Modified Waste Materials for Removal of Cationic Dye from Liquid Effluents and Their Kinetic Studies

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IN the present paper, natural adsorbents such as starch, sawdust (collected from a local sawmill) and orange peel were grafted in order to remove C.I. Basic Blue 41 (BB 41) from aqueous solution by adsorption. Batch mode experiments were conducted at 30ºC to study the effects of pH, adsorbent mass and contact time (0-240 min). Equilibrium adsorption isotherms and kinetics were investigated. The experimental adsorption data were analyzed by the Langmuir and Freundlich isotherms. The results showed that adsorption capacity is dependent on the pH, initial concentration of dye and contact time. Changes in the surface chemical groups in the adsorbent starch, orange peel and sawdust waste materials were investigated via Fourier transform infrared (FTIR). In the case of starch and sawdust the OH group after grafting is reduced while the carboxylic group is increased and vice versa after adsorption of a dye, indicating that the adsorption of dye is occurred between carboxylic groups and cationic group in basic dye. But in the case of orange peel the result is conversely. Equilibrium isotherms were well described by the Langmuir equation, giving maximum adsorption capacity of 19.2 mg/g by sawdust adsorbent at 30ºC. The adsorption kinetics can be well represented by the pseudo-second-order model equation.

Keywords: Starch, Orange peel and sawdust, Basic blue, Adsorption isotherm, Equilibrium and Kinetics.

The removal of dye from textile effluents is one of the most significant environmental problems. Dyes are used widely in modern industrial society. Since they have a synthetic origin and complex aromatic molecular structures which make them inert and difficult to biodegrade when discharged into waste streams. Also, many dyes and their break down products may be toxic for living organism. So, the removal of dyes and organics from water in an economical way remains an important problem. There is no general method for the removal of color from dye wastewater[1, 2]. Many treatment methods have been adopted to remove dyes from wastewater, which can be divided into physical, chemical, and biological methods[3]. Processes such as membrane separation, coagulation and ion exchange are also used for the removal of color from dye waste water, but the cost of the process is the main drawback of these techniques[4]. A number of non-conventional low cost adsorbents used for dye removal, includes fruit waste of Prosopisn juliflora, sawdust, waste orange peel, banana pith and maze cobs. The ability of coconut bunch waste, an agricultural waste available in large

quantity in Malaysia, to remove basic dye (methylene blue) from aqueous solution by adsorption was studied[5]. A batch sorption system using tree fern as biosorbent was investigated to remove Basic Red 13 from aqueous solutions[6]. Papaya seed (PS) was modified using chemically esterification of carboxyl group to improve performance in adsorption capacity for removal of cationic and anionic dye from aqueous solution[7]. The feasibility of quartenised sugar cane bagasse as an adsorbent for the removal of a cationic dye and an anionic dye from single and binary dye solutions was investigated[8]. On the other hand, the chemical modification of Ficus carica fiber was done with acrylic acid using ceric ammonium nitrate as initiator to change the surface morphology of the natural fibers for the improvement of interfacial adhesion between matrix and fibers to remove a hazardous methyl orange dye from aqueous system[9]. Activated carbon prepared from a sadiracted (neem) Seed Hull was used for removal of Rhodamine–B dye from aqueous solution[10]. Sawdust possesses porous structures consisting of various cell walls, which are mainly composed of biopolymers, *i.e.*, carbohydrate polymers of cellulose and hemicelluloses and phenolic polymers of lignin. The cellular structure of sawdust endows it with high strength-to weight ratio. Because of this, some high-quality sawdust can be used as structural materials, besides, as the most abundant functional group in sawdust cell walls is the hydroxyl group[11]. Many efforts have been made to investigate the use of various low cost organic adsorbents, so the aim of the present study was to prepare natural adsorbent such as starch, sawdust and orange peel by grafting with acrylic acid (30%OWS) and potassium bromate/thiourea (6mmole/100g substrate) as redox system to use it as a removal of C.I. Basic Blue 41, from the effluent solution at temperature 30°C.

Experimantal

Materials and methods

   C.I. Basic Blue 41 (BB 41) was supplied from Dongwu Dyestuff Co. Ltd. (China). Molecular Formula: $C_{20}H_{26}N_4O_6S_2/C_{21}H_{27}ClN_4O_3S$. Molecular Weight: 482.57/450.98 .Cationic dyes are more toxic than anionic dyes and the structure is shown in Fig. 1 [12].
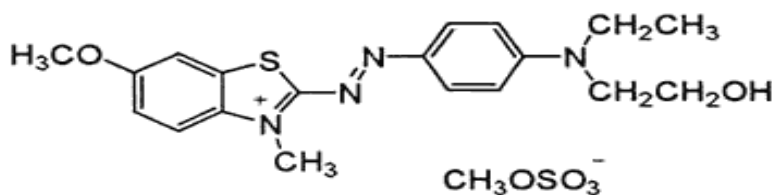

Fig. 1. Molecular structure of C.I. Basic Blue 41 (BB 41).

Egyptian native maize starch supplied by the Egyptian Starch and Glucose Manufacturing Company, Cairo Egypt, sawdust collected from a local sawmill and orange peels. Acrylic acid, thiourea, potassium bromated, sodium hydroxide and sulfuric acid were all laboratory grade reagents.

Preparation and characterization of adsorbent
Preparation of grafted adsorbent

Orange peel and sawdust are washed and grind, 50g of (starch, sawdust and orange peel) was put into glass vessel containing 60 ml distilled water followed by gradual addition of alkali solution with concentration of 25mmole/100g substrate. The reaction vessel was then placed in a thermostatic water bath at 50°C for 30 min under mechanical stirring; the pH of the reaction medium was turned to the neutral by addition of dilute sulfuric acid. This was followed by subsequent addition of potassium bromated solution (6m.mole/100g substrate), acrylic acid 30% (OWS) and thiourea (6m.mole/100g substrate). The whole course of grafting was carried out under constant stirring, temperature 50^0C for 1 hr at liquor ratio 1:2.5.

Measurements
Infrared spectral analysis

Using (FT/IR−4100, Jasco, Japan) spectrometer, the structure and bond formation of the samples were confirmed. All spectra were recorded in the range (4000–400 cm^{-1}), the number of scans was 32, and the resolution was 4 cm^{-1} and scan speed 2mm /s. The KBr technique was used.

Adsorption studies of C.I. Basic Blue 41 (BB 41)

To assess the adsorption capacity of the prepared resins for removing C.I. Basic Blue 41 (BB 41) as shown in Fig. 1**,** the batch experiments were undertaken at the optimum pH 9 and room temperature at 30°C. A dye stock solution of 1000 mg/L was prepared by dissolving 1 g in 1L distilled water for subsequent adsorption experiment. Initial concentrations from 50 to 200 mg/L of the dye were prepared by serial dilution of the stock solution. The equilibrium studies were performed by shaking 100 ml of known initial concentrations of a dye with 0.1 g of each resin in 250 ml conical flaks for 4 hr.

The effect of initial solution pH value ranging from 2 to 11 on the removal of Basic Blue 41 (BB 41) was studied by mixing 100 ml of 100mg/L dye solution with 0.1 g of adsorbent sample in various flasks of different pH values at 30°C. The required pH value was adjusted by drop-wise addition of 0.1M of NaOH or HCl solution and recorded using pH meter. The flasks tested pH solutions were then covered with rubber caps and placed on a shaker at a fixed agitation speed of 200 rpm for 4 hr. In addition the effect of resin dose was studied by conducting 0.25, 0.5, 1 and 2 g per 100 ml of 100 mg/L dye solution. The kinetic studies of basic blue dye 41 adsorbed by the herby resins were investigated by withdrawing aliquots of the solution containing 100 mg/L dye (0.1g adsorbent/100

ml) after desired contact time (0-240 min) and then measured the absorbance of residual concentration of dye studied.

The concentrations of the dye before and after adsorption were estimated by using a Janway 6405 UV-VIS spectrophotometer, U.K., at a maximum wavelength of 480 nm. The amounts of the adsorbed dye at equilibrium (q_e, mg/g) and at time t (q_t, mg/g) were calculated using equations 1 and 2 as follows:

$$q_e = \frac{(C_0 - C_e)}{m} V \qquad (1)$$

$$q_t = \frac{(C_0 - C_t)}{m} V \qquad (2)$$

where C_0, C_e, and C_t are the liquid-phase concentrations (mg/L) of dye at initial, equilibrium and time t, respectively. V is the volume of solution (L) and m is the mass of dried resins (g). In order to assess the reproducibility and error of the experimental results, all the absorbance measurements were performed in triplicate runs. It was found that the relative standard deviations are about ±3 %.

Results and Discussion

*Investigation of principal surface groups by FTIR*

Figure 2 shows the assigned of the main components from native starch and grafted starch and starch adsorbed dye at equilibrium and differences between them can be detected by FTIR. A strong broad band of OH stretching vibration at 3431 cm⁻¹ its intensity decreased in grafted starch. It is evidenced an increase in the intensity band of OH in starch adsorbed dye at equilibrium and became brooded and shifted to higher wavenumber at 3447 cm⁻¹. The carbonyl absorption band at 1732 cm⁻¹ (C=O) is increased in grafted starch than that native and adsorbed starch. The absorption peak at 2928 cm⁻¹ was attributed to the C−H stretching vibration of carbohydrates; the peak at 1732 cm⁻¹ corresponded to the C=O stretching vibration, indicating the presence of an acetyl group in starch. The absorption peak at 1649 cm⁻¹ corresponded to the C=O stretching vibration within –CHO, the peaks at 1460 and 1425 cm⁻¹ were attributed to the C−O−C plane bending vibration and the peak at 1380 cm⁻¹ was ascribed to the O−H bending vibration. In addition, starch adsorbed dye has new band at 1581 cm⁻¹. The band at 1158 cm⁻¹ was attributed to the asymmetric C−O−C stretching vibration, indicating the presence of −O−CH₃, and in the region between 1200 and 900 cm⁻¹, several strong absorption peaks assigned to the C–C and C–O stretching modes appeared [13].
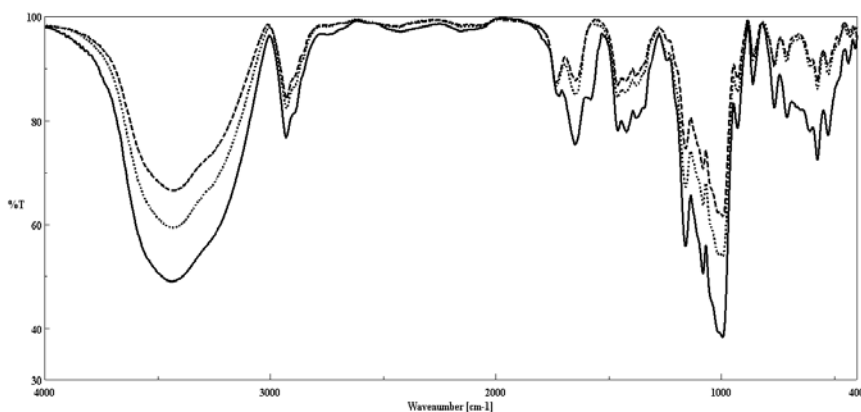
Fig. 2. FTIR spectra of investigated adsorbents .
**....   native starch   ------- grafted starch   — starch adsorbed dye**

Figure 3 shows the FTIR spectra of sawdust, grafted sawdust and sawdust adsorbed dye at equilibrium. Clear differences can be detected in the infrared spectra. A decrease in the intensity of the O–H band at 3442 cm^{-1} was observed in the grafted sawdust and then shifted to a lower wavenumber at 3435 cm^{-1}, and became sharp and increased its intensity in sawdust adsorbed dye at equilibrium. On the other hand, the intensity of carbonyl absorption band at 1735 cm^{-1} (C=O) increased in sawdust after grafted than another one[14].
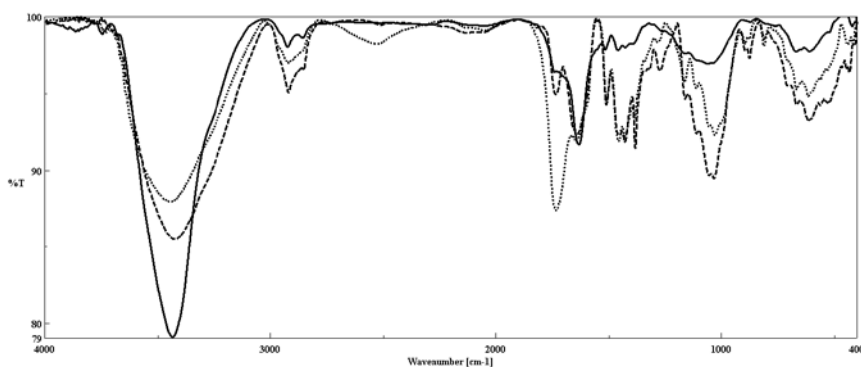
Fig. 3. FTIR spectra of investigated adsorbents .
------- sawdust ……. grafted sawdust   — sawdust adsorbed dye

The FTIR spectrum of the orange peel is shown in Fig. 4, the broad and intense absorption peaks around 3423 cm^{-1} are indicative of the absorption of water molecules, resulting from the O–H stretching mode of hydroxyl groups which is a characteristic of adsorbed water. Generally, the increase in OH and carboxyl groups (– COOH) follows the order: orange peel > grafted orange > orange adsorbed dye at equilibrium, respectively [15-20].
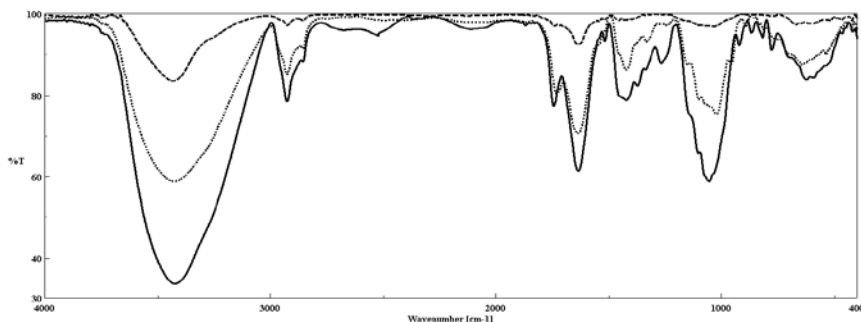
Fig. 4. FTIR spectra of investigated adsorbents .
——— orange   ……. grafted orange   -------- orange adsorbed dye

Effect of pH

The change in pH of dye solution affects the surface charges of adsorbents which lead to variation in the degree of ionization of the adsorptive molecule and hence the surface properties of adsorbents. Adsorption of various anionic and cationic species on such adsorbents has been explained on the basis of the competitive adsorption of H^+ and OH^- ions with the adsorbate[21]. It is a common observation that the surface adsorbs anions favorably at lower pH due to the presence of H^+ ions whereas; the surface is active for the adsorption of cations at higher pH due to adsorption of OH^- ions[22]. Figure 5 shows the adsorbed amounts of dye by grafted natural adsorbents under different pH of dye solution. A lower adsorbed amount was found at pH 2 (acidic medium) while the higher amount occurred at pH 9 (basic media), attaining a constant removal at pH 11. This trend may be ascribed to the occurrence of electrostatic interaction resulting in the increase in negative surface charges of the adsorbent and the basic blue dye adsorbate. Also, it was found that the sawdust resin showed the highest adsorption of dye at pH 9.
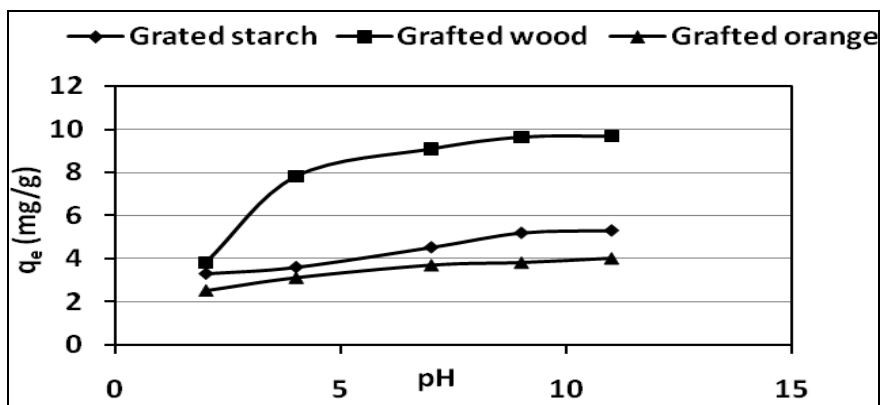
Fig. 5. Influence of pH on removal of C.I. Basic Blue 41 (BB 41) .
Conditions: sorbent dosage 0.1 g/100 ml, temperature 30 °C, 200 rpm for 4 hr

Effect of resin dose

The amount of adsorbent represents an important parameter due to its strong effect on the capacity of an adsorbent at a given initial concentration of the adsorbate (100 mg/L). Figure 6 expresses the effect of adsorbent dosage on the removal of basic blue dye. This figure reveals that the adsorbed amount was decreased with increasing the grafted natural adsorbents dose from 0.25 up to 2 g/100 ml. Thus the higher adsorbed amount of dye was found with 0.25g resin/100ml dye solution, although the other adsorption experiments were carried out with 1 g resin/100 ml dye solution. The decrease in amount of dye adsorbed, q_e (mg/g) with increasing adsorbent mass, is due to the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the adsorbent[23].
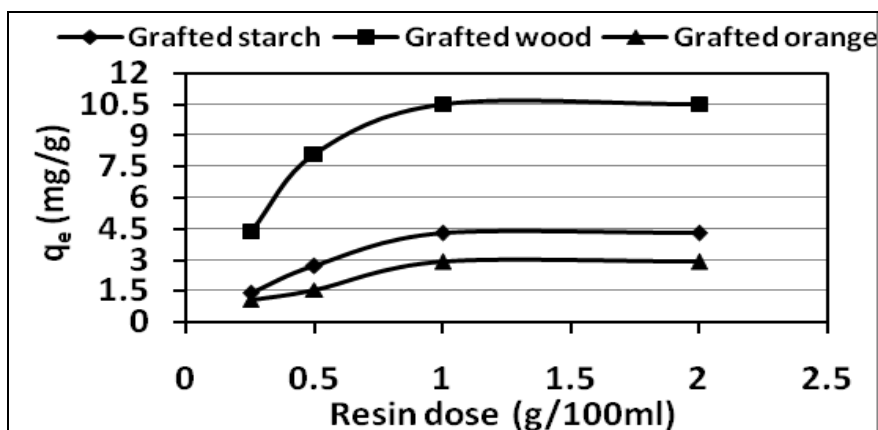

Fig. 6. Influence of resin dose on adsorbed amount of dye .
Conditions: sorbent dosage 0.1 g/100 ml, temperature 30 °C, 200 rpm for 4 hr, ph 9

Effect of contact time

The effect of contact time on the adsorption of basic blue dye was investigated at different initial dye concentration onto pine cone adsorbent, and results are presented in Fig. 7. It was also found that the amount of adsorption, *i.e.* milligrams of adsorbate per gram of adsorbent, increases with increasing contact time at an initial dye concentration of 100 mg/L, and equilibrium is attained within 120 min. The removal of dye by adsorption on grafted natural adsorbents is very fast at the initial period of contact but slowed down with time. This kinetic experiment clearly showed that the adsorption of C.I. Basic Blue 41 (BB 41) dye on grafted natural adsorbents is a more or less two step process: a very rapid adsorption of dye to the external surface followed by possible slow intraparticle diffusion in the interior of the adsorbent with increasing in the time. Generally, the rapid kinetics have significant practical importance, as it facilitates smaller reactor volumes, ensuring high efficiency and economy.
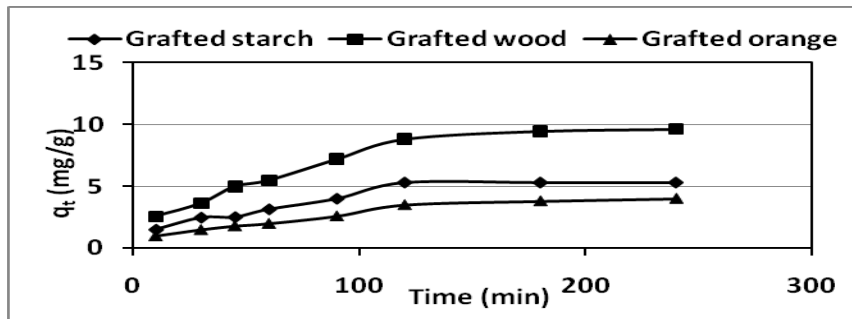
Fig. 7. Influence of contact time on the adsorption of dye .
Conditions: time 0-120 min., pH 9, temperature 30 °C, 200 rpm for 4 hr

Adsorption isotherm models

The Langmuir and Freundlich isotherm models were employed for fitting the experimental data. The Langmuir model describes the assumption that the surface of the sorbent is totally homogeneous, whereas the Freundlich isotherm is suitable for a highly heterogeneous surface.

The linear form of the Langmuir isotherms:

$$C_e / q_e = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \qquad (3)$$

where q_m is the maximum amount adsorbed assumed to be the monolayer adsorption capacity, both expressed in (mg.g^{-1}) and K_L is the Langmuir constant (mg.L^{-1}) relating to the free energy of sorption as expressed ($K_L \, \alpha \, e^{-\Delta G/RT}$).

Thus the free energy of adsorption, ΔG (kJ.mol^{-1}) can also be evaluated from the parameter K_L according to the expression; $\Delta G = -RT \ln K_L$. The linear form of the Freundlich equation is given as:

$$Ln \, q_e = ln \, K_F + 1/n \, ln \, C_e \qquad (4)$$

where K_F is the Freundlich constant related to the adsorption capacity, in which 1/n is a constant related to the adsorption strength, *i.e.*, the adsorbent- adsorbate interaction. In addition the essential features of Langmuir adsorption isotherm can be expressed in terms of a dimensionless separation factor (R_L), which is given by equation:

$$R_L = \frac{1}{1 + C_0 K_L} \qquad (5)$$

where C_0 is the initial metal ions concentration (mg/l). The R_L value indicates the shape of the isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable isotherm ($R_L > 1$). Also, R_L values are represented in Table 1, which confirmed that the prepared carbons are highly favorable for adsorption of basic dye from wastewater under the reported conditions used in this study. Moreover, the negative value of Gibbs free energy ($\Delta G^o = -22.5$ to -29.4 kJ.mol^{-1}) confirms the feasibility and spontaneous nature of the adsorption of this dye onto the tested resins. Parameters of Langmuir and Freundlich models and their corresponding regression coefficients (r^2) are listed in Table 1. Figure 8 shows the adsorption isotherms of a Basic Blue 41 (BB 41) onto the grafted resins, representing L-type of adsorption isotherm. In the range of tested initial concentrations, Langmuir ($r^2 = 0.959$-0.999) and Freundlich models ($r^2 = 0.940$-0.972) fit the adsorption data well. The maximum adsorption capacity values for dye adsorbed onto the tested grafted natural adsorbents; Starch, Sawdust and Orange were 7.85, 19.2 and 4.90 mg.g^{-1}, respectively (Table 1).
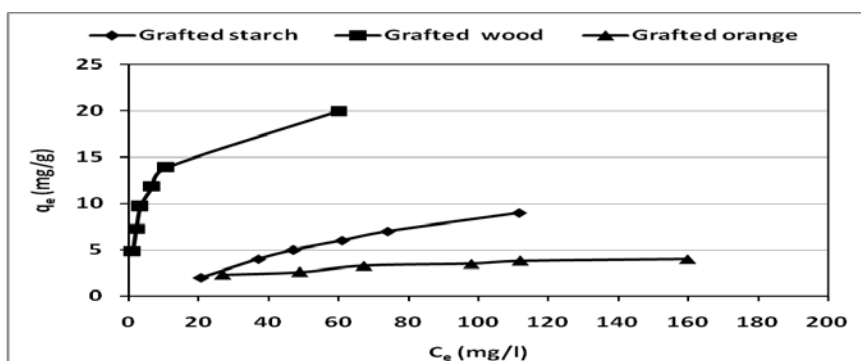

Fig. 8. Adsorption isotherms of BB41 dye onto the adsorbent grafted natural adsorbents .

TABLE 1. Parameters calculated from Langmuir and Freundlich isotherm models for adsorption of basic blue dye onto the prepared grafted natural adsorbents.

Equilibrium models	Grafted natural adsorbents		
	Grafted Starch	**Grafted sawdust**	**Grafted Orange**
Langmuir q_m *(mg.g^{-1})* K_L *(L.mg^{-1})* R_L ΔG^o *(kJ.mol^{-1})* r^2	7.58 0.0176 0.811 - 22.5 0.959	19.2 0.2756 0.411 -29.4 0.999	4.90 0.0281 0.637 -23.7 0.990
Freundlich K_F *(mg.g^{-1} (L/mg)$^{-1/n}$)* *1/n* r^2	0.212 0.802 0.972	5.31 0.377 0.940	1.30 0.330 0.953

Kinetics of adsorption

The adsorption kinetic process is largely dependent on the physical and/or chemical characteristics of both the adsorbent and adsorbate[24- 27]. Figure 9 shows the controlling mechanism in the adsorption of the basic blue 41 (BB41) with initial concentration of 100 mg/L at 30°C examined using various kinetic models such as pseudo-first order, pseudo-second order and Elovich models in order to determine whether the process is such as mass transfer and/or chemical reaction were evolved:

$$log \ (q_e - q_t) = log \ q_e - \frac{k_1 t}{2.303} \qquad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

where q_e and q_t are the amounts of solute adsorbed at equilibrium and at a time mg/g, respectively, k_1 is the pseudo-first order sorption rate constant (min^{-1}), and k_2 is the pseudo-second order sorption rate constant (g. mg^{-1} min^{-1}). In a further attempt to study the nature of sorption, another equation, namely, Elovich equation, normally applicable to chemisorption on energetically heterogeneous solid surface, and given by:

$$q_t = \beta \ ln \ (\alpha \beta) + \beta \ ln \ t \qquad (8)$$

where α and β, respectively the initial adsorption rate (mg. g^{-1}min^{-1}) and the desorption coefficients (g. mg^{-1}), respectively. These can be computed from plots of q_t versus *ln t*. The calculated values of model parameters are given in Table 2. The regression coefficients of the linear form of model (r^2), which are a measure of goodness of fit in Table 2, indicate that the pseudo-first-order model (r^2= 0.962-0.987) more frequently describes the adsorption data with the pseudo-second-order model (r^2= 0.919-0.972). Calculated q_e values from pseudo-first order showed good consistency with the detected values in experiment (5.3, 9.8 and 4.5 mg/g, respectively).

The values of α and β and the corresponding R^2 are listed in Table 2. Evidently the Elovich plots are non-linear with values of R^2=0.897 to 0.939. The initial rate of adsorption (α) of sawdust resin was higher than those of other resins. On the other hand, the corresponding desorption rate coefficient values ($\beta)$ are lower than α values. This confirms that the adsorption of the dye on the resin was held at energetically uniform sites, and perhaps at chemically different sites.
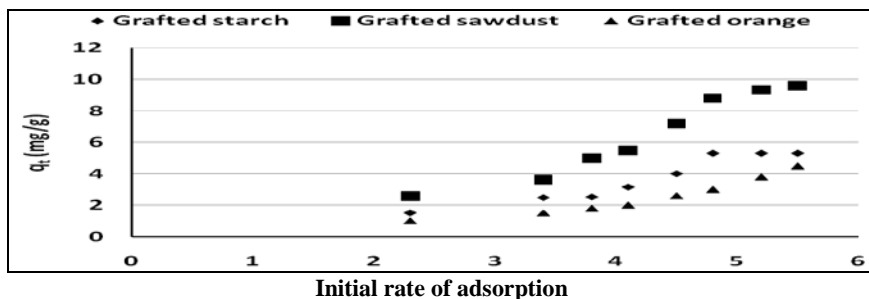
Initial rate of adsorption

Fig. 9. Elovich kinetic plots for the adsorption of dye on the adsorbents (adsorbent dose = 1g; pH = 9; Temp., = 30°C; contact time = 4 hr).

TABLE 2. Kinetic modles parameters for the adsorption of basic dye onto the prepared grafted natural adsorbents.

Samples	First order kinetic			Second order kinetic				Elovich model		
	q_e (mg/g)	k_1 (min^{-1})	r^2	q_e (mg/g)	k_2 (g/mgmin)	h (mg/g.min)	r^2	α	β	r^2
Grafted Starch	4.44	0.0115	0.964	6.62	2.92×10^{-3}	0.128	0.964	1.05×10^{-3}	1.374	0.907
Grafted sawdust	10.9	0.0184	0.987	12.0	1.46×10^{-3}	0.210	0.972	4.90×10^{-3}	2.496	0.939
Grafted orange	4.13	0.0138	0.962	5.81	1.88×10^{-3}	0.063	0.919	1.76×10^{-11}	1.086	0.897

Conclusions

In this work, grafted natural adsorbents such as starch, orange peel and sawdust (collected from a local sawmill) were grafted with acrylic acid and potassium bromated/thiourea as redox system after alkali treatment to remove basic blue dye 41 (BB41) from the aqueous solution by adsorption. Characterization of the natural adsorbents by the FTIR spectra was performed. The carbonyl absorption band at 1732 cm^{-1} (C=O) is increased in grafted starch more than that native and adsorbed starch, and becomes sharp and an increase in its intensity in the sawdust adsorbed dye was obtained. The OH group is increased in orange peel grafted but carboxylic group is decreased. This result is different from the FTIR spectra of starch and sawdust and compatible with the adsorption studies of Basic Blue 41 Dye. Overall, the carboxylic groups are increased after grafting of starch and sawdust, and hence the active adsorption sites available for the adsorption of Basic Blue 41 dyes. Batch adsorption results showed that the removal of basic dye from aqueous solution was investigated in the following order; sawdust > starch >orange. Also, these results were analyzed using two principal isotherm models, Langmuir and Freundlich. It was found that the equilibrium isotherms were well described by the Langmuir equation, giving a maximum adsorption capacity of 19.2 mg/g by sawdust at 30°C. Furthermore, the adsorption kinetics can be well represented by the pseudo-second-order model equation[24-27].

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إزالة الصبغة الكاتونية من المحاليل المتبقية بعد الصباغة بواسطة
مواد طبيعية محورة مع الدراسة الكينيتكية

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تهدف هذه الدراسة الى ازالة الصبغة الكاتيونية ذات الشحنة الموجبة وذلك بمواد طبيعية مطعمة مثل النشا ونشارة الخشب وقشر البرتقال . وقد اجريت التجارب فى درجة حرارة C° 30 ومقدار ثابت من المادة 1جم. وذلك لدراسة تأثير عدة عوامل علي سير التفاعل مثل اختلاف الاس الهيدروجيني واختلاف كم من درجة الحرارة والزمن . وقد تم تحليل البيانات والنتائج عن طريق معادلات لانجمير وفرندليش . واظهرت النتائج ان قدرة امتصاص الصبغة من المحلول تكون عند احسن مستوياتها عند درجة اس هيدروجيني 11 و زمن 120 دقيقة . وقد تم اجراء FTIR للمواد المطعمة ووجد تغير فى المجموعات الفعالة المكتسبة للمواد المطعمة بعد امتصاصها للصبغة .