Eriochrome Black T dye adsorption onto natural and modified orange peel

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Abstract

Adsorption of Eriochrome Black T dye from aqueous solution onto the orange – peel and chemically modified orange peel by either sodium hydroxide or cetyl trimethyl ammonium bromide has been studied using a batch technique. The adsorption studies were determined as a function of pH, contact time, initial dye concentration, biosorbent dosage and temperature. Experimental data obtained were analyzed with Langmuir, Freundlich and Temkin isotherm models and in each case, the Freundlich model appears to have better regression coefficients.

Thermodynamic parameters ΔG^o, ΔH^o and ΔS^o were calculated indicating that the absorption of Eriochrome Black T dye is a spontaneous and endothermic process. The kinetic study showed that that the biosorption of the dye followed pseudo-second-order. The results of this study showed that orange peel and modified orange peel can be efficiently used as a low-cost alternative for the removal of Eriochrome Black T Dye from aqueous solutions.

Keywords: Eriochrome black T dye, pollution, orange peels, cetyl trimethyl ammonium bromide, adsorption, thermodynamic, kinetics.

Introduction

Water pollution is a threat to our modern society. The substantial progress in industrial and agricultural activities led to generate many types of toxic pollutants. Contaminated wastewater must be discharged and returned to the aquifers or land. Dyes are an important category of contaminants that came in large quantities from the textile, dyeing, pulp, tanning and paint industries[1]. Dyes are always left as the main waste in these industries. Due to their chemical structures, dyes are fading resistant when exposed to light, water and many chemicals, therefore are difficult to be decolorized once released into the aquatic environment[2]. Most of these dyes pose severe ecosystem problems, which are toxic and possess carcinogenic properties that make water inhibitory for aquatic life because of their chemical composition[3]. It has already been shown that dyes significantly affect photosynthetic activity[4].

Furthermore, many dyes are toxic and even carcinogenic affecting aquatic organisms and human health[5,6]. Eriochrome black T (EBT) is an aromatic compound and a complex metric that forms part of complex metric calibration. EBT dye is used also in the water hardness determination process. It is an azo and anionic dye and its protonated state is blue. It changes to red when it forms a complex with sodium, magnesium, or other metal ions. Its chemical formula is $HOC_{10}H_6N{=}NC_{10}H_4$ (OH) (NO_2) SO_3Na[7]. EBT dye is dangerous as such and its degradation products like naphthoquinone are cancer causing[8]. Agrarian byproducts such as fruit peel are comparatively low cost and show high adsorption ability for organic and inorganic pollutants.

The usage of orange peel (OP) as biologically modified adsorbent substances offers powerful potential because the main component presents cellulose, pectin, hemicellulose and lignin acid carrying various functional polar groups including carboxyl and phenol acid groups[9]. Surfactants are moisturizers that reduce the surface tension of the liquid, resulting in easier dispersion and reduced surface tension between the liquid.[1]. Cetyl trimethyl ammonium bromide (CTAB) is a cationic surfactant that contains two long-chain alkyl groups, namely dialkyl dimethyl ammonium chloride, with alkyl groups with a chain length of 8-18 carbon atoms.

'Generally, these types of surfactants are sparingly soluble in water than the mono alkyl quaternary solvents, but they are usually used in detergent as disinfectant fabric[12]. This research work presents the study of biosorption characteristics of OP and modified OP by NaOH and CTAB for removing the EBT dye from its aqueous solution via batch process.

Material and Methods

Adsorbent preparation

Raw OP*:* The OP was obtained from trees planted in Iraq. OP was rinsed well with distilled water to remove dust and left to dry at room temperature. After drying, the peel was crushed and ground to a soft powder in a grinding mill (Retsc RM 100) and shifted to get size fraction less than 44 µm. OP powder was dried in an oven at 60^0C for 24h and stored in a desiccator to prevent adsorption of water before its use for the batch experiments.

Chemical modification with sodium hydroxide (NaOH): Sixty grams of the dried OP were immersed in 250 ml of (0.1M) NaOH solution for 24 hours under shaking. After decantation and candidacy, the product was washed with bi-distilled water several time until the pH of the filtrate reached 7.

Chemical modification with CTAB: 40 g of OP powder was mixed with 100 ml CTAB and stirred with magnetic stirrer at room temperature for 2 h. The OP –CTAB mixture obtained was washed with distilled water until free from Br as indicated by an $AgNO_3$ test. The samples were then put in an oven at 60°C for 6h in order to dry.

Preparation of EBT dye solutions: Eriochrome black T (Fluka, 99% purity) was used without any further purification in this study. The stock solution (60mg/L) was prepared by dissolving 0.06 g EBT dye in 1 L distilled water. Experimental solutions were obtained by dilution. UV-VIS Spectrophotometer (UV-Visible spectrophotometer, Double beam, Shimadzu. PC 1650, Japan) was used in order to determine dye concentration at λ_{max} 526 nm.

Batch Adsorption Study: Batch adsorption experiments were carried out by changing solution pH, adsorbent dose (OP, SOP and OP-CTAB), as well as contact time, initial concentration of dye, in addition to temperature. In this study, the amount of adsorbents was weighed accurately and added to100 mL of aqueous EBT dye solution. After that, 250 mL of the reaction mixture was taken in a conical flask and agitated at 120 rpm in a rotary shaker. The sample was analyzed after filtration by filter paper (Whatmann No. 42). Each procedure was repeated three times and the results obtained were their average values. The percentage removal (R%) of EBT dye was then calculated using the data obtained through batch studies by using the following relation:

$$\% \text{ Dyes removal} = ((C_o-C_e)/C_o) \times 100 \quad (1)$$

where C_O and C_e are the initial and equilibrium concentrations (mg/L) of the dye concentrations respectively. The amount of adsorption was calculated based on the difference between the initial and final concentrations as follows:

$$Q_e = (C_o-C_e)\, V/M \quad (2)$$

where Q_e is the amount of dye adsorbed (mg/g), V is the volume of the solution (L) and M is the mass of the adsorbent (g).

Results and Discussion

Surfaces Chemistry of Adsorbents

FTIR of OP, SOP and CTAB-OP: FTIR spectra for orange peel (OP), orange peel – NaOH (SOP) and orange peel-CTAB (OP-CTAB) powders are shown in figures (2a, b and c). The spectra show a number adsorption band distinguishing the complex nature of the adsorbents.

SEM of OP, SOP and CTAB-OP: The scanning electron microscope (SEM) (Inspect S 50 FEI company) micrographs showed the highly heterogeneous porous structure of the orange peel (OP)[13]. The SEM for OP after being treated with sodium hydroxide showed a more irregular and porous structure than OP[14]. The SEM for orange peel after modification by CTAB showed rougher image than natural orange peel[15]. Figure (3a, b and c) illustrate the SEM images for adsorbents.

AFM of OP, SOP and CTAB-OP: The orange peels and modified orange peel are characterized by AFM (SPM-AA 3000, Advanced Angestrum Inc.) to determine r average particle size and its distribution. The AFM images in three – dimensional and granularity distribution charts for orange peels (OP), sodium orange peels (SOP) and orange peel-CTAB (OP-CTAB) were represented in figures 4 and 5. The average diameter was 109.40, 94.45 and 62.46 nm for orange peel (OP), sodium orange peel (SOP) and OP - CTAB respectively. These results indicate the lower average diameter for modified orange peel than orange peels.

Surface area measurements (BET measurements): The results of surface area (BET) (Micromeritics ASAP 2020 V3.04G analyzer (micromeritics, Inc., USA) for the OP, SOP, and CTAB-OP are 0.71 m^2/g, 1.1705 m^2/g and 1.3 m^2/g. The surface area of CTAB-OP is larger than that of both OP and SOP. The presence the CTAB layer on the surface of OP leads to morphological changes. The surface of CTAB-OP is more uneven than that of OP and refers to the CTAB adhered physically or chemically bonded onto the surface of orange peel.

Effect of parameters on the EBT dye adsorption

Effect of contact time: The contact time between Eriochrome black T dye aqueous solution and adsorbents surfaces (OP, SOP and OP -CTAB) reaches equilibrium at 298 K by using a fixed concentration (C_o=9 ppm) studied at different periods (10,15.20,25 and 30) min. Fig. 6 shows that the percentage removal of Eriochrome black T dye increases with increasing the contact time until reaches a maximum value. The percentage removal of EB T dye at 25 minute of contact time is 75% for OP, 54% for SOP and 95% for OP- CTAB surfaces.

Effect of adsorbent dose: The adsorbent dosage effect on the adsorption process of the OP, SOP and OP- CTAB was studied at 298 K by using a fixed concentration (Co=9 ppm) and different weight of adsorbents (0.01-0.09) gm. The contact time is fixed at 25 min. Fig. 7 shows that the percentage removal of Eriochrome black T dye was increased with increasing the adsorbents dosage. The percentage removal was found to be maximum at 0.05 g of dosage, 76 for OP, 65 for SOP and 96 for CTAB –OP. These results may be attributed to the fact that the adsorption sites remain unsaturated during the adsorption reaction where as the number of a site available for adsorption site increases by increasing the adsorbent dose[17].

Effect of pH: EBT dye uptake was found to depend on pH of the solution, as shown in fig. 8, solutions pH was adjusted at 3, 4, 9 and 12. EBT dye was found to be maximum at pH=3.

Adsorption isotherms: Adsorption isotherms of EBT dye on OP, SOP and CTAB-OP were studied at three different temperatures (298. 308 and 318) K and at pH=3 that involved different initial concentrations (3,6, 9 ,12 and 15) ppm. Figures 9a, b and c show the graphical representation of the adsorption isotherm obtained by plotting Qe values (the amount of solute adsorbed on the surface of the adsorbents) against Ce (the equilibrium concentration of the solute in the solution)**.** The common shapes of the adsorption isotherm of EBT dye on the OP, SOP and CTAB-OP are S-curve according to Gile's classification.

S-curves are indicative of vertical or flat orientation of adsorbed. There is strong inter-molecular attraction within the adsorbed layer and the adsorbate is monofunctional. The initial section of S-curve refers to presence of more solute that is already adsorbed, the easier it is for additional amounts to become fixed[18]. The S-curve is attributed to Freundlich isotherm about the heterogeneity of the surface. The S-curve isotherm demonstrated that the type of adsorption is a physical adsorption rather than chemical adsorption.

Adsorption isotherm theories

Langmuir isotherm: The Langmuir isotherm was applied for monolayer adsorption on to surface. This model depends upon being a fixed number of adsorption sites on adsorbent surface, each site capable of holding one molecule of adsorbate. All sites are equivalent in their affinity for adsorption of molecules and the surface is uniform so that there is no interaction between the adsorbed molecules.

$$Ce/Qe = 1/k_L\, q_{max} + (1/q_{max})\, Ce \quad (1)$$

where C_e is the equilibrium concentration (mg/L), Q_e is the amount of dye adsorbed at equilibrium concentration (mg/g)) q_{max} and k_L are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The linear plot of Ce/Qe vs Ce shows that the adsorption obeys Langmuir isotherm model in fig. 10. q_{max} (mg/g) and k_L (L/mg) were determined from the slope and intercept of the plot.

The main characteristics of Langmuir isotherm can be expressed in term of dimensionless constant separation factor for equilibrium parameter, R_L[19] which is defined by

$$R_L = 1/ (1+k_L\, C_o) \quad (2)$$

The dimensionless factor (R_L) indicates the shape of isotherm as follows:

RL < 1	Favorable
RL >1	Unfavorable
RL = 1	Linear

Freundlich isotherm: Freundlich equation may be derived by assuming a heterogeneous surface with adsorption on each class of sites obeying the Langmuir equation**.** The heterogeneous adsorption sites have different potential energies and different geometrical shapes on the surface, so the affinity from site to site toward the same molecule is different, the adsorption process can be expressed as[20]:

$$Log\ Qe = Log\ k_F + 1/n\ Log\ Ce \quad (3)$$

where k_F is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg/g) and 1/n is the adsorption intensity. k_F and 1/n can be determined from the slope and intercept of the linear plot of Log Qe vs. Log Ce in figure 11.

Temkin isotherm: Temkin isotherm contains a factor that explicitly takes into account adsorbing species- adsorbent interaction. This isotherm assumes that:

(i) The heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent – adsorbate interactions.

(ii) The adsorption is characterized by a uniform distribution and that energy up to some maximum binding energy and is represented as follows[21]:

$$Qe = B_T\, Ln\, A_T + B_T\, Ln\, Ce \quad (4)$$

where B_T is a constant related to adsorption heat (J/mol) and A_T is the equilibrium binding constant (L/g), corresponding to maximum binding energy. A plot of Qe vs. ln (Ce), is used to determine isotherm constants from the slope and intercept in figure 12.

From the results tabulated in table 1, the correlation coefficient to (R^2) of the plots of Freundlich model are 0.975-0.991 at different temperatures and they support the Freundlich isotherm model application referring that the adsorption of EBT dye on OP, SOP and CTAB-OP surfaces is physical adsorption.

Adsorption thermodynamic: Thermodynamic functions[22, 23], change in Gibbe free energy ΔG , enthalpy change ΔH and entropy change ΔS were calculated according to following equation:

$$\Delta G = \Delta H - T\,\Delta S \quad (5)$$
$$k_{eq} = Qe/\ C_e \quad (6)$$
$$Ln\ k = -\Delta H / RT + \Delta S / R \quad (7)$$

where k is the equilibrium constant. Q_e is the adsorbed amount of dye on surface (mg/g), C_e is the equilibrium concentration (mg/L), R is a gas constant (8.315 $J.K^{-1}.mol^{-1}$) and T is an absolute temperature. ΔH and ΔS were calculated from the slope and intercept of a plot of ln keq against 1/T Fig. (13) and the data obtained are presented in table (2).

When the temperature of the system increases, the adsorption capacity decreases obviously from the values of k_{eq} which decrease with increasing in temperature that refers that the adsorption process is exothermic and it is confirmed by the negative values of ΔH. The negative ΔG values indicate that the nature of the adsorption process is thermodynamically spontaneous. The negative value of ΔS shows the decreasing randomness at solution– sorbate interface during the adsorption process.

Adsorption kinetics: Determination of order of the EBT dye removal and the rate constants were calculated from Lagergrens pseudo first-order model, pseudo-second order model and intraparticle diffusion model[23,24] and were applied to the experimental data:

$$\text{Ln}\,(q_e - q_t) = \ln q_e - k_1/2.303t \quad (8)$$

$$t/q_e = 1/k_2 q_e^2 + 1/q_e\, t \quad (9)$$

$$q_t = k_D\, t^{1/2} + c \quad (10)$$

where q_e is the amount of dye adsorbed at equilibrium (mg/g), q_t is the amount of dye adsorbed at any time (mg/g), k_1 is pseudo-first order (min^{-1}), k_2 is pseudo-second order (g/mg.min), k_D is diffusion constant ($mg/g.min^{1/2/}$) and t is the time (min).

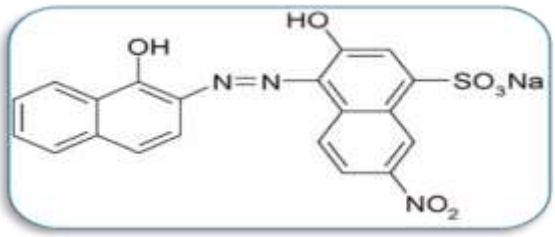
The kinetics rate constants and the correlation coefficient (R^2) were shown in table 3. Figures 15, 16 and 17 were used to determine the pseudo first-order, pseudo second- order rate constants and q_e value respectively. The adsorption constants with correlation for the pseudo- first order, pseudo second-order models and intraparticle diffusion are shown in table 5. Inspection of table 3 reveals that the values of R^2 obtained by applying the pseudo first- and pseudo second-order kinetic equations are comparable. However, more inclined to apply is the pseudo second -order model because it gives higher R^2 values.

Although the regression of intraparticle diffusion was linear, the plot did not pass through the origin, suggesting that adsorption of EBT dye on orange peels and its modified forms involved intraparticle but was not the only rate-controlling step. The values of k_D indicate that modification of OP with CTAB to give CTAB-OP resulted in a considerable increase in k_D from 0.035 to 0.127 i.e. a nearly 4-fold increase. It appears that modification with CTAB of OP resulted generally in increase in k_D also k_D values which are less than k_2 and have also confirmed that the intraparticle diffusion was rate-controlling step[25].

Table 1
Langmuir, Fruendlich and Temkin constants for EBT dye adsorption on (OP), (SOP) and CTAB-OP at three different temperatures.

Adsorbent	T (K)	Langmuir constants				Freundlich constants		
		q_{max}	k_L	R_L	R^2	n	k_F	R^2
OP	298	0.667	0.457	0.195	0.972	0.251	2.811	0.981
	308	1.131	0.363	0.234	0.968	0.344	2.254	0.987
	318	1.716	0.247	0.310	0.947	0.431	2.282	0.975
SOP	298	0.339	0.263	0.297	0.933	0.192	175.348	0.991
	308	0.377	0.253	0.305	0.982	0.199	154.882	0.977
	318	0.365	0.249	0.308	0.995	0.200	155.597	0.975
CTAB-CTAB-OP	298	0.903	1.028	0.098	0.951	0.256	11.146	0.977
	308	0.747	1.007	0.099	0.953	0.204	11.003	0.978
	318	0.594	0.987	0.101	0.984	0.193	9.378	0.989

	T	Temkin constants		
OP	(K)	A_T	B_T	R^2
	298	1.004	285.058	0.991
	308	1.003	349.532	0.913
	318	1.000	754.507	0.889
SOP	298	1.027	267.041	0.895
	308	1.026	286.186	0.799
	318	1.025	290.573	0.772
CTAB-OP	298	1.043	192.009	0.975
	308	1.051	58.508	0.976
	318	1.046	63.291	0.945



Molecular formula: $C_{20}H_{12}N_3O_7SNa$
Molecular weight: 461.381 g/mol
λ_{max} = 526 nm

Fig. 1: Structure of Eriochrome Black T Dye.

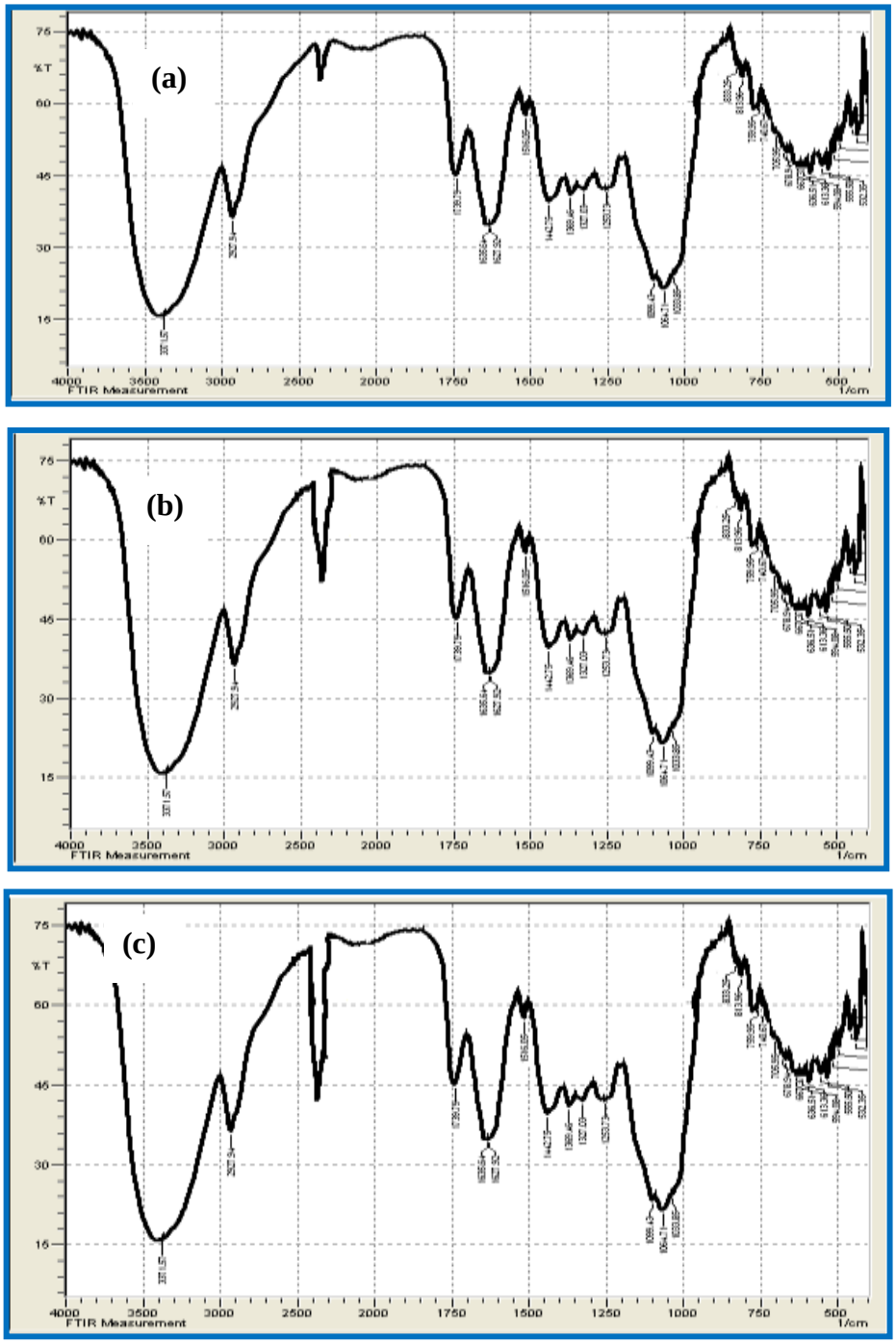


Fig. 2: FTIR spectra of a) OP, b) SOP, c) CTAB-OP powders

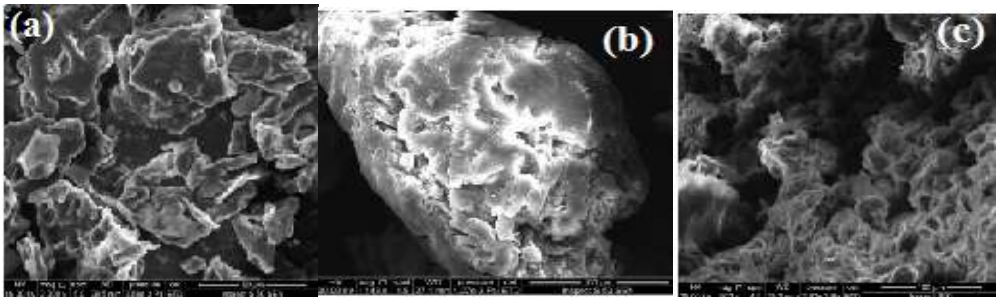


Fig. 3: SEM images of a) OP, b) SOP, c) CTAB-OP

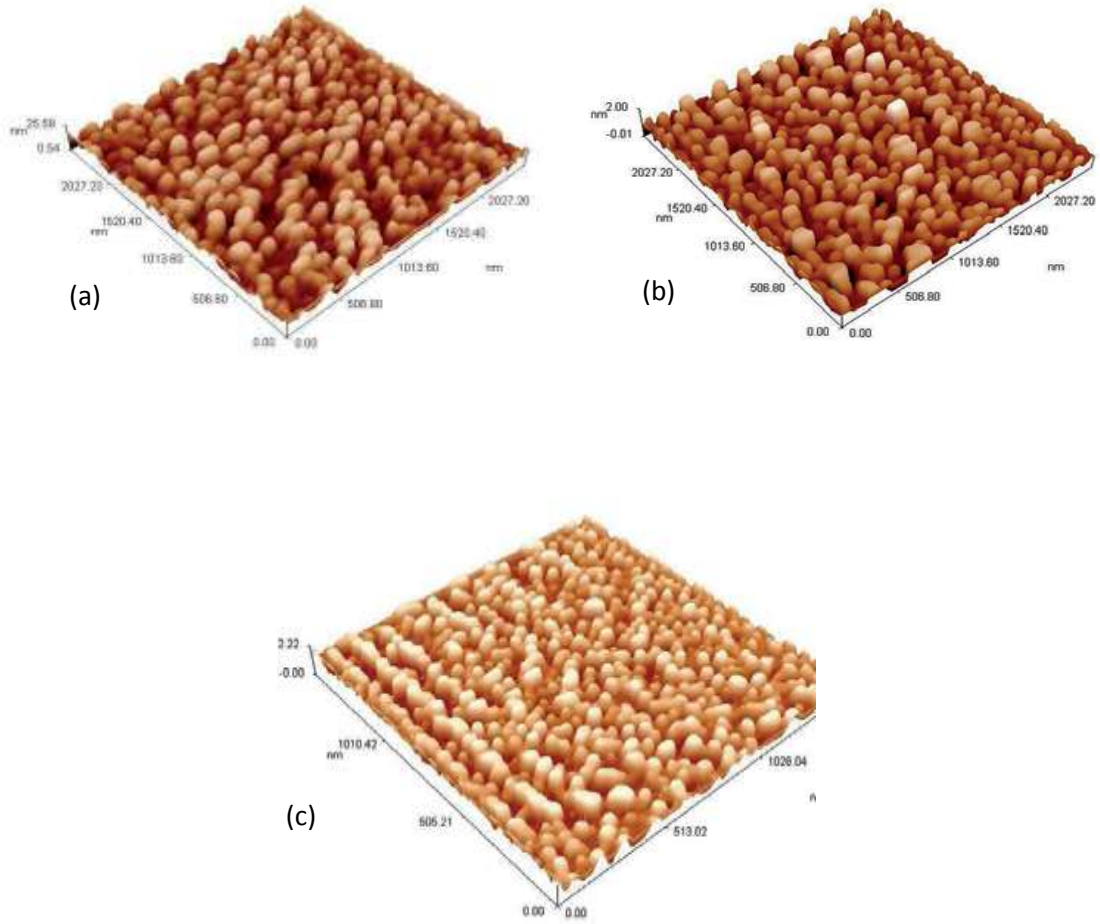


Fig. 4: AFM images of a) OP, b) SOP, c) CTAB-OP

Table 2
Thermodynamic parameters of EBT dye sorption on to OP, SOP and CTAB-OP

Surfaces	T(K)	k_{eq}	$-\Delta H$ kJ/mol	$-\Delta S$ J /mol.K	$-\Delta G$(kJ/mol)
OP	298	1.183	18.234	51.322	2.931
	308	0.957			2.451
	318	0.720			1.904
SOP	298	0.411	1.073	0.209	1.018
	308	0.387			0.991
	318	0.384			1.015
CTAB-OP	298	2.055	1.677	11.514	5.093
	308	2.056			5.266
	318	2.012			5.320

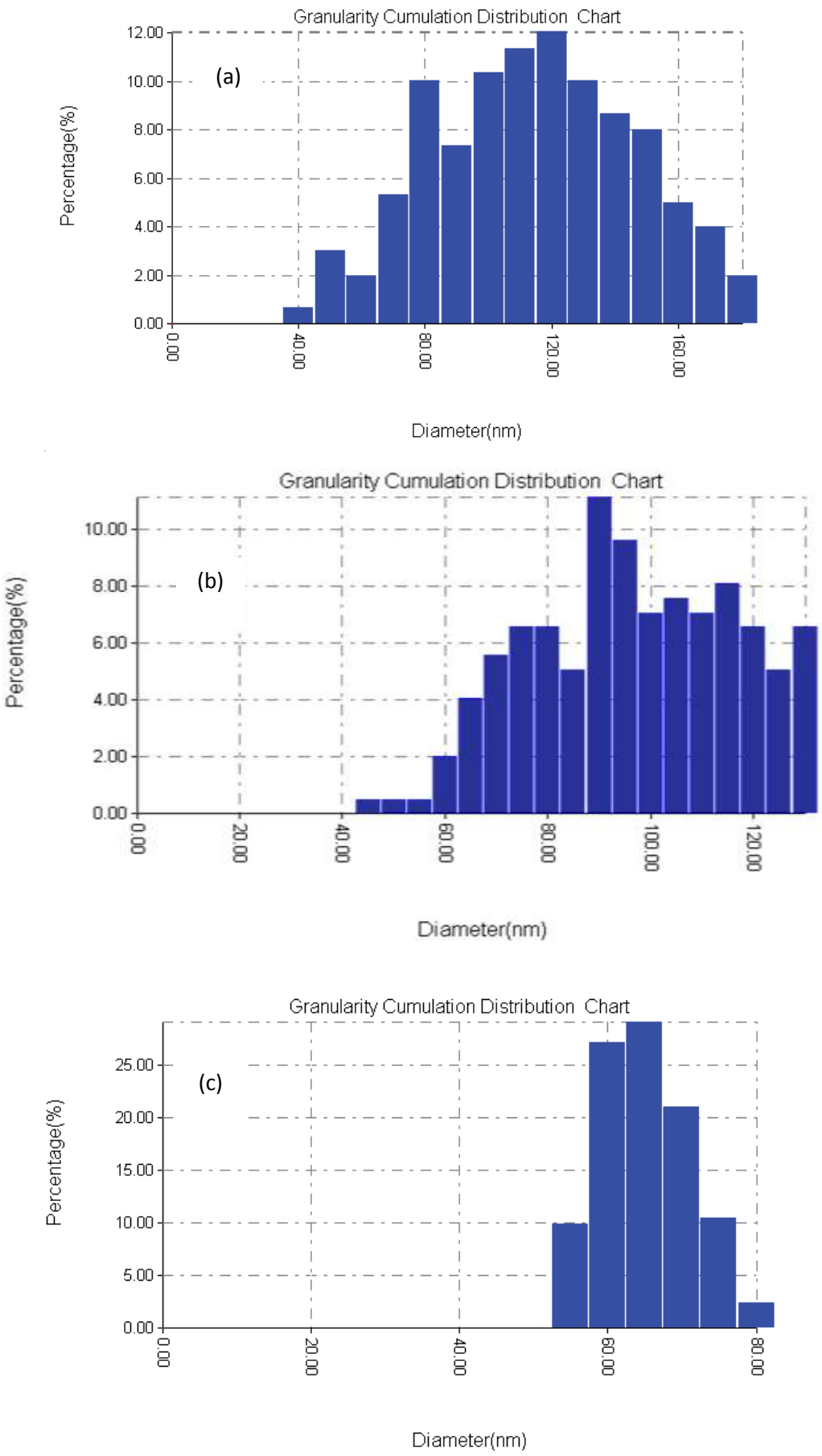


Fig. 5: Granularity Cumulating Distribution Chart of a) OP, b) SOP, c) CTAB-OP

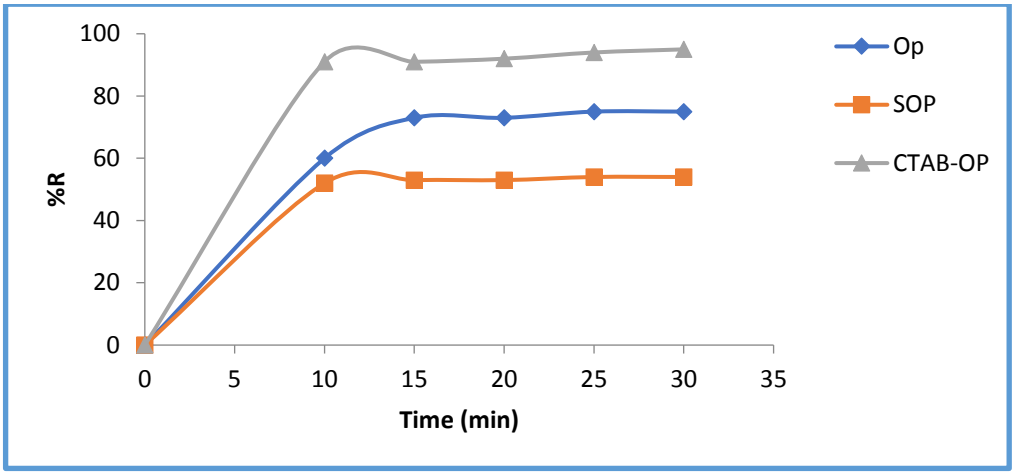


Fig. 6: Effect of contact time on adsorption of EBT dye on three sorbent surfaces

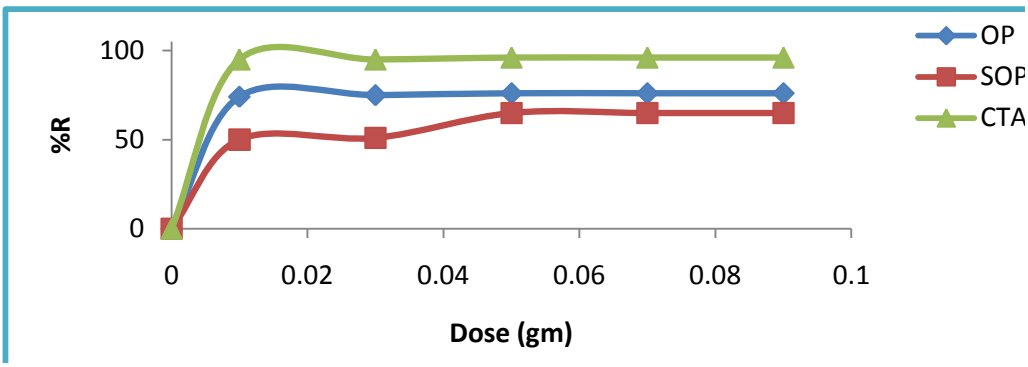


Fig. 7: Effect of adsorbents dose on adsorption of EBT dye on three sorbent surfaces.

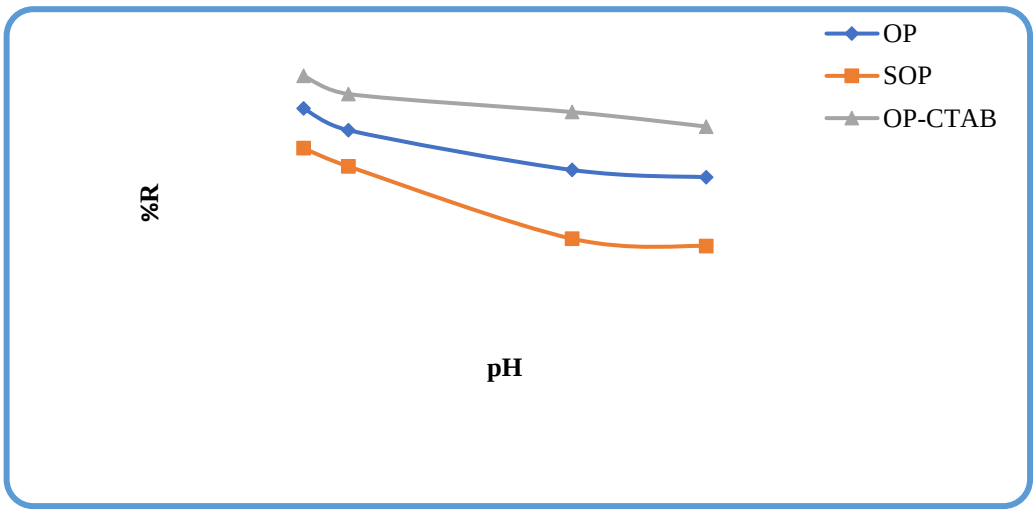


Fig. 8: Effect of pH on adsorption of EBT dye on three sorbent surfaces.

Table 3
Kinetics constants for adsorption EBT dye on OP, SOP and CTAB-OP.

Adsorbents	Pseudo-first order			Pseudo-second order			Intraparticle diffusion	
	k_1 (1/min)	q_e (mg/g)	R^2	k_2 (g/mg.min)	q_e (mg/g)	R^2	k_D (mg/g.moin$^{1/2}$)	R^2
OP	0.049	9.072	0.909	0.059	4.013	0.991	0.035	0.793
SOP	0.059	32.226	0.916	0.529	2.519	0.999	0.051	0.983
CTAB-OP	0.013	2.203	0.906	0.358	4.322	0.999	0.127	0.633

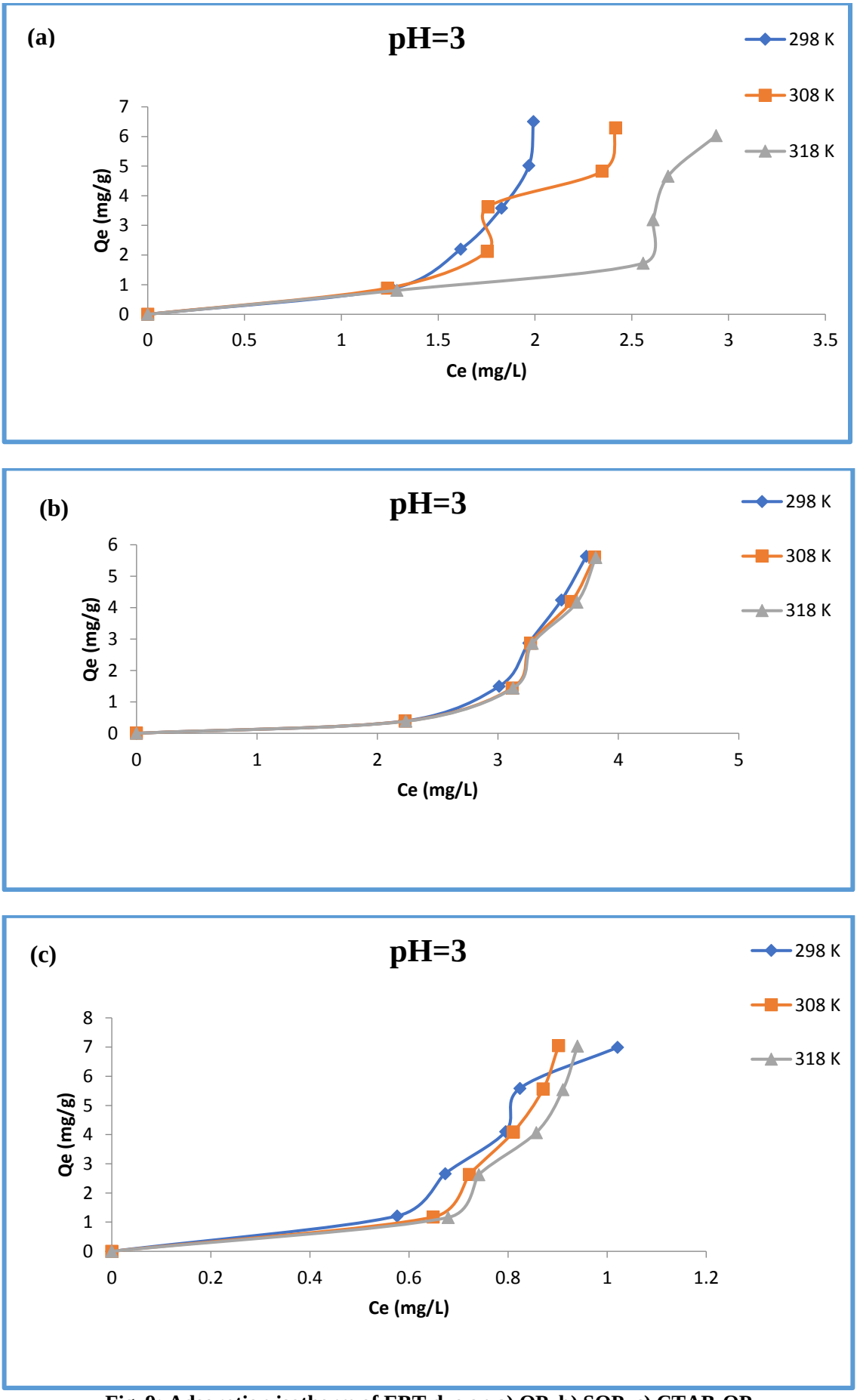
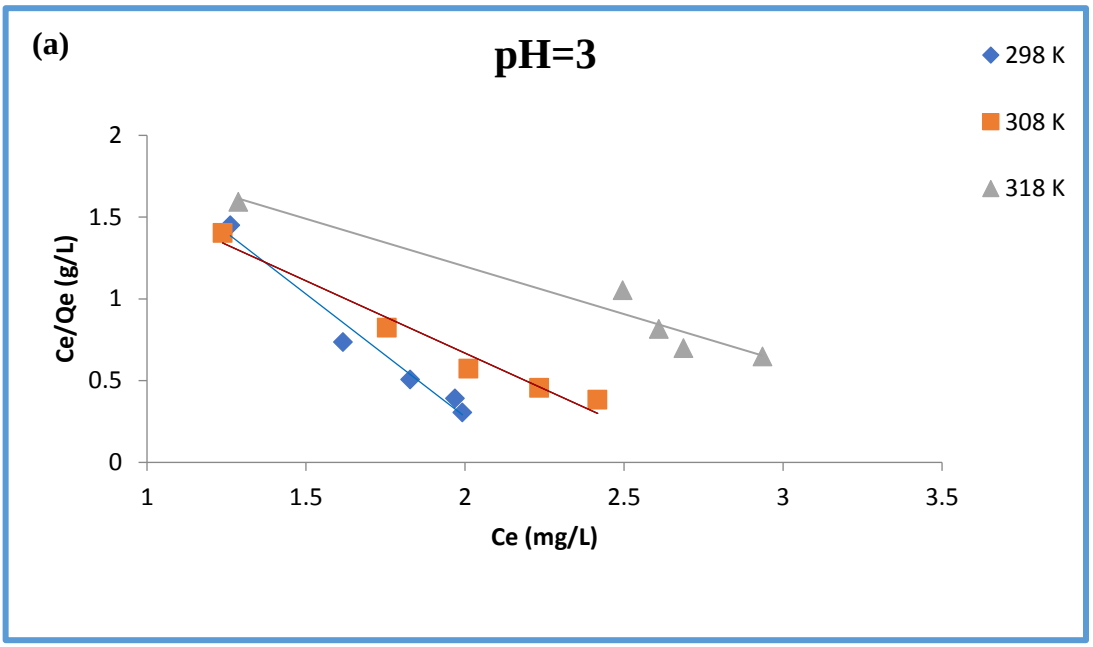
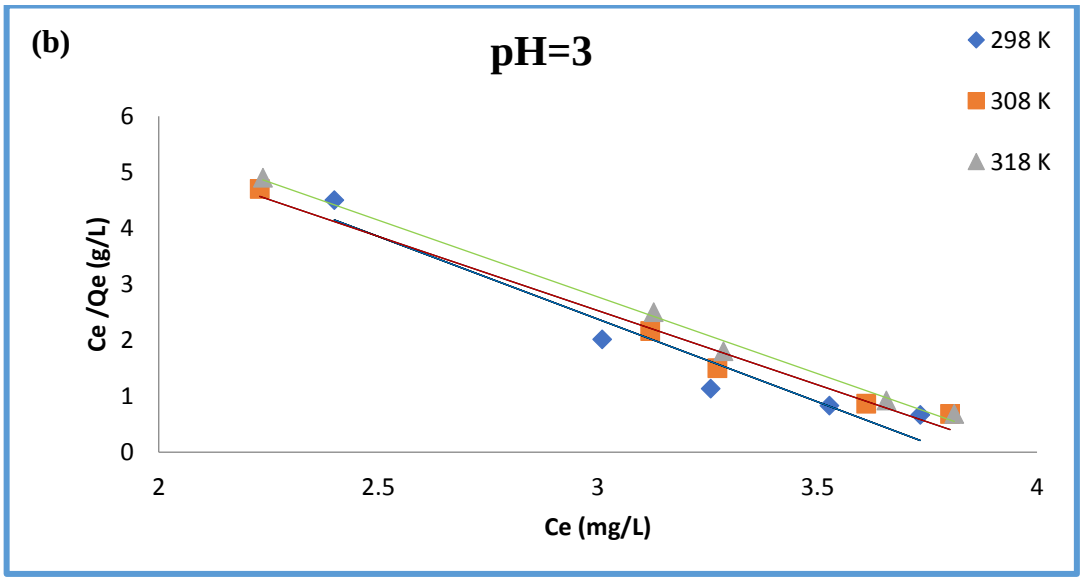


Fig. 9: Adsorption isotherm of EBT dye on a) OP, b) SOP, c) CTAB-OP





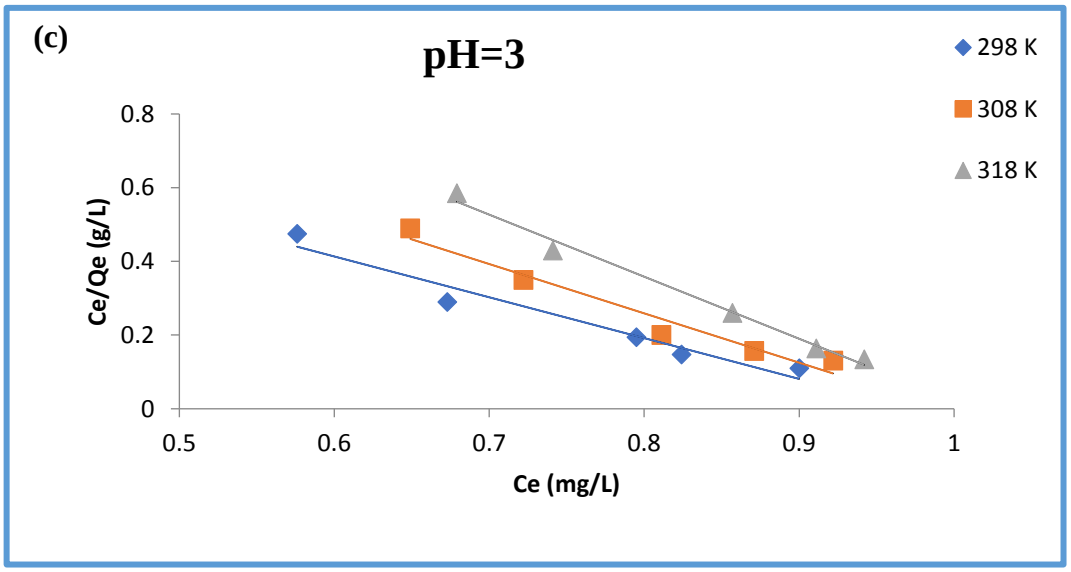


Fig. 10: Langmuir isotherm for a) OP and b) SOP, c) CTAB-OP

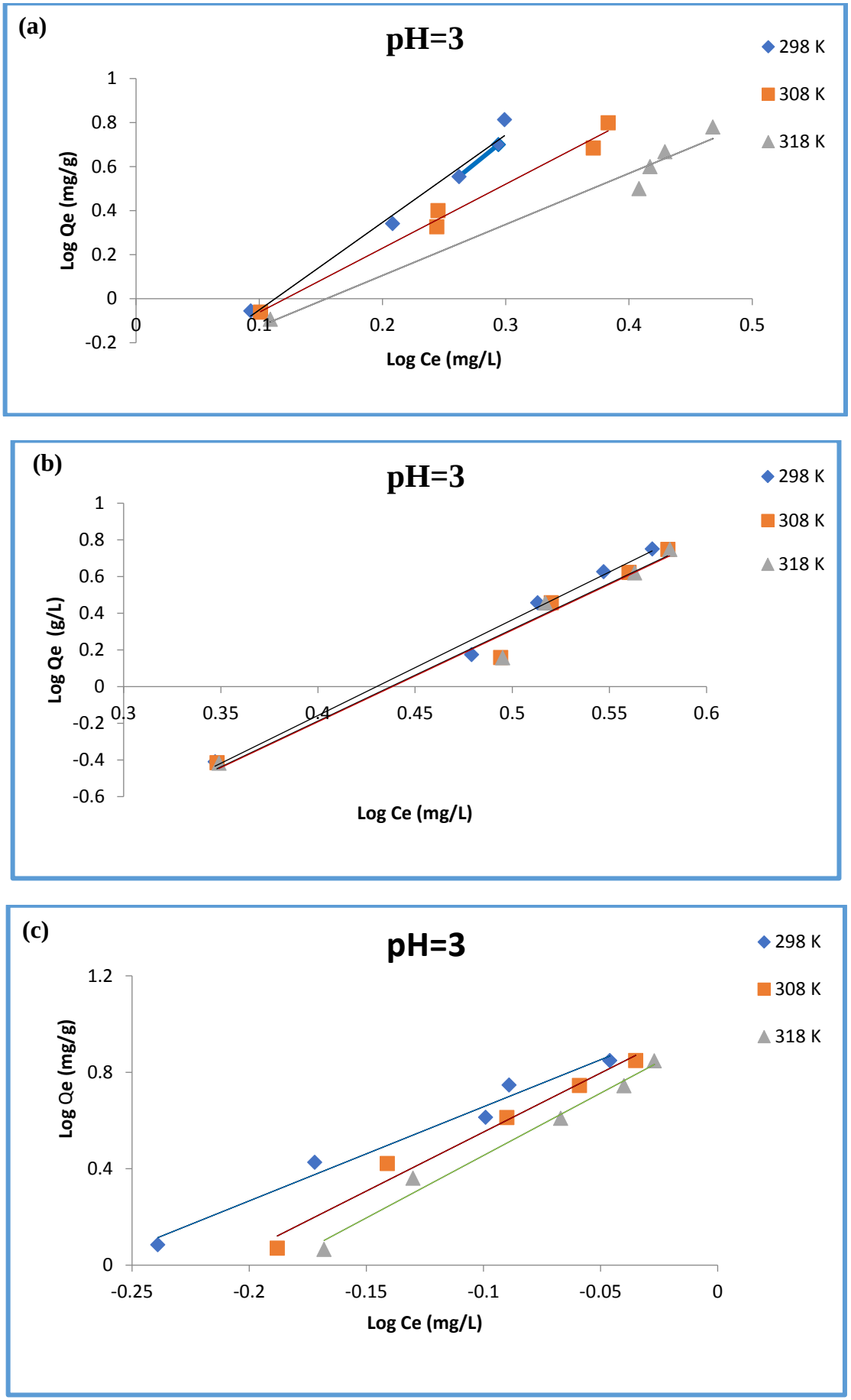


Fig. 11: Freundlich isotherm for a) OP, b) SOP, c) CTAB-OP

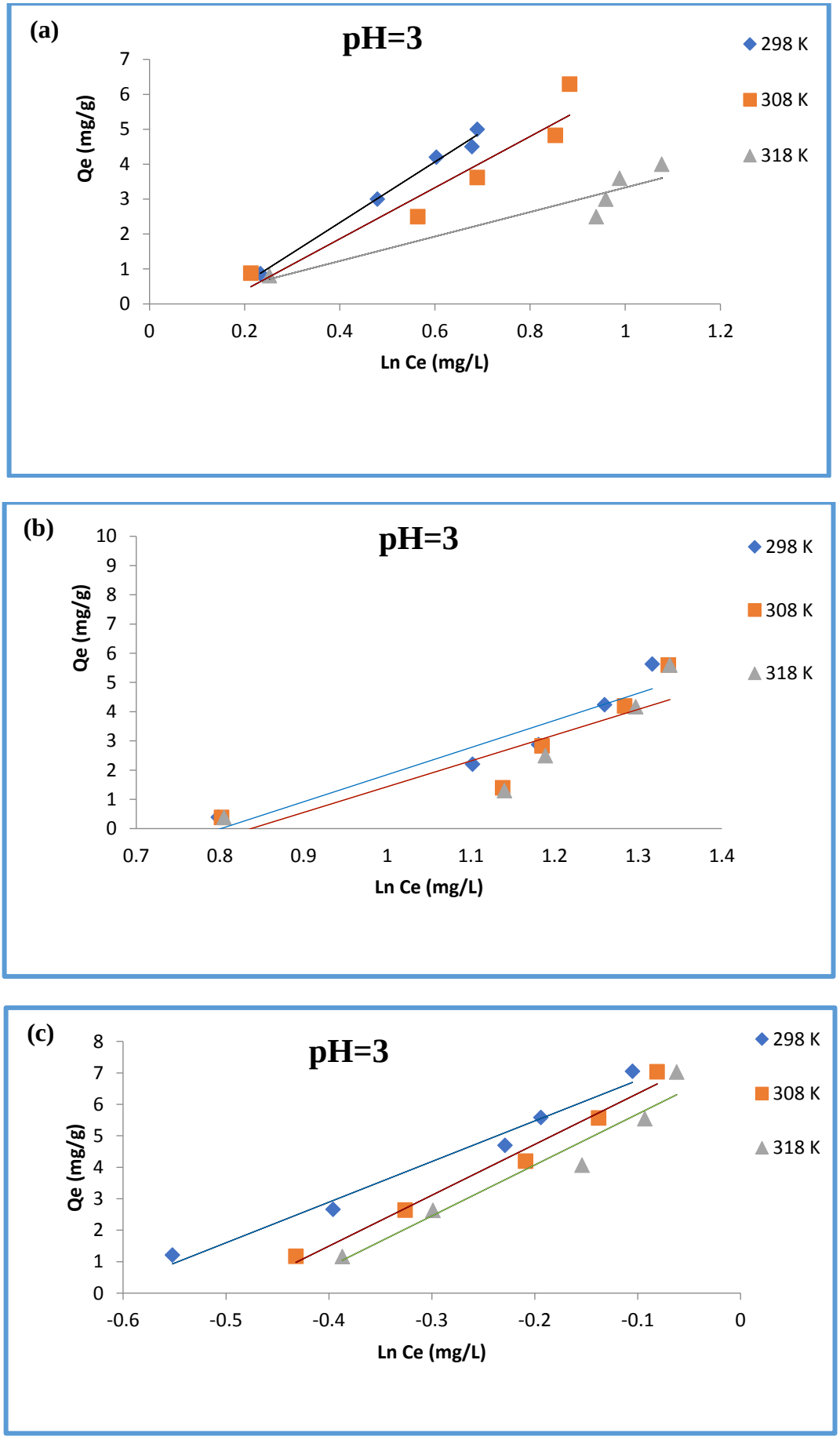


Fig. 12: Temkin isotherm for a) OP, b) SOP, c) CTAB-OP.

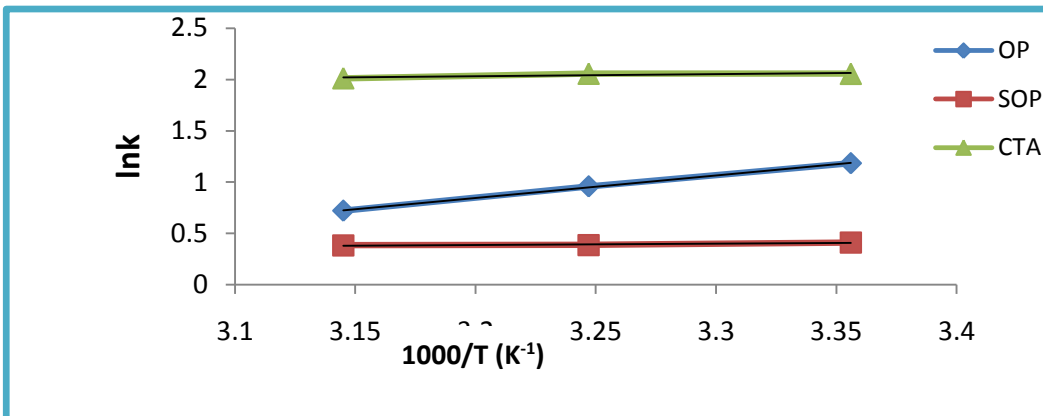


Fig. 13: Plot of Ln K against Reciprocal Absolute Temperature for adsorption of (EBT) Dye on OP, SOP and CTAB-OP Surfaces at Different Temperature

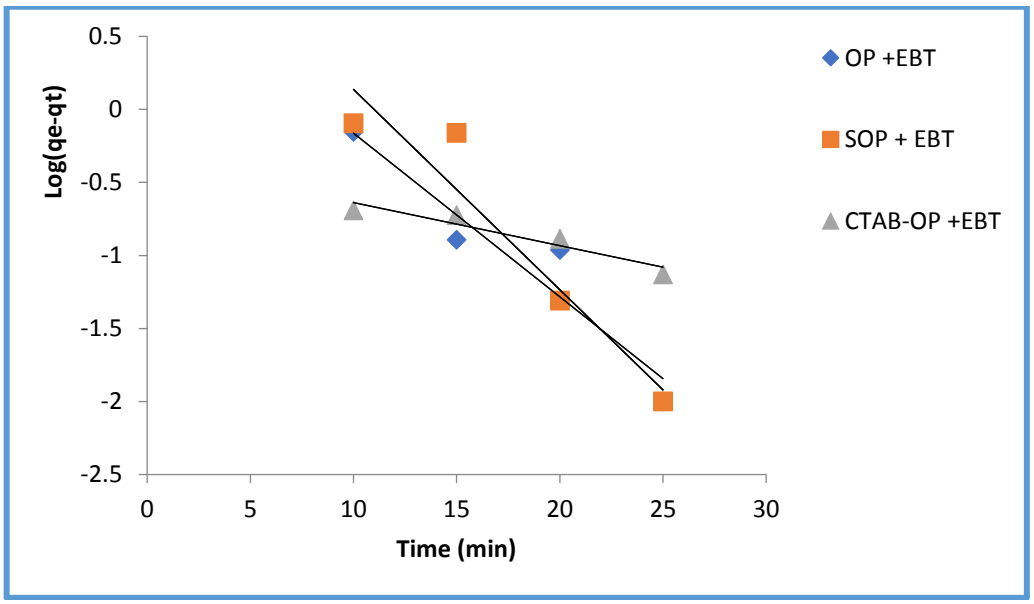


Fig. 14: Pseudo first-order model for adsorption of EBT dye on OP, SOP and CTAB-OP.

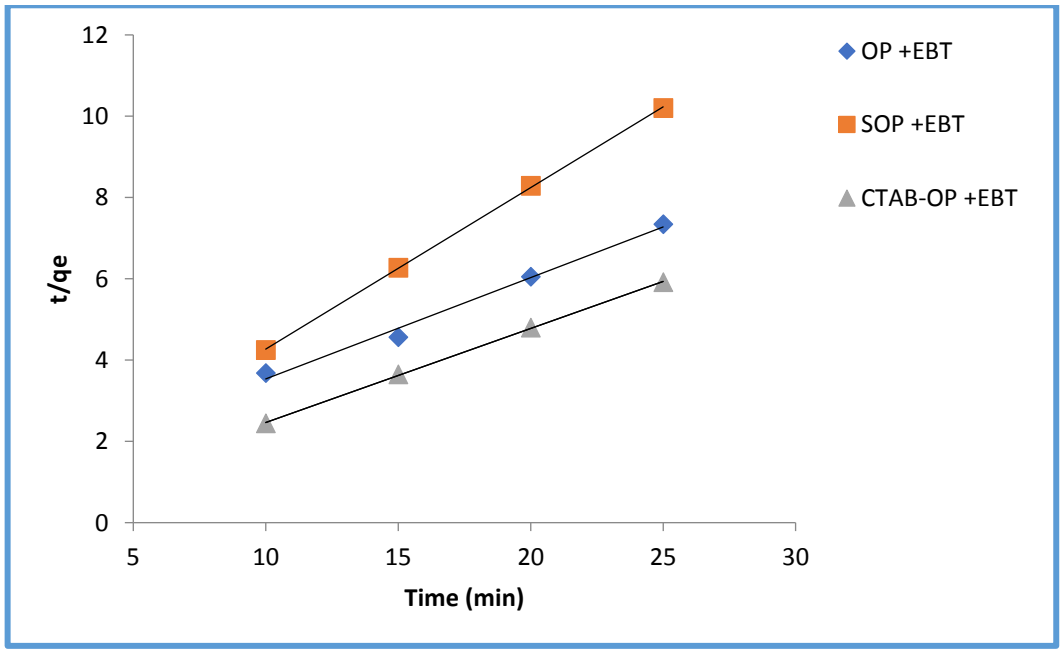


Fig. 15: Pseudo second-order model for adsorption EBT dye on OP, SOP and CTAB-OP.

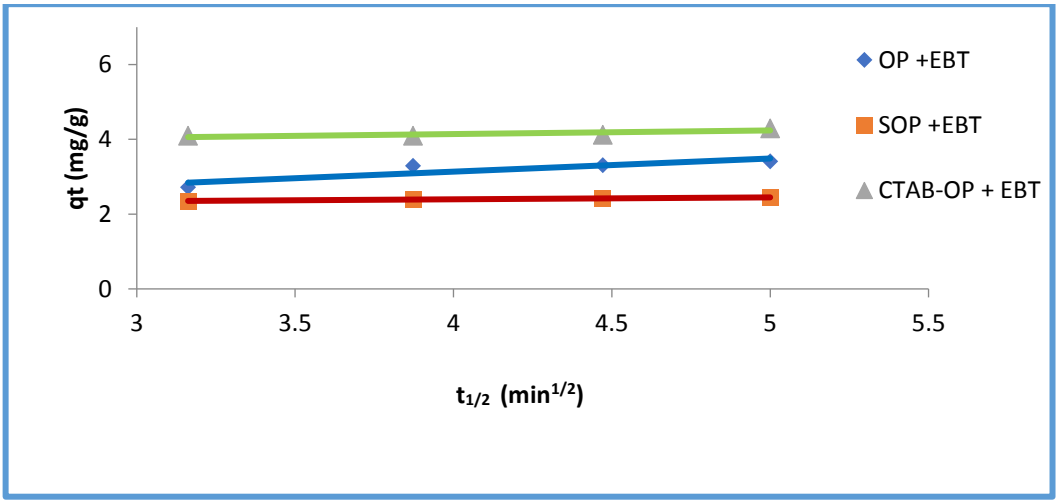


Fig. 16: Intraparticle diffusion model for adsorption EBT dye on OP, SOP and CTAB-OP

Conclusion

Cetyl trimethyl ammonium bromide (CTAB) is a cationic surfactant that has been used to increase the orange peel efficiency for removal of anionic dye (EBT dye) from aqueous solutions, thus the adsorption of EBT dye was highly adsorbed on CTAB-OP form. The higher percentage removal for EBT dye on OP, SOP and CTAB-OP surfaces at acidic media (pH=3) are 76, 65 and 96 for OP, SOP and CTAB –OP respectively. The type of adsorption was physiosorption and the adsorption data were found to fit Freundlich isotherm. EBT dye adsorption process on OP, SOP and CTAB-OP surfaces was exothermic and spontaneous. The adsorption kinetics of EBT dye on studied adsorbents followed pseudo-second order model.

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