Removal of Reactive Blue 19 dye from Aqueous Solution Using Natural and Modified Orange Peel

Sohair A. Sayed Ahmed*, Laila B. Khalil and Thoria El-Nabarawy

Department of Physical Chemistry, National Research Centre, Dokki, Cairo, Egypt

Article Info

Received 30 July 2012

Accepted 11 September 2012

*Corresponding Author

E-mail: sohairabdelaziz@yahoo.com

Tel: +2-0233371499

Open Access

DOI: <http://dx.doi.org/10.5714/CL.2012.13.4.212>

This is an Open Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

Abstract

Orange peel (OP) exhibits a sorption capacity towards anionic dyes such as reactive blue 19 (RB19). Cetyltrimethylammonium bromide (CTAB) as a cationic surfactant was used to modify the surface nature of OP to enhance its adsorption capacity for anionic dyes from an aqueous solution. Four adsorbents were investigated: the OP, sodium hydroxide-treated OP (SOP), CTAB-modified OP and CTAB-modified SOP. The physical and chemical properties of these sorbents were determined using nitrogen adsorption at 77 K and by scanning electron microscope and Fourier transform infrared spectroscopy techniques. The adsorption of the RB19 dye was assessed with these sorbents at different solution pH levels and temperatures. The effect of the contact time was considered to determine the order and rate constants of the adsorption process. The adsorption data were analyzed considering the Freundlich, Langmuir, Elovich and Temkin models. The adsorption of RB19 by the assessed sorbents is of the chemisorption type following pseudo-first-order kinetics. CTAB modification brought about a significant increase in RB19 adsorption, which was ascribed to the grafting of the sorbent with a cationic surfactant.

Key words: orange peel, cetyltrimethylammonium bromide modified orange peel, reactive blue 19, adsorption and kinetic studies

1. Introduction

Dyes are extensively used in various industries, particularly in the textile, paper, rubber, plastic, leather, cosmetics, food, and drug industries. Effluents from the dyeing and finishing processes in these industries are highly colored, and their discharge into rivers makes the water unfit for domestic, agricultural and industrial purposes. Dye wastewater discharged from various industries creates certain hazards and environmental problems. Recently, all governments have been under severe pressure by their people to stop this type of effluent into the public water courses unless it is treated properly. Some dyes are toxic, and the biodegradation of others yields carcinogenic products such as aromatic amines [1,2].

Activated carbons pollutants are commonly used for the removal of dyes from potable water and wastewater due to their high sorption capacities for organic and inorganic pollutants despite their high cost. Agricultural byproducts such as fruit peel have been used [3-6]. Extensive studies have been run to improve the sorption capacities of agricultural byproducts for dye removal via physical or chemical modification [7-10]. Reactive dyes are typically iso-based chromospheres combined with different types of reactive groups. They differ from other classes of dyes in that they bind to textile fibers such as cotton via the formation of covalent bonds. Thus, they are widely used compared to other dyes.

Various techniques have been employed for the removal of dyes from wastewater, including adsorption [11-14], photocatalytic degradation [15], electrokinetic coagulation [16],

<http://carbonlett.org>

pISSN: 1976-4251

eISSN: 2233-4998

Copyright © Korean Carbon Society

advanced chemical oxidation [17,18], ozonation [19], liquid-liquid extraction [20] and biological processes [21,22]. However, adsorption proved itself as the most feasible and efficient technique for the removal of dyes and other organic and inorganic pollutants from wastewater. Among the different sorbents, activated carbons have been reported to be the most efficient. Unfortunately, activated carbons are now expensive such that the trend is now to use agricultural byproducts as sorbents for dyes and other pollutants in potable and wastewater. To enhance the sorption capacities of agricultural byproducts, physical and/or chemical modifications are made [23,24]. Grafting of the sorbent surface with functional groups or surfactant molecules has been done [25,26]. However, less attention has been devoted to the use of surfactants to modify the surfaces of agricultural byproducts for dye adsorption purposes.

The aim of this work was to modify orange peel (OP) with a cationic surfactant (cetyltrimethylammonium bromide, CTAB) before or after the pretreatment of raw OP with sodium hydroxide (NaOH) to enhance the adsorption capacity of the by-product and to investigate the adsorption of reactive blue 19 (RB19) dye on it. The study includes a characterization of the adsorbents and the determination of the factors affecting the sorption, including the contact time, the temperature, and the pH. The adsorption data were analyzed using the Langmuir, Freundlich and Tempkin equations. The kinetic characteristics of adsorption were studied with pseudo first- and second-order equations, the Elovich equation, and the intraparticle diffusion model.

2. Materials and Methods

2.1. Adsorbent preparation

2.1.1. Raw OP

The OP was obtained from a local fruit field. It was cut into small pieces, washed several times with distilled water and dried at 70°C for 24 h. The product was then crushed and sieved through a screen to an average particle size of less than 0.5 mm and was designated as OP.

2.1.2. Chemical modification with sodium hydroxide

One hundred grams of dried OP was immersed in 1 L of NaOH for 24 h under occasional shaking. After decantation and filtration, this saponified product (NaOH-treated OP, SOP) was washed with distilled water until the pH of the filtrate reached 7.0.

2.1.3. Modification with cationic surfactant

Twenty grams of each sample (OP and SOP) was treated with 100 mL of CTAB, amounting to 1.24 g, approximately equivalent to a CMC value of 2.6×10^{-3} mol/L [27]. Preliminary experiments showed that the amount of CTAB that had been sorbed remained unchanged even after the sample had been shaken for more than 2 h. The sorbent-CTAB mixture was stirred for 30 min. using a mechanical stirrer. The CTAB-OP and CTAB-SOP were washed several times with distilled water until they were Br⁻-free, as indicated by an AgNO₃ test. The samples were then dried in an oven at 80°C.

Fig. 1. Chemical structure of anion RB19.

2.1.4. Preparation of RB19 dye

RB19 dye was used as an adsorbate in the form of a commercial salt, which is widely used in the textile industry. Its molecular formula is written as C₂₂H₁₆O₁₁N₂S₃Na₂ (mol.wt. 626.59 g/mol), the corresponding structure is illustrated in Fig. 1.

2.2. Techniques

2.2.1. Instruments used for adsorbent characterization

Nitrogen adsorption isotherms at 77 K were constructed using a conventional volumetric apparatus. The sample was degassed at 70°C for 6 h under a reduced pressure of 10⁻⁵ torr. The different types of functional groups were identified by Fourier transform infrared (FT-IR) spectroscopy in the range of 4000-400 cm⁻¹ using a Perkin Elmer Paragon 1000 FT-IR spectrometer (USA), and the KBr disc technique. Surface morphologies of the adsorbents were identified using a JOEL JSM device.

2.2.2. Adsorption of RB19

The batch sorption experiments were conducted by mixing adsorbent (0.2 g) with 50 mL of dye solutions at the desired concentrations (20-300 mg/L) in a 100 mL sealed conical flask using a shaking thermostat machine at a speed of 120 r/min for an equilibrium time of 24 h. The effect of the solution pH value on the equilibrium adsorption of the dye was investigated by mixing 0.2 g of sorbent with 50 mL of dye solution between pH values of 2.0-8.0. In the kinetic experiments, a sample of dry adsorbent (~0.5 g) was added to 300 mL of the aqueous adsorbate solution at an initial pH of 4.0 and a temperature of 30°C. The uptake of the adsorbate per unit mass of the sorbent was followed over time by withdrawing 2 mL of sample at fixed time intervals to determine the concentration at each time. C₀, C_e and C_t were measured spectrophotometrically at a wavelength of 590 nm with a Shimadzu model UV-Vis spectrophotometer.

The amount adsorbed at equilibrium q_e or at time (t) q_t was determined from the corresponding initial concentration using Eq. (1).

$$q_e \text{ or } q_t = \frac{(C_0 - C_e \text{ or } C_t)V}{m} \quad (1)$$

Where, C₀, C_e and C_t are the initial, equilibrium and concentration at time (t) (mg/L), respectively, V is the volume of the adsorption solution (L), and m is the mass of the sorbent (g).

Fig. 2. Fourier transform infrared spectroscopy spectra of OP, SOP, CTAB-OP and CTAB-SOP. OP: orange peel, SOP: sodium hydroxide-treated OP, CTAB: cetyltrimethylammonium bromide.

3. Results and Discussion

3.1. The chemistry of the surface of OP, SOP, CTAB-OP and CTAB-SOP

The chemistry of the adsorbent is equally important to its textural properties in determining the adsorption capacity of this adsorbent, particularly in the case of adsorption from a solution.

Infrared techniques have been used for the identification of adsorbents. Usually, the band at $3640\text{--}3510\text{ cm}^{-1}$ denotes the OH stretching of polymeric compounds. The band at $3000\text{--}2800\text{ cm}^{-1}$ is the stretching vibration of C-H. The band at $1740\text{--}1725\text{ cm}^{-1}$ is the stretching vibration of COO and C=O. The $1130\text{--}1000\text{ cm}^{-1}$ band is the vibration of C-O-C, C-O-P and O-H of the polysaccharides.

The FT-IR curves of OP, SOP, CTAB-OP and CTAB-SOP are shown in Fig. 2. This figure shows that some peaks disappeared after OP was pretreated with NaOH and that new peaks are observed after further cationic surfactant (CTAB) modification.

NaOH is good saponifying agent for the conversion of ester groups to carboxyl groups. It indicated the weakening intensity of the peak at 1744 cm^{-1} after the NaOH pretreatment, which can enhance the binding ability of the biomass. Fig. 2 also shows that the intensity of peaks 2926 cm^{-1} increased from 66 to 95.3 (44%) after modification of OP with CTAB and increased from 75.6 to 97.2 (29%) after modification of SOP with CTAB, indicating that the presence of the surfactant (CTAB) increases the number of $-\text{CH}_2-$ groups.

The scanning electron microscope (SEM) micrographs clearly reveal the surface texture. SEM micrographs of the OP, SOP, CTAB-OP and CTAB-SOP samples are shown in Fig. 3. The surface morphology of OP (Fig. 3a) is different from that of SOP (Fig. 3b). After being treated with NaOH, SOP has a more irregular and more porous structure than OP and therefore a larger surface area. The surface areas of OP and SOP were determined to be 4.28 and $6.82\text{ m}^2/\text{g}$ by the BET method. The surface morphology of the CTAB-OP and CTAB-SOP samples are rougher compared with the CTAB-free samples. Also, the surface areas of OP and SOP are smaller than those of CTAB-OP ($5.15\text{ m}^2/\text{g}$) and CTAB-SOP ($8.25\text{ m}^2/\text{g}$). The existence of the CTAB layer on the surface

Fig. 3. Scanning electron microscope images of (a) OP, (b) SOP, (c) CTAB-OP and (d) CTAB-SOP. OP: orange peel, SOP: sodium hydroxide-treated OP, CTAB: cetyltrimethylammonium bromide.

Fig. 4. Effect of the initial pH solution of RB19 on the equilibrium adsorption capacity of OP, SOP, CTAB-OP and CTAB-SOP ($C_0 = 100\text{ mg/L}$, temperature = 30°C , stirring rate = 100 rpm and $w = 0.2\text{ g}$). OP: orange peel, SOP: sodium hydroxide-treated OP, CTAB: cetyltrimethylammonium bromide.

of the biomass leads to these morphological changes. It can be seen that the surfaces on the surfactant-modified OP and SOP samples are more uneven than those of the OP and SOP samples, which indicates that CTAB is chemically bonded and/or physically adheres to the surface of OP. A similar result was reported with copolymer-grafted OP [28].

3.2. Effect of solution pH on dye uptake

Fig. 4 shows the effect of the pH on the removal of RB19 from an aqueous solution. The figure shows that the maximum removal of RB19 occurs at $\text{pH} = 4$. A trend similar to that of the pH effect was observed for the adsorption of DR28 and acid violet on activated carbon prepared from coir pith [29,30]

Fig. 5. Effect of the contact time on the uptake of RB19 at 30°C (pH = 4 and $w = 0.2$ g). OP: orange peel, SOP: sodium hydroxide-treated OP, CTAB: cetyltrimethylammonium bromide.

as well as for the adsorption of direct blue 2B and direct green B on activated carbon prepared from mahogany sawdust [31]. As the surfaces of OP and CTAB-OP are both positively charged at a low pH value, a significantly strong electrostatic attraction is expected with the negatively charged anion RB19. On the other hand, an increase of the pH value led to an increase in the number of negatively charged sites and a decrease in the number of positively charged sites. A negatively charged surface site on the OP or modified OP does not favor the adsorption of anion RB19 molecules due to electrostatic repulsion. Moreover, the decrease in the adsorption of anion RB19 with an increase in of the pH value is also due to the competition between the anionic dye and the excess OH ions in the solution. A pH of 4 was selected for the additional experiments.

3.3. Effect of the contact time and adsorption kinetics

Fig. 5 depicts the amount of RB19 removed by OP and its modified forms at 30°C and pH 4.0 as a function of the contact time. The figure shows that dye adsorption at the initial stages is quite rapid and then decreases with time, approaching a plateau. Evidently, equilibrium was attained after 30 min in the case of RB19 adsorption onto OP and SOP but after 60 min in case of the adsorption of the same dye onto CTAB-OP and CTAB-SOP,

indicating completely adsorbed monolayers.

Determination of order of the dye adsorption process and the rate constant were obtained by applying Lagergren's pseudo first-order kinetic model [32], a pseudo second-order kinetic model [33], the Elovich equation [34] and the intraparticle diffusion model [35]. The kinetic rate constants and the corresponding correlation coefficients R^2 are listed in Table 1.

The Lagergren equation reads

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (2)$$

where q_e and q_t (mg/g) are the amounts of the dye adsorbed at equilibrium and at time t , respectively, and where k_1 is the pseudo first-order rate constant (min^{-1}). Lagergren plots of RB19 sorption onto the biosorbents are shown in Fig. 6a. Table 1 lists the calculated results together with the corresponding values of R^2 , which were all ≥ 0.995 . The values of q_e as calculated from the Lagergren equation are generally equal to their experimental counterparts. This suggests that RB19 dye adsorption by the investigated sorbents follows pseudo first-order kinetics.

The pseudo second-order equation is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (3)$$

where q_e and q_t (mg/g) are the amounts adsorbed at equilibrium and at time t , respectively, and where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the pseudo second-order rate constant. The calculated values are listed in Table 1.

Inspection of Table 1 reveals that the values of R^2 obtained by applying the pseudo first- and pseudo second-order kinetic equations are comparable. However, the authors are more inclined to apply the pseudo first-order model because it gives calculated q_e values of the same order of magnitude as those determined experimentally.

The Elovich equation is another rate equation. It is expressed as

$$q_t = \alpha \ln(\alpha \beta) + \alpha \ln t, \quad (4)$$

where β is the initial adsorption rate mg (gmin)^{-1} and α is the desorption constant (gmin^{-1}). Elovich plots of RB19 adsorption on the investigated adsorbents are shown in Fig. 6b. The figure shows that the q_t versus $\ln t$ plots are linear, indicating the ap-

Table 1. Kinetic constants of adsorption RB19 onto OP, SOP, CTAB-OP and CTAB-SOP with the pseudo first-order and second-order kinetics, the Elovich equation and intraparticle diffusion models

Sample	Pseudo first-order				Pseudo second-order			Elovich model			Intraparticle diffusion	
	$q_e(\text{exp})$ (mg/g)	k_1 (L/min)	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	R^2	β (mg/g min)	α (g/mg)	R^2	k_{ad} (mg/g min ^{1/2})	R^2
OP	1.80	0.0212	1.32	0.9982	0.019	2.94	0.9976	0.483	3.49	0.9984	0.3530	0.9982
SOP	0.90	0.0237	1.1	0.9985	0.0389	1.69	0.9980	0.367	4.70	0.9989	0.2975	0.9969
CTAB-OP	37.5	0.0426	37.30	0.9978	0.0013	47.6	0.9970	10.66	0.073	0.9976	6.78	0.9987
CTAB-SOP	43.0	0.0133	44.7	0.9975	0.0011	48.6	0.9979	12.17	0.059	0.9979	8.67	0.9988

OP: orange peel, SOP: sodium hydroxide-treated OP, CTAB: cetyltrimethylammonium bromide.

Fig. 6. Linear plots of (a) kinetic first-order (b) Elovich model and (c) intraparticle diffusion of RB19 dye sorption at 30°C onto OP, SOP, CTAB-OP and CTAB-SOP. OP: orange peel, SOP: sodium hydroxide-treated OP, CTAB: cetyltrimethylammonium bromide.

plicability of the Elovich equation to the present adsorption system. Table 1 lists the values of α and β for each dye-adsorbent experiment, showing that the β values of the dye-CTAB-OP and dye-CTAB-SOP are higher than the values of β obtained from the OP and SOP sorbents. On the other hand, the desorption constants α of the CTAB-modified sorbent are lower than those of CTAB-free sorbents.

The mechanism of the diffusion of dye molecules during adsorption was studied considering the intraparticle diffusion model, which is expressed as

$$q_t = k_{id}t^{1/2}, \quad (5)$$

Fig. 7. Adsorption isotherms for RB19 onto OP, SOP, CTAB-OP and CTAB-SOP at pH = 4. OP: orange peel, SOP: sodium hydroxide-treated OP, CTAB: cetyltrimethylammonium bromide.

where k_{id} is the intraparticle diffusion rate constant ($\text{mg/gmin}^{1/2}$). Plots of q_t versus $t^{1/2}$ are shown in Fig. 6c. The values of k_{id} for the dye-adsorbent systems investigated are listed in Table 1.

Fig. 6c shows the initial curved portions followed by the linear portions. The initial curved portions of the plots refer to boundary layer diffusion, whereas the linear portions correspond to intraparticle diffusion. However, the linear portion does not pass through the origin, indicating that intraparticle diffusion is not the only process controlling dye sorption.

The values of k_{id} listed in Table 1 indicate that modification of OP with CTAB to give CTAB-OP resulted in a considerable increase in k_{id} from 0.2975 to 6.78, i.e., a nearly 23-fold increase. The same is also evident when the k_{id} values of CTAB-SOP and k_{id} of SOP are compared. k_{id} of the former = 8.67 and that of the latter = 0.353, referring to the modification of SOP with CTAB, is associated with a nearly 24.6-fold increase in the value of k_{id} . It appears that modification with CTAB of both OP and SOP resulted in generally the same increase in k_{id} .

3.4. Equilibrium adsorption modeling

We have already determined the appropriate pH value for the sorption of RB19 for the sorbents investigated here (pH = 4). It was also shown from the kinetic curves in Fig. 6 that beyond 100-120 min of contact, no significant increase in the sorption over time is observed. This equilibrium time is much shorter than that reported for the adsorption of dyes by activated carbons, as the latter contain a large fraction of the surface located on microspores [1].

Typical sorption isotherms of RB19 dye on the investigated sorbents at 313 K are shown in Fig. 7. These isotherms are typical type L isotherms according to the classification reported by Zheng et al. [2] for adsorption from dilute solutions. Three models were applied for the equilibrium data of RB19: the Langmuir, Freundlich and Tempkin models.

The Langmuir adsorption model [36] assumes that adsorption occurs at specific homogeneous adsorption sites within the adsorbent and that intermolecular forces decrease rapidly with the distance from the adsorption surface. The model is based on the assumption that all adsorption sites are energetically identical and that adsorption occurs on a structur-

Fig. 8. Representative (a) Langmuir plot, (b) Freundlich plot and (c) Tempkin plot of the adsorption of RB19 onto the investigated biomass samples. OP: orange peel, SOP: sodium hydroxide-treated OP, CTAB: cetyltrimethylammonium bromide.

ally homogenous adsorbent. The linear form of the Langmuir equation is written as

$$\frac{1}{q_e} = \frac{1}{K_L} + \frac{1}{K_L b} \cdot \frac{1}{C_e}, \quad (6)$$

where K_L is a parameter related to the maximum adsorption capacity (mg/g), q_e is the amount of dye sorbed at equilibrium per unit mass of sorbent, C_e is the equilibrium concentration of the dye in the solution (mg/L) and b is the equilibrium adsorption

Table 2. Langmuir, Freundlich and Tempkin model parameters for RB19 biosorption equilibrium on surfactant-modified OPs

model	biosorbents		CTAB-OP	CTAB-SOP
	OP	SOP		
Langmuir				
K _L	45.5	25.0	100.0	166.6
b	0.083	0.075	0.227	0.024
R ²	0.998	0.996	0.997	0.998
Freundlich				
K _F	2.85	6.68	24.5	44.7
1/n	0.54	0.46	0.38	0.38
R ²	0.875	0.814	0.941	0.932
Tempkin				
b	2509.5	434.3	130.9	125.9
A	0.812	0.596	2.55	9.9
R ²	0.998	0.996	0.999	0.999

OP: orange peel, SOP: sodium hydroxide-treated OP, CTAB: cetyltrimethylammonium bromide.

constant related to the energy of the adsorption (L/mg) Fig. 8a.

The Langmuir parameters and correlation coefficients of the experimental data are shown in Table 2. The values of R^2 are ≥ 0.997 , clearly indicating the excellent fitting of the adsorption data to Langmuir's model. The maximum uptake of RB19 by SOP is lower than that taken by OP. The alkaline saponification decreased the RB19 uptake, which may be ascribed to the conversion of the ester groups to carboxylic groups on the surface of OP.

The modification of OP and SOP by CTAB brought about a 2.2-fold increase in the dye uptake amount by OP, whereas a 6.66-fold increase occurred by SOP. The chemical modification mechanism of OP and SOP can be explained as follows. The cationic surfactant (CTAB) combined with cellulosic hydroxyl groups of OP to form an ester linkage and introduce $-CH_2-$ groups to the fiber. As expected, the cationized OP was effective in removing anionic dyes from an aqueous solution. This behavior may be attributed to coulombic attraction between the cationized cellulose and the anionic dyes, whereas coulombic repulsion could occur in the case of cellulose as a result of the partial negative charge developed on the surface in the aqueous solution [37].

Unmodified OP was previously used to remove different dyes from aqueous solutions [5,38-40]. The maximum capacity of dye removal (mg/g) is listed in Table 3. The maximum capacity (166.6 mg/g) obtained for CTAB-modified OP is higher than that obtained for unmodified OP.

The adsorption data was also analyzed by the Freundlich model. The Freundlich model [41] is given by the equation

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e, \quad (7)$$

Table 3. Reported maximum dye adsorption amounts obtained for orange peel

Dye name	Maximum adsorption (mg/g)	References
Congo red	22.44	[5,38]
Procion orange	1.33	[5]
Rhodamine B	3.23	[5,38]
Methyl violet	11.5	[38]
Black IOB	7.9	[38]
Methylene blue	18.6	[38]
Methyl orange	20.5	[38]
Direct red 23	10.72	[39,40]
Direct red 80	21.05	[39,40]

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), K_F is a constant related to the maximum amount adsorbed and $\frac{1}{n}$ is a measure of the binding energy between the sorbate molecule and the sorbent surface.

The applicability of the Freundlich sorption isotherm was also analyzed using the same set of experimental data by plotting $\ln q_e$ versus $\ln C_e$ (Fig. 8b). The data obtained from a linear Freundlich isotherm plot for the adsorption of the RB19 onto the investigated samples are given in Table 2. The correlation coefficients R^2 are less than 0.886, indicating less fitting of the adsorption data to the Freundlich model. This can be taken as evidence that the adsorption of RB19 by the investigated biosorbent is chemical adsorption.

Tempkin's adsorption model [42] was used to evaluate the adsorption potentials of the OP and its modified forms for RB19. Tempkin's equation suggests a linear decrease of the sorption energy as the degree of completion of the sorptional centers of an adsorbent is increased. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbent-adsorbate interactions. The adsorption is characterized by a uniform distribution of the binding energies up to some maximum. The Tempkin isotherm is generally applied in the following form:

$$q_e = \frac{RT}{b} \ln(A C_e)$$

It can be linearized as

$$q_e = \beta \ln A + \beta \ln C_e, \quad (8)$$

where $\beta = RT/b$, b is the Tempkin constant related to the heat of sorption (J/mol), A is the Tempkin isotherm constant (L/g), R is the gas constant (8.314 J/molK), and T is the absolute temperature (K). Therefore, plotting q_e versus $\ln C_e$ Fig. 8c enables one to determine the constants A and b , and the correlation coefficient, R^2 with the experimental data are listed in Table 2.

The correlation coefficients R^2 are clearly higher than 0.995, indicating excellent fitting of the dye adsorption data to the Tempkin model. The heat of RB19 adsorption onto OP and its modified forms was found to decrease from 2509.5 to 131 J/

mole to result in 434 to 126 J/mol for the CTAB-modified SOP. The R^2 values obtained are comparable to those calculated from the Langmuir isotherm. Regarding values of the heat of adsorption as determined from the Langmuir and Tempkin models, the values are considerably higher than 45 J/mole, suggesting that dye adsorption by the investigated sorbents is of a chemical nature.

3.5. Effect of temperature

The adsorption of RB19 by CTAB-OP and CTAB-SOP was assessed at 303, 313 and 333 K. The adsorption increased with the increase in the temperature from 303 to 313 K and then decreased with a further rise of the adsorption temperature from 313 to 333 K. This may be explained as follows. The increased adsorption by the CTAB-modified sorbents with the increased temperature from 303 to 313 K may be ascribed to the enhancement of the rate of diffusion of the dye molecules to the adsorption sites. A further increase of the temperature from 313 to 333 K may be sufficient to weaken the binding energy between the sorbent sites and sorbate molecules, thus resulting in a considerable decrease in the amount adsorbed, i.e., desorption.

4. Conclusions

OP, SOP, and their CTAB-modified forms were prepared and characterized for their physical and chemical properties using nitrogen adsorption at 77 K, SEM, and FT-IR. The adsorption of the anionic dye RB19 was highly adsorbed on CTAB-modified forms, particularly at pH 4. The adsorption was of the chemisorption type and the adsorption data followed the Langmuir and Tempkin models and followed pseudo first-order kinetics.

References

- [1] Boeniger MF. In carcinogenicity of azo dyes derived from benzidine, Department of Health and Human Services (NIOSH), Cincinnati, OH, Publication No. 8-119 (1980).
- [2] Zheng T, Holford TR, Mayne ST, Owens PH, Boyle P, Zhang B, Zhang YW, Zahm SH. Use of hair colouring products and breast cancer risk: a case-control study in Connecticut. *Eur J Cancer*, **38**, 1647 (2002). [http://dx.doi.org/10.1016/S0959-8049\(02\)00138-7](http://dx.doi.org/10.1016/S0959-8049(02)00138-7).
- [3] Robinson T, Chandran B, Nigam P. Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. *Water Res*, **36**, 2824 (2002). [http://dx.doi.org/10.1016/S0043-1354\(01\)00521-8](http://dx.doi.org/10.1016/S0043-1354(01)00521-8).
- [4] Sivaraj R, Namasivayam C, Kadirvelu K. Orange peel as an adsorbent in the removal of Acid violet 17 (acid dye) from aqueous solutions. *Waste Manage*, **21**, 105 (2001). [http://dx.doi.org/10.1016/S0956-053X\(00\)00076-3](http://dx.doi.org/10.1016/S0956-053X(00)00076-3).
- [5] Namasivayam C, Muniasamy N, Gayatri K, Rani M, Ranganaathan K. Removal of dyes from aqueous solutions by cellulosic waste orange peel. *Bioresour Technol*, **57**, 37 (1996). [http://dx.doi.org/10.1016/0960-8524\(96\)00044-2](http://dx.doi.org/10.1016/0960-8524(96)00044-2).
- [6] Hameed BH, Mahmoud DK, Ahmad AL. Sorption of basic dye from aqueous solution by pomelo (*Citrus grandis*) peel in a batch

- system. *Colloids Surf Physicochem Eng Aspects*, **316**, 78 (2008). <http://dx.doi.org/10.1016/j.colsurfa.2007.08.033>.
- [7] Gong R, Zhong K, Hu Y, Chen J, Zhu G. Thermochemical esterifying citric acid onto lignocellulose for enhancing methylene blue sorption capacity of rice straw. *J Environ Manage*, **88**, 875 (2008). <http://dx.doi.org/10.1016/j.jenvman.2007.04.004>.
- [8] Gong R, Sun J, Zhang D, Zhong K, Zhu G. Kinetics and thermodynamics of basic dye sorption on phosphoric acid esterifying soybean hull with solid phase preparation technique. *Bioresour Technol*, **99**, 4510 (2008). <http://dx.doi.org/10.1016/j.biortech.2007.08.061>.
- [9] Gong R, Zhu S, Zhang D, Chen J, Ni S, Guan R. Adsorption behavior of cationic dyes on citric acid esterifying wheat straw: kinetic and thermodynamic profile. *Desalination*, **230**, 220 (2008). <http://dx.doi.org/10.1016/j.desal.2007.12.002>.
- [10] Ong ST, Lee CK, Zainal Z. Removal of basic and reactive dyes using ethylenediamine modified rice hull. *Bioresour Technol*, **98**, 2792 (2007). <http://dx.doi.org/10.1016/j.biortech.2006.05.011>.
- [11] Valderrama C, Cortina JL, Farran A, Gamisans X, de las Heras FX. Evaluation of hyper-cross-linked polymeric sorbents (Macronet MN200 and MN300) on dye (Acid red 14) removal process. *React Funct Polym*, **68**, 679 (2008). <http://dx.doi.org/10.1016/j.reactfunctpolym.2007.11.005>.
- [12] Gomez V, Larrechi MS, Callao MP. Kinetic and adsorption study of acid dye removal using activated carbon. *Chemosphere*, **69**, 1151 (2007). <http://dx.doi.org/10.1016/j.chemosphere.2007.03.076>.
- [13] Pavan FA, Mazzocato AC, Gushikem Y. Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent. *Bioresour Technol*, **99**, 3162 (2008). <http://dx.doi.org/10.1016/j.biortech.2007.05.067>.
- [14] Cengiz S, Cavas L. Removal of methylene blue by invasive marine seaweed: *Caulerpa racemosa* var. *cylindracea*. *Bioresour Technol*, **99**, 2357 (2008). <http://dx.doi.org/10.1016/j.biortech.2007.05.011>.
- [15] Sleiman M, Vildoza D, Ferronato C, Chovelon JM. Photocatalytic degradation of azo dye Metanil Yellow: optimization and kinetic modeling using a chemometric approach. *Appl Catal B: Environ*, **77**, 1 (2007). <http://dx.doi.org/10.1016/j.apcatb.2007.06.015>.
- [16] Zidane F, Drogui P, Lekhlif B, Bensaid J, Blais JF, Belcadi S, kacemi KE. Decoloration of dye-containing effluent using mineral coagulants produced by electrocoagulation. *J Hazard Mater*, **155**, 153 (2008). <http://dx.doi.org/10.1016/j.jhazmat.2007.11.041>.
- [17] Sires I, Guivarch E, Oturan N, Oturan MA. Efficient removal of triphenylmethane dyes from aqueous medium by in situ electrogenerated Fenton's reagent at carbon-felt cathode. *Chemosphere*, **72**, 592 (2008). <http://dx.doi.org/10.1016/j.chemosphere.2008.03.010>.
- [18] Kim DS, Park YS. Comparison study of dyestuff wastewater treatment by the coupled photocatalytic oxidation and biofilm process. *Chem Eng J*, **139**, 256 (2008). <http://dx.doi.org/10.1016/j.cej.2007.07.095>.
- [19] Khadhraoui M, Trabelsi H, Ksibi M, Bouguerra S, Elleuch B. Discoloration and detoxification of a Congo red dye solution by means of ozone treatment for a possible water reuse. *J Hazard Mater*, **161**, 974 (2009). <http://dx.doi.org/10.1016/j.jhazmat.2008.04.060>.
- [20] Mahmoud AS, Ghaly AE, Brooks MS. Removal of dye from textile wastewater using plant oils under different pH and temperature conditions. *Am J Environ Sci*, **3**, 205 (2007). <http://dx.doi.org/10.3844/ajessp.2007.205.218>.
- [21] Sirianuntapiboon S, Sadahiro O, Salee P. Some properties of a granular activated carbon-sequencing batch reactor (GAC-SBR) system for treatment of textile wastewater containing direct dyes. *J Environ Manage*, **85**, 162 (2007). <http://dx.doi.org/10.1016/j.jenvman.2006.09.001>.
- [22] Isik M, Sponza DT. Anaerobic/aerobic treatment of a simulated textile wastewater. *Sep Purif Technol*, **60**, 64 (2008). <http://dx.doi.org/10.1016/j.seppur.2007.07.043>.
- [23] Attia AA, Shouman MA, Khedr SA, El-Nabarawy T. Removal of Cu(II) and Cd(II) ions onto water hyacinth based carbonaceous materials. *Carbon Lett*, **7**, 249 (2006).
- [24] El-Nabarawy T, Sayed Ahmed SA, Youssef AM. Removal of pesticide (oxamyl) from water using activated carbons developed from Apricot stones. *Carbon Lett*, **8**, 299 (2007).
- [25] Sayed Ahmed SA. Removal of toxic pollutants from aqueous solutions by adsorption onto organo-kaolin. *Carbon Lett*, **10**, 305 (2009).
- [26] Lugo-Lugo V, Hernandez-Lopez S, Barrera-Diaz C, Urena-Nunez F, Bilyeu B. A comparative study of natural, formaldehyde-treated and copolymer-grafted orange peel for Pb(II) adsorption under batch and continuous mode. *J Hazard Mater*, **161**, 1255 (2009). <http://dx.doi.org/10.1016/j.jhazmat.2008.04.087>.
- [27] Liao WS, Bi ZC. Adsorption and interfacial properties of the cationic gemini surfactant of ethanediyl- α,β -bis(cetyldimethylammonium bromide). *Adsorpt Sci Technol*, **21**, 697 (2003). <http://dx.doi.org/10.1260/026361703773581768>.
- [28] Feng N, Guo X, Liang S. Adsorption study of copper (II) by chemically modified orange peel. *J Hazard Mater*, **164**, 1286 (2009). <http://dx.doi.org/10.1016/j.jhazmat.2008.09.096>.
- [29] Namasivayam C, Kavitha D. Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dyes Pigments*, **54**, 47 (2002). [http://dx.doi.org/10.1016/S0143-7208\(02\)00025-6](http://dx.doi.org/10.1016/S0143-7208(02)00025-6).
- [30] Namasivayam C, Radhika R, Suba S. Uptake of dyes by a promising locally available agricultural solid waste: coir pith. *Waste Manage (Oxford)*, **21**, 381 (2001). [http://dx.doi.org/10.1016/S0956-053X\(00\)00081-7](http://dx.doi.org/10.1016/S0956-053X(00)00081-7).
- [31] Malik PK. Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. *J Hazard Mater*, **113**, 81 (2004). <http://dx.doi.org/10.1016/j.jhazmat.2004.05.022>.
- [32] Lagergren S, Svenska BK. Zur theorie der sagenannten adsorption geloeester stoffe. *Vaternska psakad Handlingar*, **24**, 1 (1898).
- [33] Ho YS, McKay G. Sorption of dye from aqueous solution by peat. *Chem Eng J*, **70**, 115 (1998). [http://dx.doi.org/10.1016/S0923-0467\(98\)00076-1](http://dx.doi.org/10.1016/S0923-0467(98)00076-1).
- [34] Ho YS, McKay G. Application of kinetic models to the sorption of copper(II) on to peat. *Adsorpt Sci Technol*, **20**, 797 (2002). <http://dx.doi.org/10.1260/026361702321104282>.
- [35] Weber WJ, Marris JC. Kinetics of adsorption on carbon from solution. *J Sanit Eng Div*, **89**, 31 (1963).
- [36] Annadurai G, Chellapandian M, Krishnan MRV. Adsorption of reactive dye on chitin. *Environ Monit Assess*, **59**, 111 (1999). <http://dx.doi.org/10.1023/a:1006072119624>.
- [37] McKay G, El Geundi M, Nassar MM. Equilibrium studies during the removal of dyestuffs from aqueous solutions using Bagasse pith. *Water Res*, **21**, 1513 (1987). [http://dx.doi.org/10.1016/0043-1354\(87\)90135-7](http://dx.doi.org/10.1016/0043-1354(87)90135-7).
- [38] Annadurai G, Juang RS, Lee DJ. Use of cellulose-based wastes for

- adsorption of dyes from aqueous solutions. *J Hazard Mater*, **92**, 263 (2002). [http://dx.doi.org/10.1016/S0304-3894\(02\)00017-1](http://dx.doi.org/10.1016/S0304-3894(02)00017-1).
- [39] Arami M, Limaee NY, Mahmoodi NM, Tabrizi NS. Removal of dyes from colored textile wastewater by orange peel adsorbent: equilibrium and kinetic studies. *J Colloid Interface Sci*, **288**, 371 (2005). <http://dx.doi.org/10.1016/j.jcis.2005.03.020>.
- [40] Doulati Ardejani F, Badii K, Yousefi Limaee N, Mahmoodi NM, Arami M, Shafaei SZ, Mirhabibi AR. Numerical modelling and laboratory studies on the removal of Direct Red 23 and Direct Red 80 dyes from textile effluents using orange peel, a low-cost adsorbent. *Dyes Pigments*, **73**, 178 (2007). <http://dx.doi.org/10.1016/j.dyepig.2005.11.011>.
- [41] Allen SJ, McKay G, Khader KYH. Equilibrium adsorption isotherms for basic dyes onto lignite. *J Chem Technol Biotechnol*, **45**, 291 (1989). <http://dx.doi.org/10.1002/jctb.280450406>.
- [42] Tempkin MT, Pyzhev V. Recent modifications to Langmuir isotherms. *Acta Physiochim USSR*, **12**, 217 (1940).