Biosorption of Eriochrome Black T (EBT) onto Waste Tea Powder: Equilibrium and Kinetic Studies

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Abstract

Biosorption of EBT molecules from aqueous solutions onto waste Tea powder (WTP) have been examined in a batch biosorption process. The biosorption procedure was found to be dependent on biosorbent dose, pH of solution, initial dye concentration, and contact time. The experimental equilibrium biosorption data were inspected by Langmuir, Freundlich, Temkin and Dubinin‗Radushkevic isotherms models. The Langmuir model gave the best fit by higher correlation coefficient(R^2 =0.997, it assumes as monolayer adsorption). The maximum biosorption capacities determined from the Langmuir, isotherm models was 111.11 mg/g, at optimum circumstances. The kinetic studies showed that the biosorption operation of the EBT dye obeyed well pseudo-second-order model. According to the determined biosorption capacity, waste tea powder is considered to be as an effective, low cost, and environmentally friendly biosorbent for the removal of EBT dye from aqueous solutions.

Keywords:Biosorption, EBT, Equilibrium and Kinetic study

Subject Classification: Physical Chemistry, Adsorption, Isotherms and Kinetics

Type (Method/Approach): Removal of Dyes from waste water by adsorption

Introduction

Extended utilize of chemicals in everyday life and utmost manufacture processes have brought considerable amount of dyes and their existence produce environmental-disposal problems. Our biological system has been polluted by high levels of organic compounds produced into the environment. Modern exercises, development, urban waste treatment, and vehicle deplete are a part of the origin causing significant amounts of organic compounds tainting in environment, water, and soil [1]. Dyes are widely applied in industries such as cosmetic, rubber, textile, paper, plastic, etc. Through these several industries, textile classify first in employment of dyes for coloration of fiber. They are carcinogenic and also catalyze allergic complications. Dyes pollutions occurs in aqueous waste streams from numerous industries constitutes one of the most dangerous pollution problems and can influence the quality of water supply and cause many problems on aquatic life [2].

Various treatment techniques have been established for the elimination of dyes from waters and waste waters like precipitation, solvent extraction, filtration, ultrafiltration, membrane ion exchange, and many others [3-12]. However, these processes are not extensively used because they are expensive, and create industrial problems. Recently, adsorption techniques have been demonstrated to be the most promising choice for the removal of organic pollutants and dyes from aqueous streams [13]. Activated carbon as an adsorbent has been extensively examined for the adsorption of dyes due to their effectiveness and versatility. However, some difficulties have been reported for activated carbon in terms of engineering problems and high-cost in commercial applications [14]. Alternatively, there are various kinds of waste byproducts which have been utilized to remove dyes such as rice husk, mushroom biomass, sunflower stalks, Eucalyptus bark, wheat bran, fruit peel of orange, and Ficus religiosa leaves [15].

In our previous work, we have studied the efficiency of waste coffee and tea, orange peels, and olive leaves powders as a biosorbents for removal of some heavy metal ions from aqueous solutions [16 - 18]. In this work,

the adsorption of EBT dye onto waste tea powder has been investigated. The adsorption capacity was evaluated under various conditions of pH, contact time, initial dye concentration, and adsorbent dosage. The adsorption isotherms were also investigated to explain the probable mechanism of adsorption and to provide several information such as maximum sorption capacity, energy of sorption, homogeneity/heterogeneity, and affinity between sorbent and adsorbent.

Materials and Methods

Reagents

All chemicals used were of analytical reagent (AR) grade. 100 ppm EBT stock solution was prepared by dissolving an appropriate amount of EBT salt in deionized water. The stock solution was diluted to the required concentrations using deionized water. The solution pH was adjusted using 0.10 M HCl or 0.10 M NaOH.

Determination of EBT Dye

The concentration of EBT dye in the solutions before and after equilibrium was determined by Molecular Absorption Spectrophotometer 6305 from JENWAY. The pH of the solution was measured with pH Meter 3505 from JENWAY. The determination of EBT dye was carried out according to the published work [19]. The range of calibration curve concentrations of dyes prepared from stock solution varies between 5-100 ppm.

Preparation of Adsorbents

The tea waste powders were collected from a coffee shop, washed with double distilled water and then dried in an oven at 70°C for 24 hrs. The dried materials were sieved through 500 μm size fraction using an American Society for Testing and Materials (ASTM) standard sieve

Adsorption Experiments

The adsorption experiments were carried out in a series of 250 mL Erlenmeyer flasks containing 200 ml of EBT dye solution, 0.100 g adsorbent powder and if necessary, an appropriate volume of HCl or NaOH solutions was used to adjust the pH of the solution. The solutions were shaken (175 rpm) at 25°C. Then solutions were filtered by Whatman filter paper. The removal percentage (% R) was calculated according to the following equation:

$$\% R = \frac{C_o - C_e}{C_o} \text{ X } 100 \qquad (1)$$

Where: C_o and C_e are initial and final concentrations in ppm, respectively. The amount of adsorbed dye Q_e mg/g (mg dye per gram adsorbent) was calculated based on the difference between the initial (C_o, ppm) and final concentration (C_e, ppm) in every flask, as follows:

$$Q_e = \frac{C_o - C_e}{M} \text{ X V} \qquad (2)$$

Where Q_e is the dye uptake capacity (mg/g), V the volume of the dye solution in the flask (L) and M is the dry mass of biosorbent (g)

Parameters Affecting Adsorption Experiments

The effects of experimental parameters such as pH, biosorbent dose, contact time, and dye concentration were investigated for EBT adsorption onto tea powders. The pH dependent study was carried out in 200 ml aqueous dye solution of 90 ppm and 0.10 g powder. The investigated pH values were from 1.50 to 7.50. The effect of contact time on dye adsorption was examined for 200 ml solutions with 90 ppm concentration and containing 0.10 g powder. The effect of biosorbent doses on dye uptake was investigated with adsorbent masses of 0.2,

0.4, 0.6, 0.8, 1.0 and 1.2 g per 200 ml of 90 ppm dye solution. Finally, various concentrations of EBT dye were investigated to study the effect of dye concentration which was: 55, 65, 75, 85, 95, ppm per 200 ml solution.
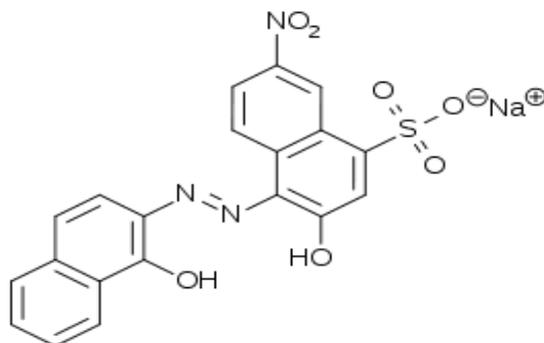
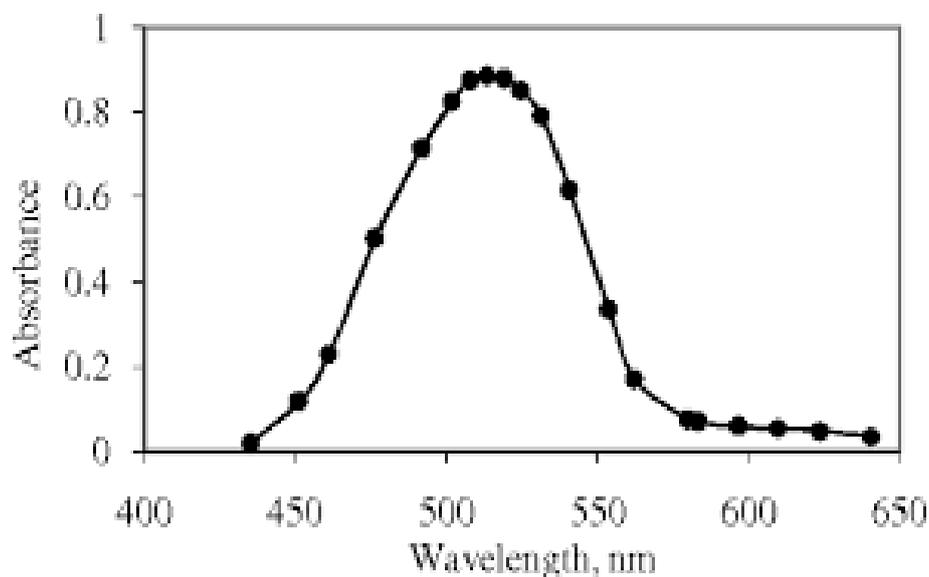## Results and Discussion

Figure 1. Structure of EBT

Figure 2. Absorption Spectrum of EBT

By UV. VIS. Spectrophotometer, the concentrations of EBT dye in the solutions were determined [19]. The range of calibration curve of dye prepared from stock solution varies between 5-100 ppm as shown in Figure 3. The response of the EBT dye was found to be linear in the investigation concentration range at λ_{max} = 528 nm and the linear regression equation was *y = 0.009X* with high correlation coefficient (R^2= 0.999). From the calibration curve, the concentrations of EBT in the solutions before and after equilibrium adsorption were determined
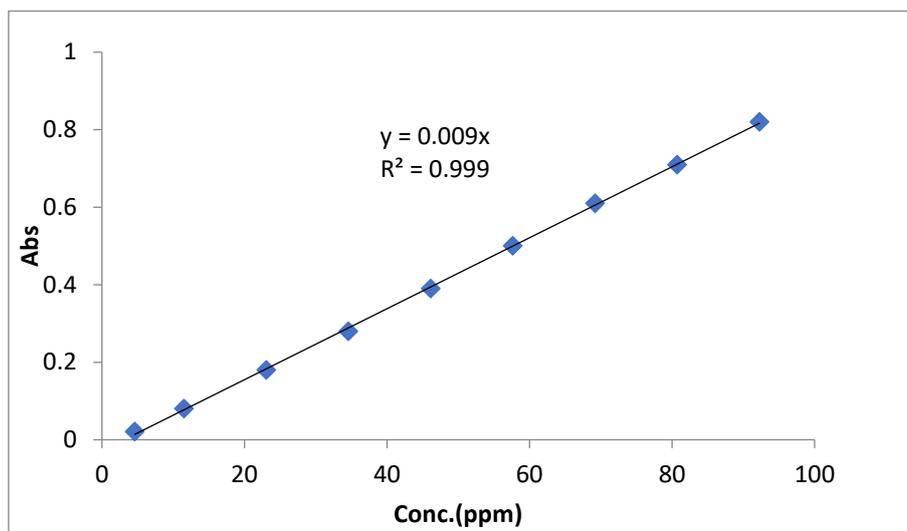
Figure 3. Calibration curve for EBT

Effect of pH

The biosorption of EBT dye from aqueous solutions are strongly affected by the pH. The pH is considered to be as the most important parameters governing dye uptake by adsorbent substrate. The adsorption of EBT dye on (WTP) was monitored over a range of pH from 1.5 to 7.5 of individual solutions as shown in Figure 4. Low percent removal were observed at low pH values (< 5.0) and also at higher pH (above pH 7). If electrostatic interaction was the only mechanism for the dye adsorption, then the removal capacity should be at a maximum within the range pH 5 – 6. In this pH range the surface of activated tea powder is positively charged (pH > 5.0) and dyes are negatively charged (pK$_a$ of dyes 6.2 and 11.6). The deprotonated groups of the dye were the sulfonate (-SO$_3^-$). At solution pH < 5, the removal capacity was expected to decrease, as the adsorbent was positively charged and dye molecules were either neutral or partially positively charged. At this acidic pH, the sulfonate groups of the dyes were almost protonated (-SO$_3$H, i.e., neutral). The large reduction in dye adsorption at highly basic conditions can be attributed to electrostatic repulsion between the negatively charged activated tea powder and the deprotonated dye molecules. Activated tea powder can also interact with dye molecules via hydrogen bonding mechanism.
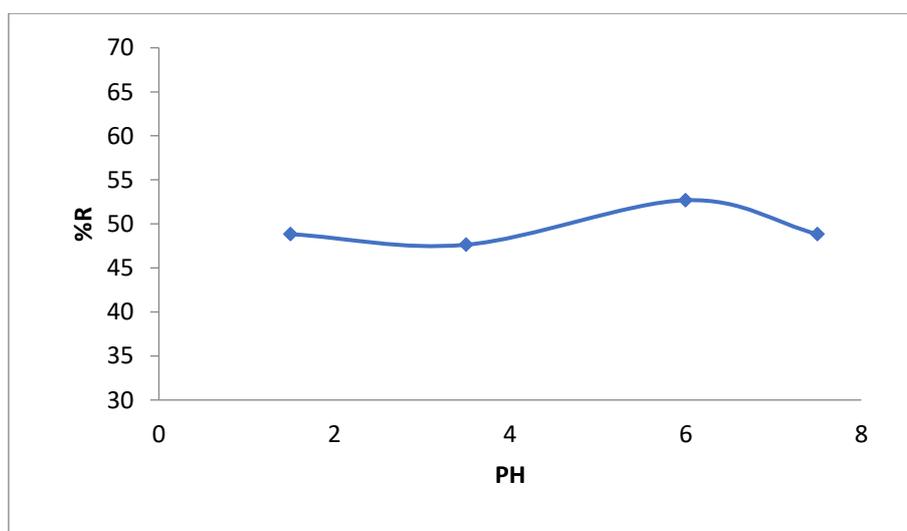

Figure 4. Effect of pH on percent removal of dye (% R) by WTP

Effect of initial concentration

The effect of different initial concentrations of dye on equilibrium of biosorption experiments onto (WTP) were investigated from 55 to 95 ppm at pH 6. The relation between equilibrium uptake Q_m (mg.g^{-1}) with initial dye concentration is shown in Figure 5. The Q_m of dye was increased gradually with an increasing the initial concentration of EBT dye as shown in Figure 5. The dye molecules adsorption is possible at lower concentrations, but as the concentration is increased, the driving force also increased, which favored the adsorption at higher concentrations. The increasing of adsorption capacity with the increasing in dye concentration is probably due to higher interaction between the EBT molecules and sequestering sites of biosorbent.
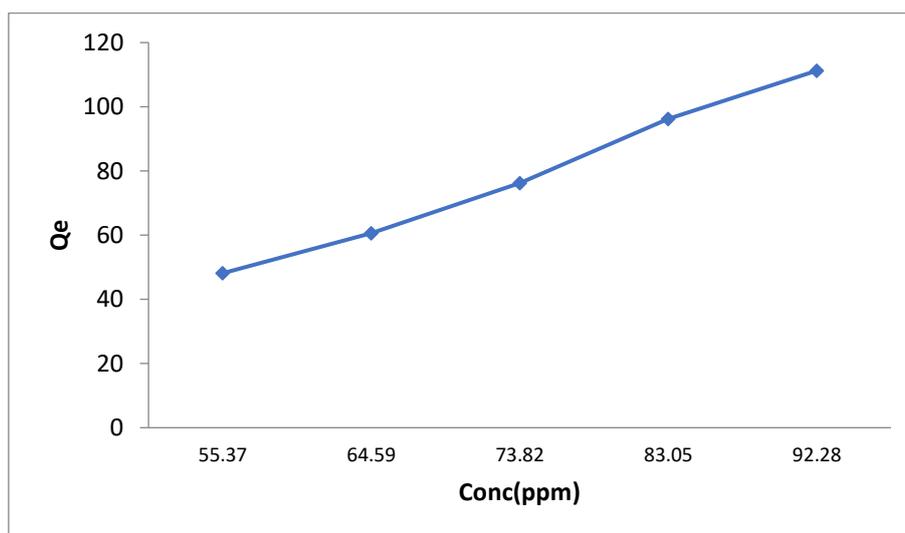

Figure 5. Effect of initial dye concentration on dye uptake Q_m onto absorbent (WTCP)

Effect of contact time

The rate of biosorption is an important for designing batch biosorption experiments. Therefore, the effect of contact time of dyes biosorption on (WTP) was investigated Figure 6 shows that the biosorption of EBT molecules on (WTP) was increased considerably until the contact time reached 80 min at 25°C. Further increase in contact time did not enhance the biosorption, so, the optimum contact time was selected as 80 min for further biosorption experiments.
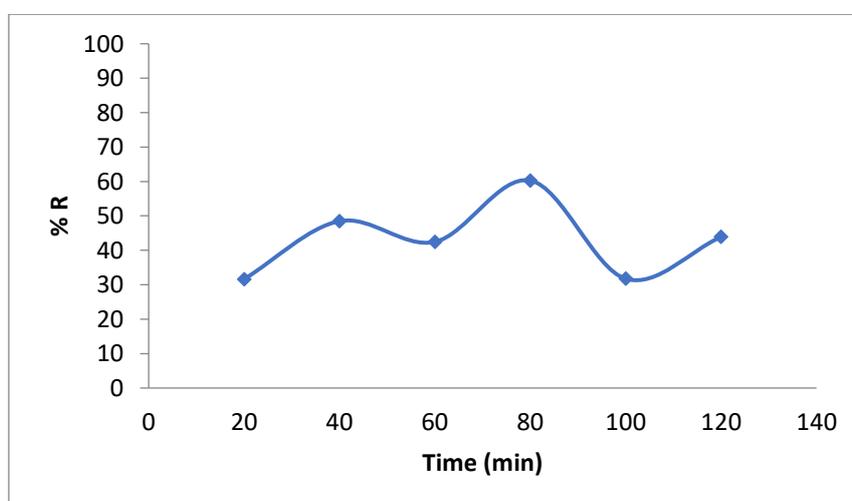

Figure 6. Effect of contact time on percent removal of dye (% R) by WTP

Effect of adsorbent dose

The biosorbent dosage of (WTP) is an important parameter because this determines the maximum capacity of a biosorbent for a given dye concentration. The biosorption efficiency for EBT molecules as a function of biosorbent dosage (WTP) was investigated, Figure 7 shows that the dye uptake was decreased with the biosorbent dose up to 0.1 g/L. This result can be explained by the fact that the biosorption sites in (WTP) remain unsaturated during the biosorption reaction whereas the number of sites available for biosorption site increases by increasing the dose of (WTP). In the further experiments, 0.1 g/L were taken as optimum biosorbent dose because a maximum capacity of the dye was attained at this value.
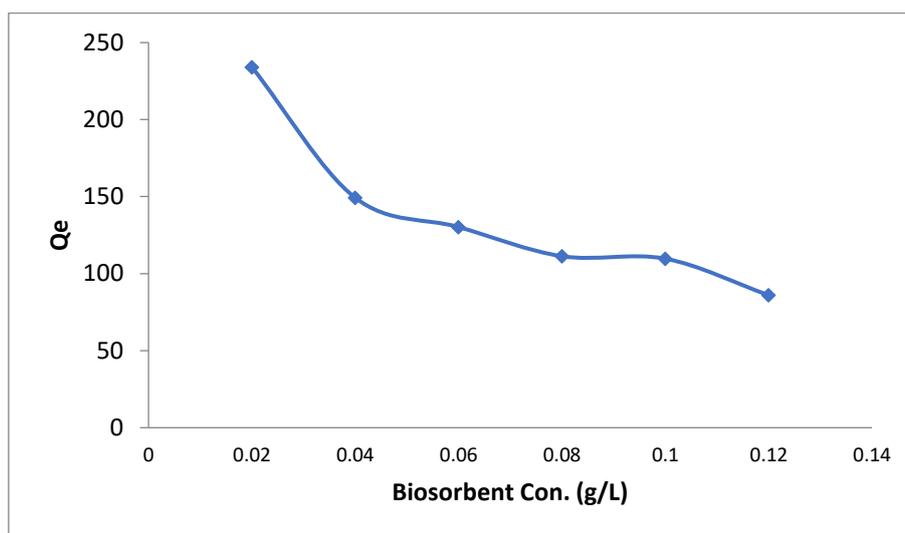

Figure 7. Effect of adsorbent dose on EBT uptake Q_m by WTP

Biosorption isotherms

Adsorption isotherms describe the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium**.** Biosorption of EBT onto waste tea powder (WTP) was modeled using four adsorption isotherms.

The Langmuir isotherm

It assumes as monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The linear form of the Langmuir isotherm model is described as [20]:

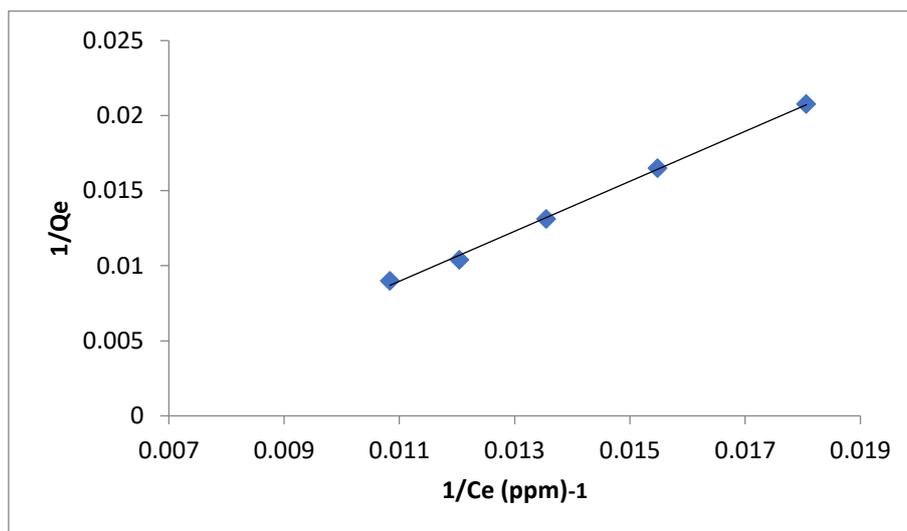$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{b\,Q_m C_e} \qquad (3)$$

Figure 8. Langmuir adsorption isotherm for the removal of EBT dye by WTP

where b is the Langmuir constant related to the energy of adsorption (L.mg^{-1}) and Q_m is the maximum biosorption capacity (the monolayer adsorption saturation capacity mg/g), Q_e (mg/g) the amount of dye molecules bound per gram of the adsorbent at equilibrium; and C_e, the residual (equilibrium) dye concentration left in the solution after binding. Values of Langmuir parameters Q_m and b were calculated from the slope and intercept of the linear plot of $1/Q_e$ versus $1/C_e$ as shown in Figure 8. Values of Q_m, b, and regression coefficient R^2 are listed in Table 1. These values indicated that Langmuir model describes the biosorption phenomena favorable. The level of conformity for tea as a good sorbent is high, according to the correlation coefficients (R^2) of 0.997. The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, R_L expressed as in the following equation:

$$R_L = \frac{1}{1 + b\,C_0} \qquad (4)$$

The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). In concentration range of 50 to 95 mg/L of EBT dye, the values R_L of biosorbed (WTP) were found to be 0.667. This is in the range of 0.0-1.0 which indicates the favorable biosorption.

The Freundlich isotherm model

It is the well-known earliest relationship describing the adsorption process. This model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules and the application of Freundlich equation. Also suggests that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. This isotherm is an empirical equation and can be employed to describe heterogeneous systems and is expressed as follows in linear form [21]:

$$\text{Log } Q_e = \text{Log } K_f + \frac{1}{n}\,\text{Log} C_e \qquad (5)$$

Where K_f is the Freundlich constant related to the bonding energy. 1/n is the heterogeneity factor and n (g/L) is a measure of the deviation from linearity of adsorption. Freundlich equilibrium constants were determined from the plot of $\log Q_e$ versus $\log C_e$, as shown in Figure 9, on the basis of the linear of Freundlich equation. The n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is a chemical process; if $n > 1$, then adsorption is a physical process. The n value in Freundlich equation was found to be 0.596 (Table 1) this indicates the physical biosorption of EBT molecules onto tea adsorbate is suitable.
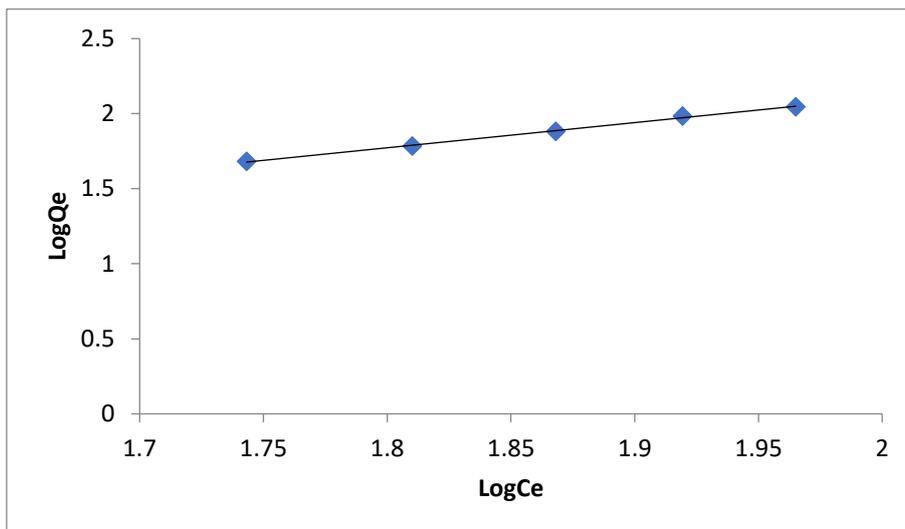
Figure 9. Freundlich adsorption isotherm for the removal of EBT dye by adsorption on (WTP)

Temkin isotherm

In literature [22] assumes that the heat of biosorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions and that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy. The Temkin isotherm has been used in the linear form as follows:

$$Q_e = B \, Log \, A + B \, Log \, C_e \qquad (6)$$

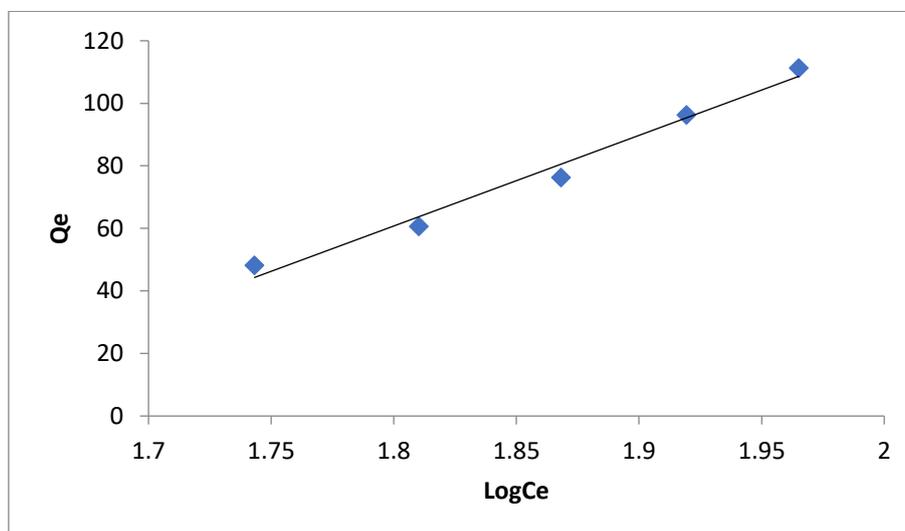**Figure 10. Temkin adsorption isotherm for the removal of EBT dye by adsorption on (WTP)**

The plot of Q_e versus $logC_e$ enables the determination of the isotherm constants B and A obtained from the slope and the intercept, Figure 10. Where A (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy and constant B is related to the heat of biosorption, Table 1.

Dubinin-Radushkevich (D-R) model

This model does not assume a homogenous surface or a constant biosorption potential as the Langmuir model, and it was also used to test the experimental data [23].

$$\text{Log } Q_e = \text{Log } Q_d - \beta \, \varepsilon^2 \qquad (7)$$

Where ε can be correlated to C_e (mg/L) by the following equation:

$$\varepsilon = \text{RT Log} \left(1 + \frac{1}{C_e} \right) \qquad (8)$$
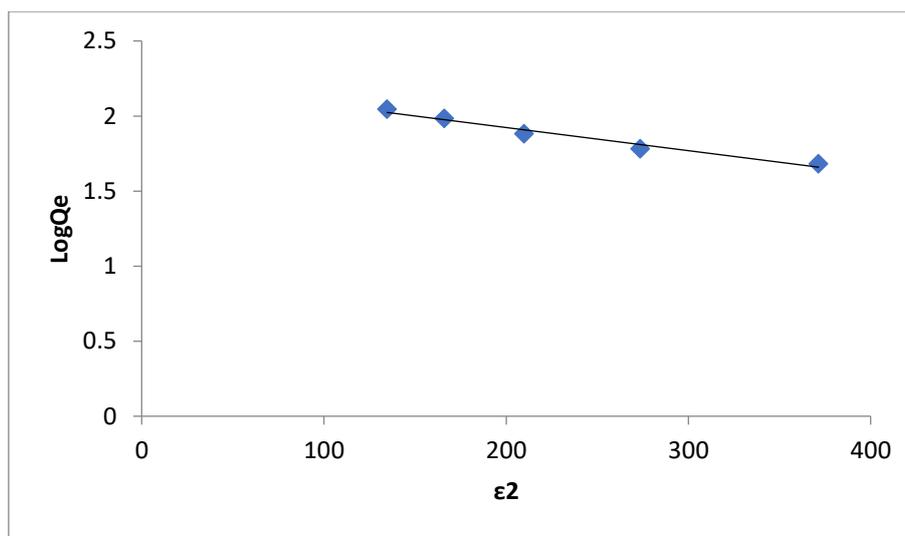

Figure 11. Dubinin-Radushkevich (D-R) adsorption isotherm for the removal of EBT dye by adsorption on (WTP)

Where R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K) . The D-R \isotherm β and Q_d were obtained from the slope and intercept of the plot of $\log Q_e$ versus ε^2, Figure 11. The calculated vales are listed in Table 1. The values of correlation coefficient were lower than that of other three isotherm values. In all cases, the D-R model represents the least fit to experimental data than the other isotherms models.

The mean free energy of biosorption, E defined as the free energy change when 1 mole of ion is transferred to the surface of the solid from infinity in solution and calculated from the β value using the following equation:

$$E = \frac{1}{\sqrt{2 \, \beta}} \qquad (9)$$

If the magnitude of E is between 8 to 16 KJ/mol then the sorption process is supposed to proceed via chemisorption reaction, while for values of E is less than 8 kJ/mol, the sorption process is of physical nature. The value of E calculated from equation (9) for the biosorption of EBT dye by waste tea powder is 0.0.018 KJ/mol. This indicates that the biosorption process is of physical nature.

Biosorption Kinetics

To examine the biosorption kinetics of dye uptake onto (WTP), the two kinetic models (pseudo first-order and pseudo second-order) were fit to experimental data.

The pseudo-first order equation of Lagergren [24] is generally expressed as follows:

$$\frac{dQ_t}{dt} = k_1 \, (Q_e - Q_t) \qquad (10)$$

Where Q_e and Q_t are the sorption capacities at equilibrium and at time t, respectively and k_1 is the rate constant of pseudo-first order sorption. The integrated form of equation (10) at boundary conditions, from Q_t= 0 to Q_t, and t = 0 to t; becomes:

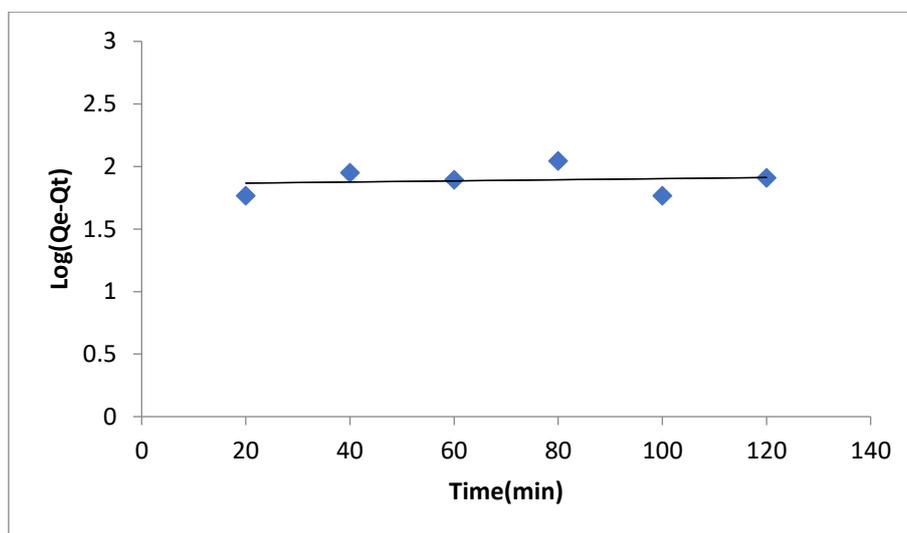$$Log \, (Q_e - Q_t) = \, Log \, Q_e - k_1 \, t \qquad (11)$$

Figure 12. Pseudo first order kinetic plots for the removal of EBT dye by adsorption on (WTP)

In order to fit the experimental data by integrated form of pseudo-first order equation, the equilibrium sorption capacity, Q_e must be known. For this reason, and for analyze the pseudo-first order model kinetics it is therefore necessary to use trial and error to obtain the equilibrium sorption capacity. In most cases in the literature, the amount sorbed is still significantly smaller than the equilibrium amount and the Lagergren equation does not fit well for the whole range of contact time process. The calculated values and their corresponding linear regression correlation coefficient values (which calculated from Figure 12) are listed in Table 2. R^2 was found to be 0.0238 which shows that this rate equation cannot be applied to predict the adsorption kinetic model.

The pseudo second-order rate expression, which has been applied for analyzing sorption kinetics rate, is expressed as [25]:

$$\frac{d \, Q_t}{dt} = k_2 \, (Q_e - Q_t) \qquad (12)$$

For the boundary conditions from Q_t= 0 to Q_t and t= 0 to t; the integrated form of equation becomes:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} \, t \qquad (13)$$

Where t is the contact time (min), Q_e and Q_t are the amount of the solute adsorbed at equilibrium and at any time t (mg/g) respectively and k_2 is the rate constant of pseudo-second order sorption, (g/mg.min).
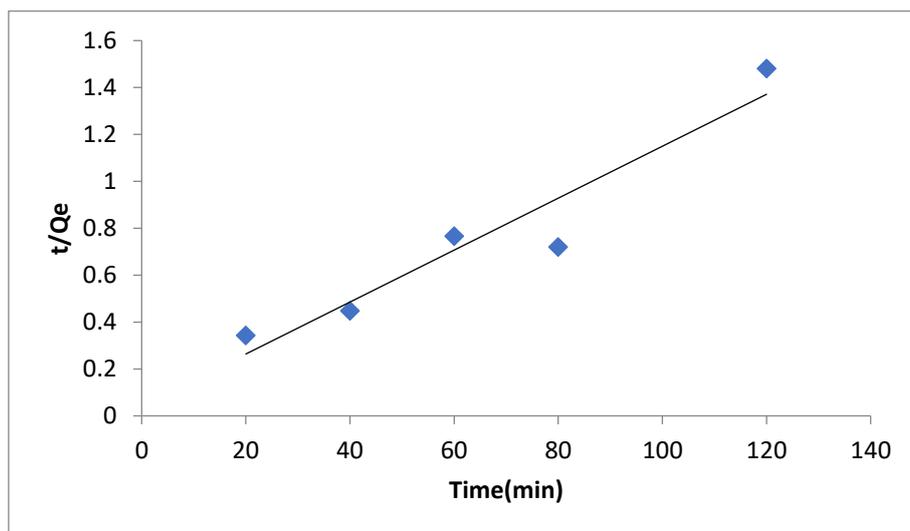
Figure 13. Second order kinetic plots for the removal of EBT dye by adsorption on (WTP)

If pseudo-second order kinetics is applicable, the plot of t/Q_t versus t of the equation should give a linear relationship, from which Q_e and k_2 can be determined from the slope and intercept of the plot, Figure 13. The pseudo-second order rate constant k_2, the calculated Q_e value and the corresponding linear regression correlation coefficient value R^2 are listed in Table 2. At all initial metal concentrations, the linear regression correlation coefficient R^2 values was high (0.9156) which confirm that the adsorption data are better represented by pseudo-second order kinetics. The calculated Q_e values agreed with the estimated experimental Q_e values 90.1 (Table 1 and 2). This enhance that the adsorption of EBT dye follows pseudo-second order kinetics

Table1. Langmuir, Freundlich, D-R and Temkin isotherm constants for biosorption of EBT onto WTCP

Langmuir	Q_m	b	R_L	R^2
Tea	111.11	0.0054	0.668	0.997
Freundlich	K_f	n		R^2
Tea	17.62	0.596		0.997
Temkin	B	A		R^2
Tea	289.84	0.025		0.9809
Dubinin-Radushkevich	Q_d	β		R^2
Tea	170.37	0.0015		0.971

Table 2.Kinetic parameters of EBT biosorption onto WTP

First Order	Q_e	k_1**(1/min)**	R^2
Tea	72.09	0.0004	0.0238
Second Order	Q_e	k_2 (g/mg min)	R^2
Tea	Graphically (90.1) Estimated (111.3)	0.0000291	0.9156

Conclusions

In our present work, we show that the waste tea powders could be used as a biosorbent for the removal of dye molecules from aqueous solutions.The removal efficiency and dye capacity were found to be dependent on pH, contact time, initial dye concentration, and biosorbent dose. Biosorption isothermal data could be well simulated by Langmuir, Freundlich, Temkin and then Dubinin-Radushkevich (D-R) models. The maximum metal capacities determined by using the Langmuir isotherm were 111.11 mg/g tea powders. The values of dye uptake capacities at equilibrium Qe calculated from equation (2) and pseudo-second-order plot were found comparable .The biosorption kinetics could be well predicted by pseudo-second-order kinetic. The results of our investigation indicate that the tea powder has a potential for use in removing EBT dye from aqueous solutions.

Conflicts of Interest

Submitting author is responsible for co-authors declaring their interests.

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