbent (mg/g) and K_L is the Langmuir adsorption constant. The Langmuir constant K_L is a measure of the affinity between adsorbate and adsorbent, $1/K_L$ value gives half maximum adsorption. A plot of C_e/Q_e Vs C_e is a straight line with slope $1/Q_{max}$ and intercepts $1/Q_{max}$ K_L. The correlation coefficient (R^2) values are given in Table 3. R^2 value for dyes are very close to 1 for RB and MY indicated that RB and MY adsorption follows the Langmuir adsorption isotherm (Figure 7). The monolayer adsorption capacity of SF for RB is 23.4852 mg /g and for MY is 23.529 mg/g.

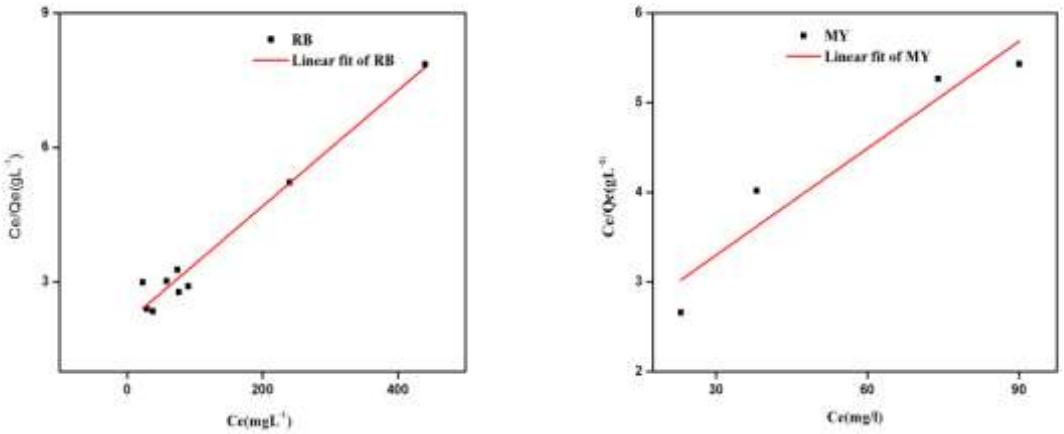

Figure 7: Langmuir adsorption Isotherm for RB and MY on SF

Table 3: Langmuir adsorption isotherm parameters

S.No	Langmuir Isotherm		
	Parameters	Cationic dye RB	Anionic dye MY
1.	Q_{max}(mg/g)	23.4852	23.5290
2.	K_L	2.1543	1.9916
3.	R^2	0.9565	0.9102

Freundlich adsorption isotherm:

The adsorption studies are carried out at various concentrations for the adsorption of RB and MY. The adsorption values are applied to the freundlich equation to verify the adsorption isotherms are shown in Table 4. The study has been carried out for understanding the multilayer adsorption on SF.

The Freundlich equation is represented as $\ln Q_e = \ln K_F + (1/n) \ln C_e$ Where, KF is the Freundlich constant and n is the number of layers. The plot of $\ln Q_e$ Vs $\ln C_e$ gave a straight line with the intercept $\ln K_F$ and the slope 1/n. The correlation coefficient for the adsorption of RB and MY dyes are close to 1(Figure 8).This result revealed that the adsorption process follows the freundlich isotherm model.

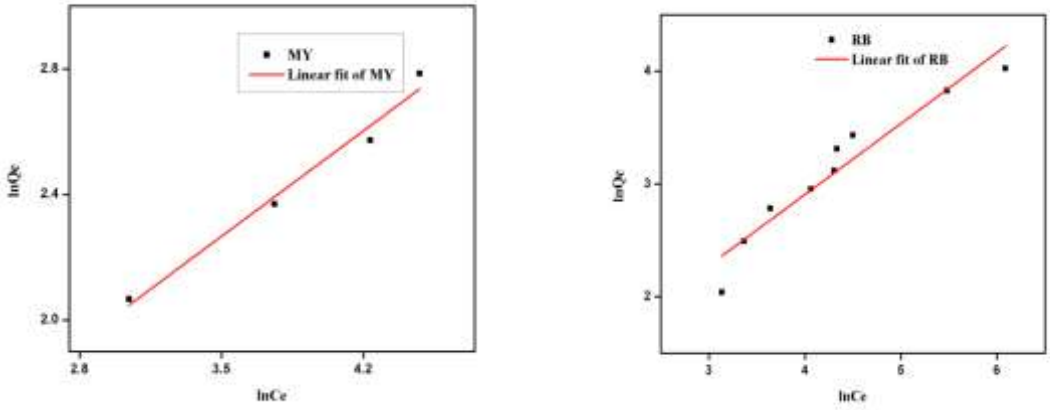

Figure 8: Freundlich isotherm for MY and RB adsorption on SF.

From the table, we know that the SF using RB and MY dye followed the Freundlich isotherm.

Table 4: Freundlich adsorption isotherm parameters

S.No	Freundlich Isotherm		
	Parameters	Cationic dye	Anionic dye
		RB	MY
1.	n	0.6301	0.4798
2.	K_F	2.557	1.7947
3.	R^2	0.9141	0.9710

Thermodynamic Properties:

Thermodynamic properties explain the spontaneity and heat change of the adsorption process. The thermodynamic parameters are calculated by the following relation,

$\Delta G = \Delta H - T\Delta S$ (1)
$\Delta G = -RT \ln K_D$ (2)
$K_D = q_e/C_e$ (3)
From the equations 1 and 2,
$\ln K_D = (\Delta S/R) - (\Delta H/RT)$ (4)

Where,

K_D is the distribution coefficient of the adsorbate, q_e and C_e are the equilibrium dye concentration on SF and in the solution. R is the universal gas constant (8.314 J/mol K) and T is the temperature (K). ΔH and ΔS parameters can be calculated from the slope and intercept of the plot (Figure 9). ΔG is calculated by the equation (1) at various temperatures. Results are summarized in Table 5. The enthalpy (ΔH) values are greater than40 kJ/mol for MY (43.526) dye indicated that the adsorption of dye on SF is chemisorptions[104] and less than 40 kJ/mol for RB (30.4269) indicated that the adsorption of dye on SF is physisorption[105]. The positive value of enthalpy indicated that the adsorption process is endothermic[106] and also the positive value of entropy indicated that the degrees of freedom increased at the solid- liquid interface during the adsorption.

In Sardine fish, the removal of MYis chemisorption and spontaneous reaction. In Rhodamine-B dye, the ΔH value less than 40 KJ mol^{-1},it is physisorption and non spontaneous reaction[22-24].

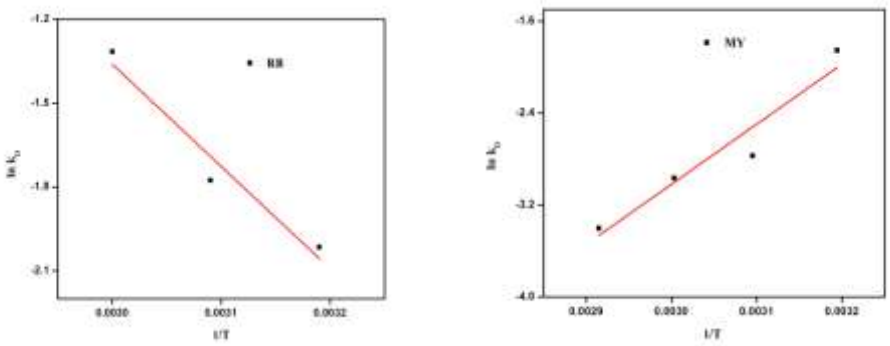

Figure 9: Adsorption thermodynamics for MY and RB adsorption on SF.

Table 5: Thermodynamic parameters for adsorption of dyes

S.No	Thermodynamic parameters (kJ/mol)	Cationic	Anionic
		RB	**MY**
1.	ΔH	-30.4269	-43.526
2.	ΔS	0.0799	0.1556
3.	ΔG		
	313 k	-5.4182	-5.1768
	323 k	-4.6192	-6.7328
	333 k	-3.8202	-8.2888
	343 k	-3.0212	-9.8448

Conclusion:

The present study shows that SF biomaterial can be used as an adsorbent for the removal of MY and RB. The amount dye adsorbed is found to vary with adsorbent dosage, concentration, contact time, temperature and pH. The rate of adsorption is found to confirm that pseudo-second order kinetic is perfectly matched. Experimental adsorption data at equilibrium condition is fitted with Langmuir and Freundlich adsorption isotherm. The adsorption thermodynamics of MY on SF is more than 40 kJ/mol**,** it proved that the MY adsorption on SF is chemisorption. It confirm that the MY adsorption on SF is not reversible. Therefore, the MY is fish toxic. However, the RB adsorption on SF is less than 40 kJ/mol. It indicates that the RB may be reversible in aqueous medium. As a result, it maynot be a permanent fish toxic dye.

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