

Removal of rhodamine B from textile wastewater using lemon waste

Dalal Z. Husein

Chemistry Department- Faculty of Science- Assiut University-
New Valley Branch-Alkharga, Egypt

Abstract

Lemon waste is an abundant waste product that could be a cost effective technique for removing rhodamine B from wastewater. The ability of two adsorbents prepared from lemon waste to remove rhodamine B from aqueous solutions was investigated. The adsorption capacity was determined as a function of contact time, pH, and adsorbent dosages. The treated lemon waste showed excellent efficiency in removing rhodamine B with percentage of removal up to 99.23% and the maximum removal has been found to be 5.75 for initial concentration of 10 mg/L. The adsorption process was found to follow Langmuir isotherm model and proceed according to the pseudo second-order kinetic model. Temperature effects proved that the adsorption was exothermic and pure physical in nature. The removal efficiencies of rhodamine B from actual samples ranged from 40.61 to 65.8%. The use of lemon waste as adsorbent is not only effective for rhodamine B removal from wastewater but also helps in solving the problem of over-abundance of agricultural waste product.

Key words: Lemon waste; adsorption; wastewater; rhodamine B

Introduction

Water is one of the most essential natural resources for human life. Only 0.3% of the total water available on earth can be used for various human activities. The demands of water have been increased due to increasing population growth and industrial prosperity, whereas the total availability of the water has remained constant. Furthermore, poor water management at industrial level has also reduced the amount of available water (Mittal and Mishra, 2014). Dyes are broadly used in many industries and they represent a contaminant of water resources, because of their poor biodegradability and high diffusion in aquatic environment (Zamouche et al., 2014).

Their tinctorial value is very high where less than 1 ppm of a dye produces obvious coloration. Consequently, dyes can harm human life, wildlife and flora (Garg et al., 2004). Conventional treatment processes present several limitations in the removal of dyes from water and are not effective for the treatment of low concentrations of these contaminants economically. Among the novel approaches developed for the removal of dyes from water; biosorption is an efficient technique. Biosorption is a physico-chemical process, simply defined as the removal of substances from solution by biomass. This is a property of living, dead organisms and their components. More attention was paid on biomass adsorbents due to its lower cost and higher adsorption capacity towards dyes. Literatures rhodamine B using biomass based adsorbents are scarce (Anandkumar and Mandal, 2009). Rhodamine B is widely used in many industries; plastics, leather tanning, paper and pulp, cosmetics, paint and pigments, and textile industries. Its carcinogenicity, reproductive and developmental toxicity, neurotoxicity and chronic toxicity towards humans and animals have been experimentally proven (Anandkumar and Mandal, 2011).

Corresponding author: Dalal Z. Husein, Chemistry Department- Faculty of Science- Assiut University, New Valley Branch- Alkharga- P.O. box:72511, Egypt. *e-mail:* dalal_husein@yahoo.com

Thus, removal and remediation of this dye from the industrial effluents is of significant environmental and commercial importance. It was reported that the adsorption capacity of the biosorbent for dyes, in general, could be improved greatly through chemical and physical modification (Kadirvelu et al. 2005, Ju et al. 2008 and Mohanty et al. 2005). Mostly, citric acid has been used as a modification agent in order to attach free carboxyl groups onto the hydroxyl of polysaccharide matrix of cellulosic waste materials (Lu et al., 2009; Wang et al., 2013; Fathy et al., 2013 and Arslanoglu et al., 2008). Lemon waste material is typically generated in large quantities by the fruit juice industry. Two different tissues are found which are colloquially called lemon peel, flavedo and albedo. Flavedo is the peel's outer layer, whose colour varies from green to yellow. It is a rich source of essential oil. Albedo is the major component of lemon peel, and is a spongy layer laid under flavedo. The thickness of the albedo fluctuates according to several variables, among them variety and degree of ripeness (Garcia-Perez et al., 2008). The lemon waste is a complex material. This material has received little scientific attention, in spite of its high quantity of cellulose, hemi-cellulose and pectin while lemon juice contains significant amount of citric acid. The lemon provides a ready source of alcoholic and polyacid groups in its different parts, which may be sufficient for the preparation of an ion exchanging resin (Arslanoglu et al., 2008). Chemical sorption may occur via the polar functional groups of lignin and cellulose such as alcohols, aldehydes, ketones, acids, phenolic hydroxides and ethers as chemical bonding and ion exchange (Ho et al., 2005).

In this study, lemon waste, is used to assess its efficiency in the removal of a cationic dye, rhodamine B, in a batch system. The effects of different parameters including contact time, pH, adsorbent dose and temperature were investigated. The adsorption kinetics, thermodynamic properties and isotherms were also explored. Application of prepared lemon waste adsorbents to real textile wastewater were performed to examine its efficiency toward rhodamine B removal.

Materials and Methods

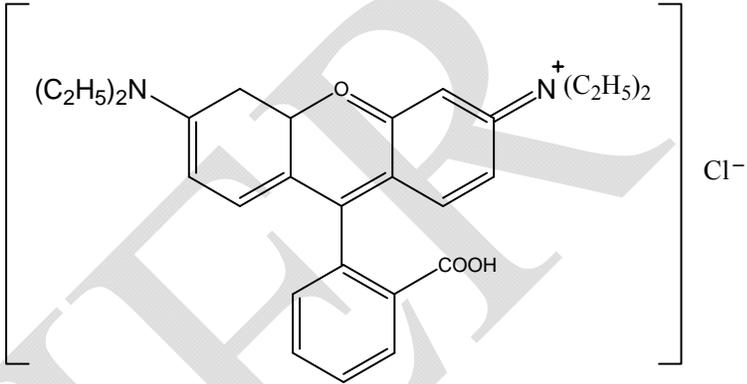
Preparation of adsorbents:

Lemon was purchased from a local grocery store. The lemon waste (LW) produced from juice processing were chopped into small pieces less than 10 mm. Seeds were picked out and the chopped material was placed on a glass tray and subjected to sun for 3 days. Resulting brown material was heated at 65°C in a convection oven for 12 h, ground, and screened into particle size less than 420 µm. The brown material obtained was grinded in a domestic mill and screened to particle size less than 420 µm. In order to remove unreacted citric acid and other soluble substances, material was boiled in deionized water for 30 min with stirring and then the slurry is filtered and washed repeatedly with deionized water till colorless filtrate. The separated gel is dried at 65°C for 24 h and grinded to particle size less than 420 µm. The resulting material is referred as BLW. Another part (25 g) of native lemon waste (LW) was boiled as aforementioned. After washing, the precipitate was treated with 100 ml 2M NaOH for 12h, washed again with deionized water to remove excess base, dried at 65°C, ground and sieved to get particle size less than 420µm and stored in tightly capped jars during the experimental study. It is labeled as NaLW.

Preparation of dye solution

Rhodamine B (RhB) supplied by Fluka company and distilled water was used to prepare all the solutions and reagents. Chemical structure and properties of the rhodamine B are listed in Table 1. The dye stock solutions were prepared by dissolving accurately weighted dye in deionized water to the concentration of 500 mg/L. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations. The pH of dye solutions were adjusted with 0.1M NaOH or 0.1M HCl using a pH meter (MP220, Mettler-Toledo, USA).

Table 1. Some properties of rhodamine B

Chemical structure	
Chemical formula	C ₂₈ H ₃₁ N ₂ O ₃ Cl
Molecular weight	479.01 g/mol
Type	Basic dye
Chemical class	Xanthenes
Solubility	Soluble in water
Wavelength	555 nm

Batch Adsorption experiments

Adsorption experiments were carried out at 120 rpm and 27°C using 50mL Erlenmeyer flasks containing 20mL different concentrations and initial pH values of rhodamine B solutions. The effect of temperature on the adsorption was carried out in order to study the thermodynamics of the process. Each study was conducted in a thermostated water-bath and the residual dye ions were analyzed. Different doses of adsorbent were added to each flask. After shaking the flasks for predetermined time the dye solutions were separated from the sorbent by filtration. Sorption kinetics experiments were carried out using 500 mL dye solution of 10 mg/L concentration and 1g of lemon waste. It was agitated at room temperature (27°C) at a pH of 5.75 and at a constant agitation speed of 120 rpm. A 5 mL series of samples were pipetted out using 10 mL syringe at different time intervals through a membrane filter 0.45µm. Dye concentrations in the supernatant solutions were performed by measuring absorbance at maximum wavelengths of rhodamine B (555 nm) with a 2550 UV-Visible spectrophotometer (Schimadzu, Japan). The amount of adsorbed rhodamine B

onto lemon waste at time t , q_t (mg/g), was calculated from the mass balance equation (1):

$$q_t = (C_e - C_t) v/m \quad (1)$$

when t is equal to equilibrium contact time, $C_t = C_e$, $q_t = q_e$ and the amount of adsorbed; RhB dye at equilibrium, q_e is calculated by using the equation (1).

The prepared lemon waste adsorbents, LW, BLW and NaLW were characterized by using FT-IR. The FT-IR spectra were registered in a spectrophotometer Model Bruker Vector 22, using OPUS 5.5 software, in the wave number range $500\text{--}3800\text{ cm}^{-1}$, using the ATR accessory.

Application treatment on real samples

Real samples of textile effluents from El-Helw Brothers, Diamond Textile and Golden Tex factories were collected. The three factories are located in 10th of Ramadan City in Egypt. The effluents from textile areas usually have more than one kind of dye in their composition. Thus, the wastewater was taken just from the outlet of the dyeing machine before it is mixed with other dye house wastewater streams in order not to contaminate with other source of wastewater in the dyeing section. Removal of RhB from actual wastewater was done as follows; 25 mL of each real sample was examined with 0.3 g lemon waste. The sorption mixtures were left for 24 h then filtered using membrane filter $0.45\text{ }\mu\text{m}$.

Results and discussion

Characterization of the adsorbents

As an important parameter for chemical characterization, IR spectra of LW, BLW and NaLW were recorded and shown in Figure 1.

The broad band between 3286 and 3316 cm^{-1} indicated the existence of hydroxyl groups of macromolecular association (cellulose, pectin, hemicellulose and lignin). The bands at 2920 and 2851 cm^{-1} were assigned to C–H stretches of methylene groups on the surface and to chelated H-bridges. Compared to the intensity of the characteristic C-H aliphatic peaks at 2920 and 2851 cm^{-1} , visible decrease for BLW and NaLW may confirm removal of soluble lignin and part of hemicellulose due to the pretreatment processes using boiling and alkali hydrolysis. Removal of lignin increases the population of pores and then decrease the crystallinity of cellulose (Taherzadeh and Karimi, 2008). Peaks observed at 1712 and 1613 cm^{-1} in the LW spectrum are indicative of free and esterified carboxyl groups which may be useful in identifying pectins present in LW (Arslangoglu et al., 2008). Compared to the intensity of the characteristic ester peak at 1712 cm^{-1} , visible decrease for BLW was observed. Disappearing of such peak at NaLW spectrum indicated that the methyl ester is hydrolyzed with alkali (Abdelkreem and Husein, 2012). Moreover, the peak that appears at $1008\text{--}1017\text{ cm}^{-1}$ is due to vibration of C-O-C and O-H of polysaccharides.

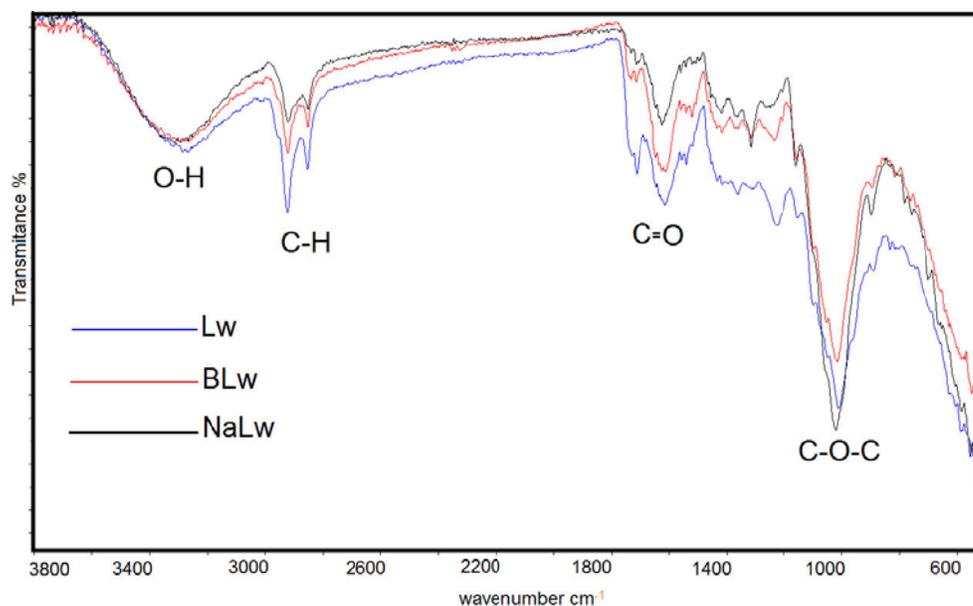


Fig. 1. FTIR spectra of lemon waste adsorbents (LW, BLW and NaLW).

Effect of pH on adsorption capacity

The role of pH is very important because of its impact on the adsorption sites of the bioadsorbent as well as ionization process of the contaminant molecules. The effect of pH on RhB removal onto BLW and NaLW was evaluated at 27°C at different initial pH values in the range of 2.60-8.5. RhB dye solution adjusted by adding either 0.1M HCl or 0.1M NaOH. Other adsorption parameters like initial dyes concentration, adsorption dose and shaking time were fixed at 10mg/L, 2.5 g/L and 3h, respectively. Both BLW and NaLW have the same pattern as shown in Figure 2. The maximum removal for RhB was found at pH 5.75. The removal decreased and reached minimum (62.54% and 68.46% for BLW and NaLW, respectively) at highly acidic condition at pH 2.60. However, when the pH of the solution was further increased to pH 3.91, the uptake of RhB increased to 82.67% and 80.46% for BLW and NaLW, respectively. With further increasing of pH to the value 5.05, the uptake of RhB decreased to be and 74.74% and 79.85% for BLW and NaLW, respectively, and return to increase at pH 5.75 to reach maximum (88.08% and 93.36% for BLW and NaLW, respectively).

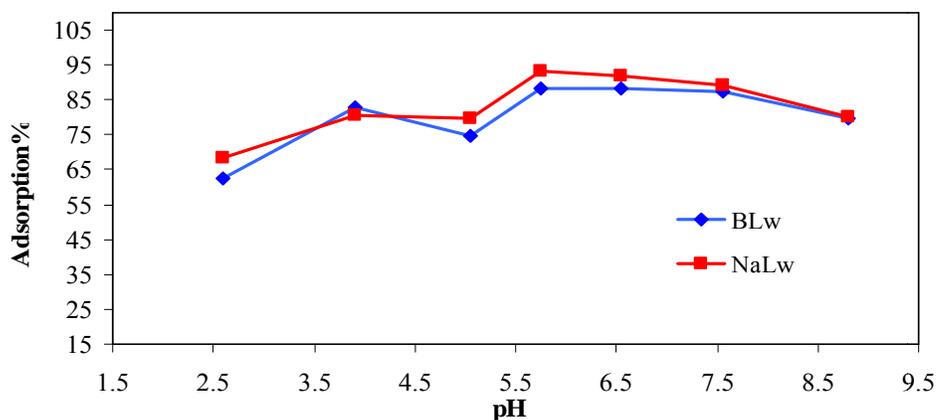


Fig. 2. Effect of pH on the adsorption of RhB onto BLW and NaLW.

Rhodamine B is an aromatic amino acid compound with amphoteric characteristics due to the presence of both the amino group ($-\text{NH}$) and the carboxyl group ($-\text{COOH}$), Table 1. Thus, the charge state of RhB is dependent on solution pH. When the solution pH is lower than 3.91, lower adsorption capacity was recorded. The rhodamine B ion takes on a positive charge on one of the nitrogens while the carboxyl group is unionized. The electrostatic repulsion between cationic RhB and positively charged lemon wastes leads to decrease of dye uptake when pH decreased from 3.91 to 2.60. At pH values lower than 3.91, the dye can enter into the pore structure of the BLW and NaLW. When solution pH increased above 3.91, the carboxyl group gets ionized and the zwitterions form of RhB is formed. The zwitterions form of RhB in water may increase dimerization of RhB, which makes the molecule too large to enter most of the pore structure of Lemon waste surface. The inaccessibility to the pore structure of BLW and NaLW, which is smaller than the dimer's effective size, resulted in a decrease in RhB removal. At a pH value higher than 5.05, excessive OH^- compete with COO^- in binding with $-\text{N}^+$ and the aggregation of RhB decreases which causes an increase in the adsorption of dye on surfaces of BLW and NaLW.

Point Zero Charge of lemon waste-RhB dye system

The point of zero charge (pH_{zpc}) is the pH at which the total number of positive and negative charges on the adsorbent surface becomes zero. The pH at the point of zero charge (pH_{zpc}) of lemon waste-RhB was measured by using the pH drift method. The pH of the solution was adjusted between 2.33-8.50 by adding either HCl or NaOH. 1g of adsorbent was added in 50 ml of the solution in Erlenmeyer flask and left at room temperature for 24 h until stabilization, and then the final pH was recorded. The graph of pHs was drawn and used to determine the points at which the initial and final pH values were equal (Vijayakumar et al., 2012). Typical curve obtained with the pH-drift technique was shown in Figure 3 for both BLW and NaLW. From Figure 3, it can be concluded that the pH_{ZPC} of lemon waste-RhB dye system is pH 5.1 and 5.25 for BLW and NaLW, respectively. With increasing in pH, the magnitude of surface charge of the lemon waste decreases and thus electronegativity increases. The decrease in removal of the positively charged RhB dye at acidic pH range is attributed to the presence of excess H^+ ions competing with the dye molecule for the adsorption sites.

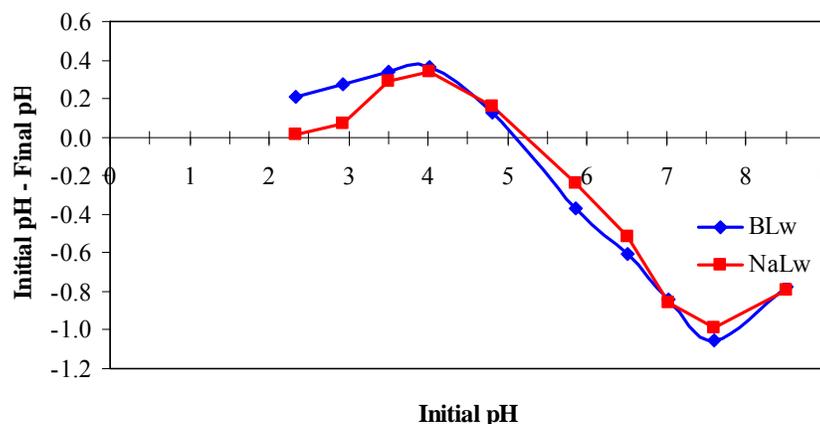


Fig. 3. Relation of initial pH's vs final pH.

Effect of adsorbent dose on RhB adsorption

The adsorbent dose is an important factor in adsorption studies because it determines the lemon waste capacity for initial RhB dye concentration. It is found that as the adsorbent dose was increased from 0.025 to 0.2 gms there was an increase in the adsorption of rodamine dye onto the surface of lemon waste, as shown in Figure 4. The increase in adsorption capacity with increase in lemon waste dose may be attributed to the increase in the availability of active sites which reflect an increase in the effective surface area. NaLW showed a little increase in adsorption of RhB dye than BLW.

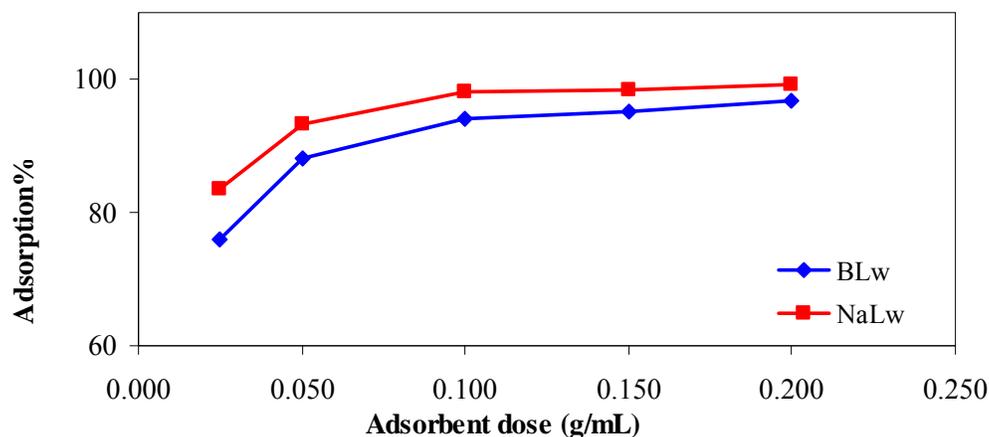


Fig. 4. Effect of adsorbent dose on the removal of RhB onto BLW and NaLW.

Adsorption isotherm studies

Adsorption isotherms describe the interaction of contaminant with the adsorbent materials. Isotherms are critical for optimization of the adsorption mechanism pathways (Husein, 2013). Accordingly, the correlation of equilibrium data by the empirical equations is intrinsic to the practical design and operation of adsorption systems (Abdelkreem and Husein, 2012). Adsorption isotherms of RhB ions by BLW and NaLW was shown in Figure 5. Relation between RhB adsorption (%) and initial dye concentrations was conducted in Figure 6. As indicated in Figure 6, the percentage adsorption was decreased as the dye concentration increased.

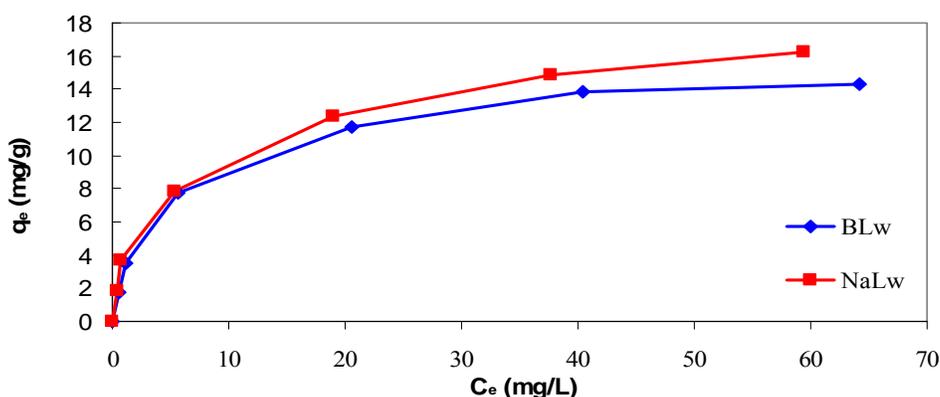


Fig. 5. Adsorption isotherms of RhB ions onto BLW and NaLW.

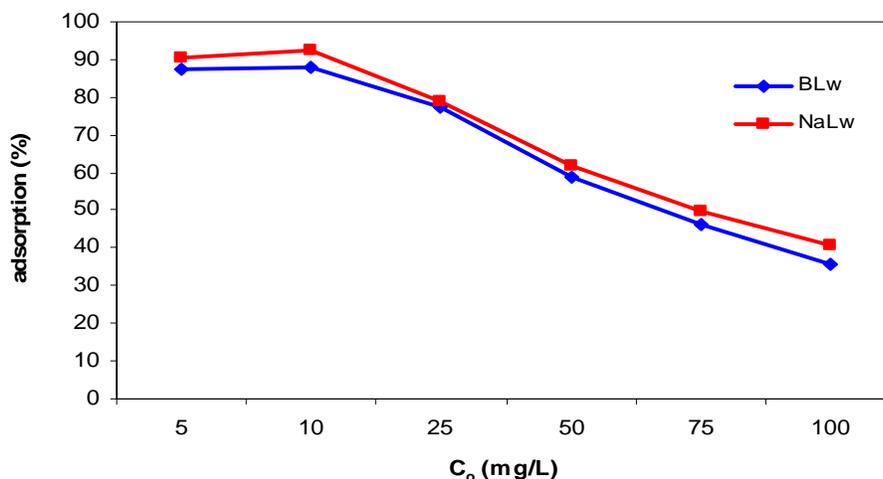


Fig. 6. Plot of adsorption (%) vs. initial concentration of RhB.

Four isotherm models, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich, were used to describe the relationship between the amount of RhB onto lemon waste and its equilibrium concentrations in solutions. Langmuir isotherm (Langmuir, 1918) has been widely applied to many real sorption processes. It assumes a monolayer adsorption onto the surface in which adsorbates are adsorbed to a finite number of definite localized sites that are identical and equivalent with no lateral interaction (Langmuir, 1918). The nonlinear form of Langmuir equation is equation (2) while the linearized is equation (3):

$$q_e = q_L K_L C_e / (1 + K_L C_e) \quad (2)$$

$$C_e / q_e = (1 / K_L q_L) + (1 / q_L) C_e \quad (3)$$

Where, q_e is the equilibrium adsorption capacity on the adsorbents BLW and NaLW (mg/g) and C_e is the equilibrium solute (or RhB ions) concentration in the solution (mg/L). Langmuir constants q_L represents the monolayer adsorption capacity of the lemon waste adsorbents (mg/g) and K_L is the energy of adsorption (L/mg). The values of K_L and q_L (Table 2) were obtained from the slope and intercept of a plot of C_e versus C_e / q_e . The greater the value of K_L , the higher is adsorption energy, reflecting a rapid increase in adsorption efficiency at low concentrations of adsorbate (Gopinath and Venugopal, 2012). When the linearized form of Langmuir (equation 3) was applied to quantify maximum adsorption capacity, the plot of C_e / q_e versus C_e (Figure 7) indicated that a linear relationship with the correlation coefficient (R^2) values as 0.999 and 0.995 for BLW and NaLW, respectively. Hence, it may be deduced that the adsorption process of RhB closely followed the Langmuir isotherm model. Accordingly, the study confirmed the monolayer coverage of rohdamine dye at the outer surface of BLW and NaLW. The values of equilibrium parameter, R_L , which can expressed as given in equation 4:

$$R_L = 1 / (1 + K_L C_{max}) \quad (4)$$

where the C_{max} represents the maximum initial RhB concentration in the solution (mg/L). Values of R_L (Table 2) were found to be between zero and one which confirm that the adsorption feature of BLW and NaLW could be well described by Langmuir

isotherm. Furthermore, it is observed, later, that the adsorption capacity is positively correlated with temperature.

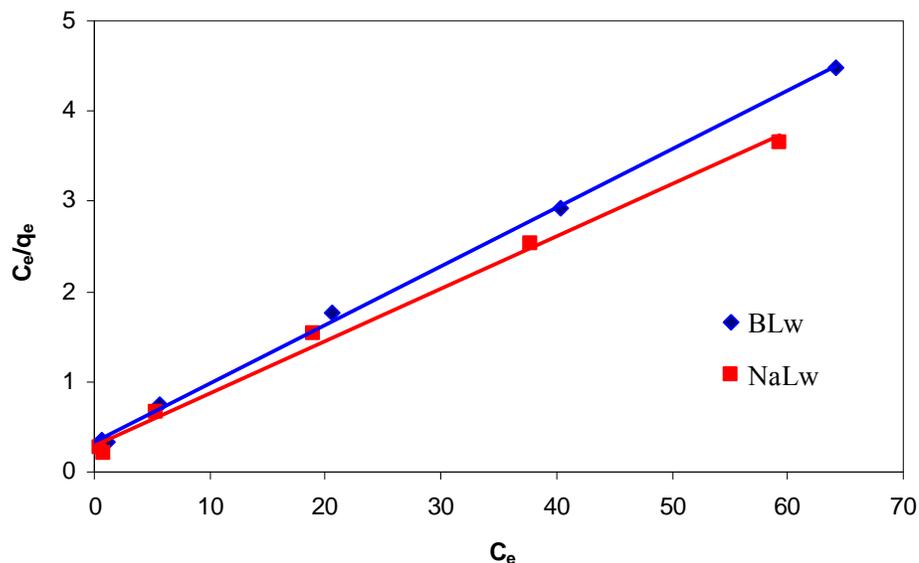


Fig. 7. Correlation coefficient, R^2 , of Langmuir model.

Unlike the Langmuir isotherm model, the Freundlich model is a nonlinear adsorption model and is given in equation 5. It advocates a multilayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interaction between sorbed RhB dye molecules (Freundlich, 1906).

$$\log q_e = \log K_F + 1/n \log C_e \quad (5)$$

Where q_e is the amount of solute adsorbed (RhB) per unit weight (mg/g) of the adsorbent (lemone waste) used, K_F is a constant relating the adsorption capacity (mg/g), $1/n$ is an empirical parameter relating the adsorption intensity which varies with the heterogeneity of the material and C_e is the equilibrium solute concentration (RhB) in the solution (mg/L). The values of K_F and n are obtained from the slope and intercept of a plot of $\log(q_e)$ versus $\log C_e$. Both the parameters K_F and $1/n$ affect the adsorption isotherm, by sharing a direct proportional relationship with the adsorption capacity (Gopinath and Venugopal, 2012). The obtained correlation coefficient (R^2) values in Table 2 are found to be less compared to Langmuir correlation coefficients which suggest that application of Freundlich isotherm model is not the best fit.

Temkin isotherm model considered the effects of some indirect sorbate/adsorbate interactions on adsorption isotherms. Temkin suggests that the heat of adsorption of all the sorbate molecules in the layer would decrease linearly with coverage due to these sorbate/adsorbent interactions (Temkin, 1940). The Temkin isotherm is represented in the following equation (6):

$$q_e = B \ln A + B \ln C \quad (6)$$

$$\text{where: } B = RT/b \quad (7)$$

where A is the equilibrium binding constant (L/g), b is related to heat of adsorption (J/mol), R represents the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K).

The Temkin adsorption isotherm parameters, A and B are obtained from the plot of q_e versus $\ln C_e$, and then recorded in Table 2. Though correlation coefficient (R^2) value in Temkin adsorption isotherm was found to be 0.997 and 0.992 for BLW and NaLW, respectively, the (R^2) values were lower than that for Langmuir Isotherm. Though both the models fit the adsorption equilibrium data satisfactorily, Langmuir had better correlation (Table 2).

The Dubinin-Radushkevich equation is commonly expressed as:

$$q_e = q_m - \beta \varepsilon^2 \quad (8) \text{ (Dubinin and Radushkevich, 1947)}$$

where ε (Polanyi potential) is equal to $RT \ln(1 + 1/C_e)$, q_e is the amount of the RhB dye adsorbed per unit lemon waste (mol/g), q_m the theoretical monolayer saturation capacity (mol/g), β is the constant of the adsorption energy (mol^2/kJ^2), R is the gas constant (8.314 KJ/mol K), and T is the temperature (K). The linear form of the D-R isotherm is given as:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (9)$$

The parameter β is related to mean adsorption energy E (kJ/mol) as:

$$E = (-2\beta)^{-1/2} \quad (10) \text{ (Acemioglu, 2004)}$$

The calculated D-R adsorption isotherm parameters are summarized in Table 2. The calculated value of mean adsorption capacity of RhB, q_m was found to be less as compared to the values of Langmuir adsorption capacity. Difference in the values of adsorption capacity by using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich, models may be impute to the different assumption taken into consideration during the formulations of these isotherm adsorption models. The R^2 values were found to be less than those recorded for Langmuir isotherm. The mean free energy of biosorption (E) was found to be 1.118 and 1.290 kJ/mol for BLW and NaLW, respectively. These values showed that the adsorption was physical in nature. Since D-R model is not being followed by this system, these (E) values assort only an estimation of the nature of the biosorption processes of RhB onto lemon waste.

Table 2. Isotherm parameters for RhB adsorption onto BLW and NaLW.

Isotherm	Isotherm constants	BLw	NaLw
Langmuir	q_L	15.41	17.24
	K_L	0.196	0.199
	R_L	0.048	0.048
	R^2	0.999	0.995
Freundlich	n	2.296	2.366
	K_F	2.830	3.310
	R^2	0.944	0.950
Temkin	A	2.969	3.797
	B	2.803	2.945
	R^2	0.997	0.992
Dubinin-Radushkevich	q_m	10.359	11.467
	E	1.118	1.290
	R^2	0.910	0.939

Adsorption kinetics

Predicting the rate at which adsorption takes place for a given system is probably the most important factor in adsorption system. Adsorption kinetics describes the relationship of solute uptake rate of adsorption and adsorption time.

The adsorption (%) of BLW and NaLW towards RhdB as a function of contact time is shown in Figure 8. A very rapid adsorption was found during the adsorption time of 5 min. However, the amount of rhodamine B adsorbed increased with time and reached a constant value after 1h. The fast adsorption rate at the initial stage may be explained by an increased availability in the number of active binding sites on the lemon waste surface. The adsorption process rapidly occurs and is normally controlled by the diffusion process from the bulk to the BLW and NaLW surface. In the later stage, the availability of active sites decreased, consequently slowing down the transfer of metal ion from solution to the lemon waste surface and the sorption is likely an attachment-controlled process.

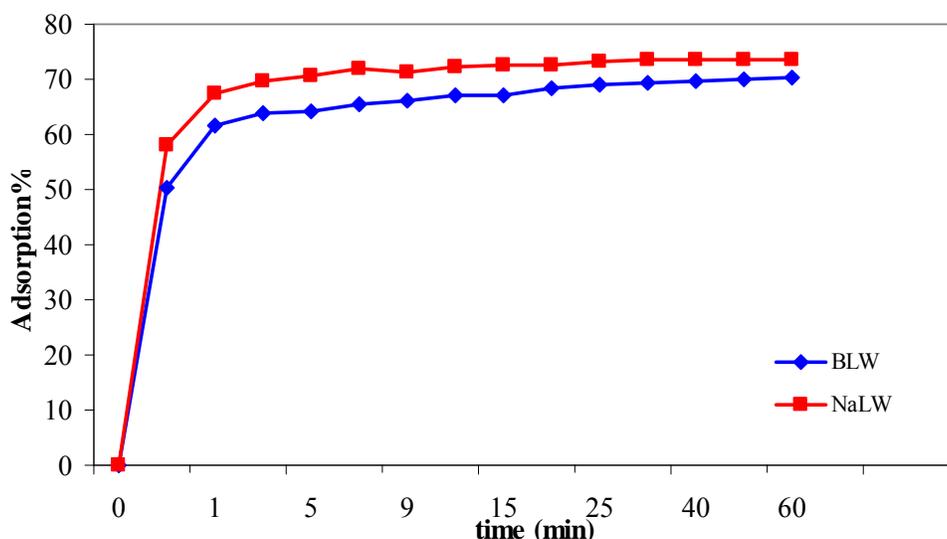


Fig. 8. Effect of contact time on RhB removal by BLW and NaLW.

In order to clarify the adsorption kinetics of RhB-lemon waste system in different kinetic models, the pseudo first-order, pseudo second-order, Elovich, and intra particle diffusion models were applied to the sorption data. The best fit among the kinetic models is assessed by the linear coefficient of determination (R^2).

- Pseudo first-order kinetics

The pseudo first-order equation (Lagergren's equation) describes adsorption in solid-liquid systems based on the sorption capacity of solid adsorbents (Lagergren, 1898). It is assumed that one RhB ion is sorbed onto one sorption site on the lemon waste surface and the linear form of pseudo first order model can be expressed as:

$$\log(q_e - q_t) = \log q_e - k_1/2.303t \quad (11)$$

where parameters; q_e and q_t (mg/g) are the adsorption capacities at equilibrium and at time t (min), respectively. Both k_1 and q_e , were experimentally evaluated using the slope and intercept of plots of $\log(q_e - q_t)$ versus t . The obtained values of R^2 are found to be very low which suggest that application of equation (11) is inappropriate

as experimental observations are nonlinear when plotted in this form. Moreover, agreement between experimentally observed equilibrium adsorption data and that derived using equation (11) is poor (Table 3). This suggests that the adsorption of RhB on BLW and NaLW did not follow pseudo first-order kinetics.

- *Pseudo second-order kinetics*

This model assumes that one RhB ion is sorbed onto two sorption sites on the lemon waste surface. The pseudo second-order rate expression, which has been applied for analyzing chemisorptions kinetics from liquid solutions (McKay and Ho, 1999), is linearly expressed as follows:

$$t/q_t = 1/(k_2q_e^2) + (1/q_e)t \quad (12)$$

where k_2 represents the rate constant for pseudo second-order adsorption (g/mg min) and $k_2q_e^2$ (mg/g min) is the initial adsorption rate. The parameters of pseudo second-order adsorption model, q_e and k_2 in equation (12) were determined by plotting t/q_t versus t (Figure 9, Table 3). Fitted equilibrium adsorption capacities obtained from equation (12) are in close agreement with those conducted experimentally. The calculated q_e values were 3.53 and 3.70 mg/g for BLW and NaLW, respectively, while the experimental values were 3.52 and 3.69 mg/g for the same order. In addition the correlation coefficients (R^2) for the pseudo second-order kinetic model fits are 0.999 and 1.00 for BLW and NaLW, respectively, much higher than the correlation coefficients derived from pseudo first-order model fits. Given the good agreement between model fit and experimentally observed equilibrium adsorption capacity furthermore to the large correlation coefficients, this suggests that RhB adsorption followed pseudo second-order kinetics. Accordingly, the dye ions were adsorbed onto the BLW and NaLW surface via chemical interaction.

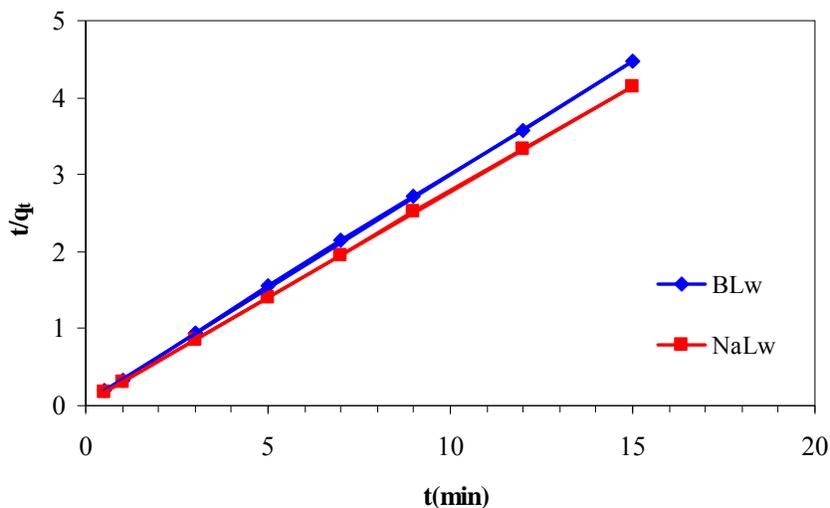


Fig. 9. Pseudo second-order kinetics for the adsorption of RhB onto BLW and NaLW.

- *Elovich model*

The Elovich equation is generally expressed as follows (Boparai et al., 2011):

$$q_t = 1/\beta \ln(\alpha\beta) + (1/\beta) \ln t \quad (13)$$

where q_t is the sorption capacity at time t (mg/g), α represents the initial sorption rate (mg/g min) and β is related to the Elovich coverage factor and activation energy

(g/mg) during any experiment. Thus, the constants β and α can be obtained from the slope and the intercept of a straight line plot of q_t against $\ln t$. Table 3 lists the kinetic constants obtained from the Elovich equation. From Table 3 it can be seen that the adsorption data deviated greatly from linearity which was evidenced by low correlation values. Kinetic data were further applied to the intraparticle diffusion model suggested by Weber and Moris.

- Intra-particle diffusion

Adsorption of adsorbate on adsorbent proceeds in several steps, involving transport of the adsorbate molecules (RhB) from the aqueous phase to the surface of the solid particulates (film diffusion). Second step is diffusion of the adsorbate molecules into the interior of the pores (of BLW and NaLW), which is usually a slow process. The intraparticle diffusion rate constant (k_{int}) is given by the Weber–Morris equation (Weber and Morris, 1963) as follows:

$$q_e = C + k_{int} t^{1/2} \quad (14)$$

where k_{int} is the intraparticle rate constant of transport in $\text{mg/g min}^{1/2}$ and C , is the boundary layer (film diffusion). When intraparticle diffusion mechanism plays a significant role in controlling the kinetics of the sorption process, the plots of q_e versus $t^{1/2}$ yield a straight line passing through the origin and the slope gives the intraparticle rate constant, k_{int} . The adsorption of RhB onto the lemon waste depends on film diffusion and intraparticle diffusion, and the more rapid one will control the overall rate of transport. The plot obtained from this work shows multi-linearity with 2 steps. The first part of the multi-linear plot is attributed to boundary layer diffusion (film diffusion), while the second to the intraparticle diffusion and the chemical reaction. The multi-linearity curve indicates that intraparticle diffusion is not a fully operative mechanism in the sorption of RhB by the BLW and NaLW. The diffusion rate constant (k_{int}) was found low (0.094, 0.068 mg/g min for BLW and NaLW, respectively), indicating that the rate of the adsorption step is not only the rate controlling step. The higher intercept values (2.93 and 3.29 for BLW and NaLW, respectively) show the greater contribution of the surface sorption in the rate limiting step.

Table 3. Comparison of the correlation coefficients of kinetic parameters for RhB adsorption onto BLW and NaLW.

Kinetic model	Adsorbents	parameter	R ²
Pseudo first-order	BLw	$q_e = 0.58$ $K_1 = 0.102$	0.776
	NaLw	$q_e = 0.40$ $K_1 = 0.137$	0.763
Pseudo second-order	BLw	$q_e = 3.53$ $K_2 = 0.599$	0.999
	NaLw	$q_e = 3.70$ $K_2 = 1.126$	1
Elovich	BLw	$\alpha = 6.2 \times 10^6$ $\beta = 6.00$	0.847
	NaLw	$\alpha = 1.6 \times 10^{10}$ $\beta = 7.87$	0.775
Intraparticle diffusion	BLw	$k_{int} = 0.094$	0.636
	NaLw	$k_{int} = 0.068$	0.518

Adsorption thermodynamics

Thermodynamic behavior of adsorption of RhB dye on lemon waste, Figure 10, was evaluated by the thermodynamic parameters - Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). These parameters were obtained from analysis of experimental data at temperature range of 300-313 K using the following equations:

$$\Delta G^\circ = -RT \ln K_C \quad (15)$$

$$K_C = C_\delta / C_e \quad (16)$$

$$\ln K_C = -\Delta G^\circ / RT = -(\Delta H^\circ / RT) + (\Delta S^\circ / R) \quad (17)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (18)$$

K_C is the distribution coefficient for adsorption, C_δ is the equilibrium RhB dye concentration on the lemon waste (mg/L) and C_e is the equilibrium dye concentration in solution (mg/L). ΔG° for adsorption of rhodamine dye onto BLW and NaLW at all temperatures was calculated by using equation (15) and was found to be -4.99, -4.95 and -5.02 kJ/mol for BLW and -6.23, -6.18 and -6.08 kJ/mol for NaLW at T=300, 306 and 313 K, respectively, as shown in Table 4. The negative value of ΔG° at all temperatures confirms the spontaneous nature and feasibility of RhB adsorption onto BLW and NaLW. Heat of adsorption, ΔH° was calculated from the slope ($= \Delta H^\circ / R$) of the linear plot of $\ln K_C$ versus $1/T$, Figure 11. The negative value of ΔH° (-5.89 and 18.37 kJ/mol for BLW and NaLW, respectively) for the removal of RhB by lemon waste from aqueous solution at pH 5.75 shows the exothermic nature of adsorption and the pure physical process (Temkin, 1940). This result confirmed the mean free energy of biosorption that conducted by using equation (10). The values of ΔS° were estimated as -3.14 and -40.91 kJ/mol for BLW and NaLW, respectively. The negative value of ΔS° implies a decrease in the randomness at the solid/solution interface during the adsorption process. The distribution of RhB dye ions in solution was obviously more disordered compared to RhB ions bound to the lemon waste surface and this resulted in net decrease in entropy.

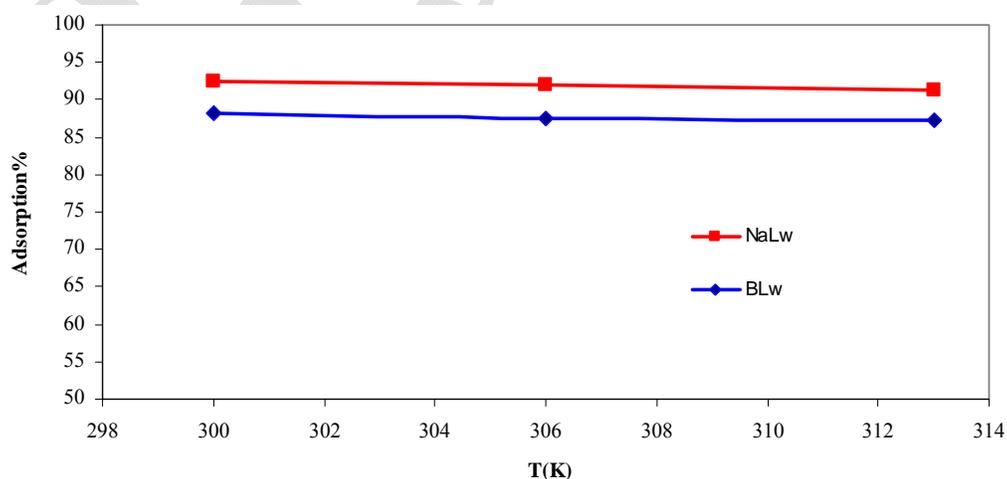


Fig. 10. Effect of temperature on adsorption of RhB onto BLW and NaLW.

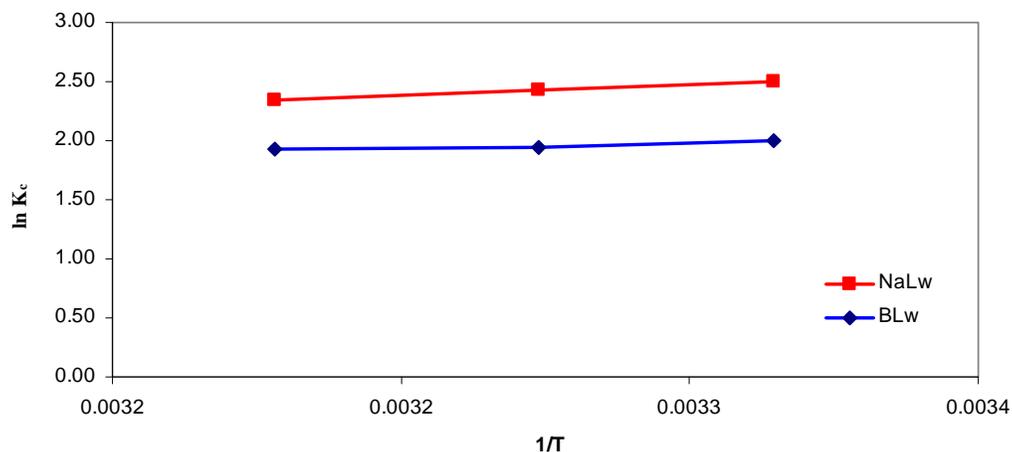


Fig. 11. A plot of $\ln K_c$ vs $1/T$ for adsorption of RhB on BLW and NaLW.

Table 4. Thermodynamic parameters for the adsorption of RhB on BLW and NaLW at different temperature.

Adsorbent	T(K)	K_c	ΔG°	ΔH°	ΔS°
BLW	300	7.40	-4.99	-5.89	-3.14
	306	6.99	-4.95		
	313	6.87	-5.02		
NaLW	300	12.16	-6.23	-18.37	-40.91
	306	11.35	-6.18		
	313	10.36	-6.08		

Treatment of textile effluent enriched with RhB dye

Textile industries release wastewater with different pH values. The effluent's natural pH was chosen to apply removal of RhB by BLW and NaLW. The characteristics of wastewater of the three textile effluent samples were illustrated in Table 5. The results have been presented in Figure 12. It can be inferred from the data that 40.61-62.8% RhB dye can be removed from the textile effluents. Therefore, it could be concluded that the adsorbents studied were efficient remover of the RhB dye which could be used for the textile effluents treatment at industrial scale.

Table 5. Characteristics of real textile wastewater samples.

Factory	pH	Total solids (mg/L)	Total dissolved solids (mg/L)	Total suspended solids (mg/L)	Turbidity (NTU)	Conductivity ($\mu\text{s}/\text{cm}$)	Concentration of RhB (mg/L)
Al-Helew brothers	5.26	81407.3	81378.8	28.49	14.96	90420.9	99.72
Diamond Textile	9.47	57262.4	57230.9	31.47	12.52	64582.4	181.47
Golden Tex	8.05	43816.8	43796.6	19.84	17.09	50227.4	68.99

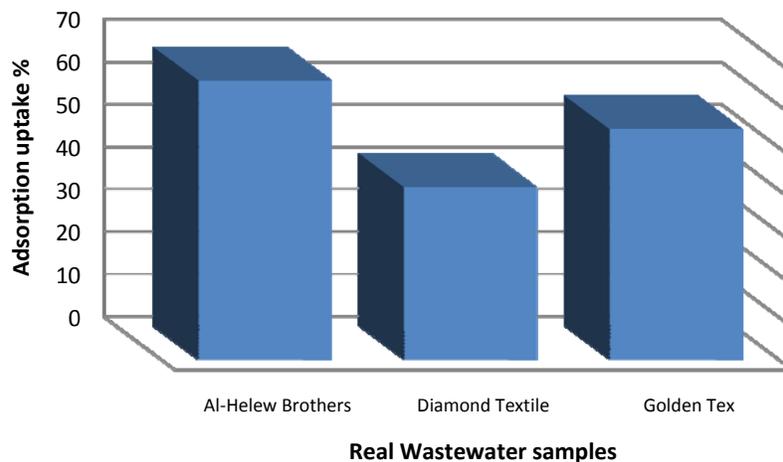


Fig. 12. Adsorption uptake of BLW and NaLW towards rhodamine B contained in real wastewater obtained from Golden Tex, Diamond Textile and El-Helew Brothers factories.

Conclusion

On the basis of the present study, The lemon waste could be used as low cost adsorbent for the removal of rhodamine B dye as indicated in Figure 13. The experimental results showed that contact time required to achieve maximum adsorption rhodamine B was 1 h, where removal was found to be 99.2%. The effect of pH for maximum removal of RhB has been found to be 5.75 for initial concentration of 10 mg/L. Langmuir isotherm model were fitting better than Freundlich, Temkin and Dubinin-Radishkevich isotherms interpreting the adsorption phenomenon of rhodamine B onto lemon waste adsorbents. RhB-lemon waste adsorption system follows pseudo second-order kinetic model. The small value of mean free energy of adsorption, E , calculated from D-R isotherm suggested that physical adsorption may play a role in the removal of rhodamine B using lemon waste. Such result confirmed the obtained values of enthalpy, ΔH° . Furthermore, depending on the negative values of ΔH° and ΔG° , the adsorption of rhodamine B onto lemon waste was exothermic and spontaneous process. The removal efficiencies of rhodamine B from actual samples ranged from 40.61 to 65.8%.

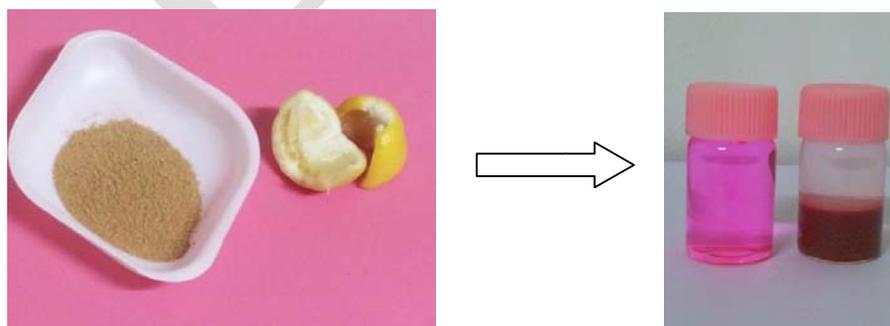


Fig. 13. Raw lemon waste powder and its application to remove rhodamine B dye from model samples.

References

- Abdelkreem M. , Husein D.Z. , 2012. Removal of strontium from aqueous solutions by adsorption onto orange peel: isotherms, kinetics, and thermodynamic studies. *EJER.*, 1 , 42-61.
- Acemioglu B. , 2004. Adsorption of congo red from aqueous solution onto calcium-rich Fly ash. *J. Colloid Interface Sci.* 274, 371-379.
- Anandkumar J. , Mandal B. , 2011. Adsorption of chromium(VI) and Rhodamine B by surface modified tannery waste: Kinetic, mechanistic and thermodynamic studies, *J. Hazard. Mater.* 186, 1088–1096.
- Anandkumar J. , Mandal B., 2009. Removal of Cr(VI) from aqueous solution using Bael fruit (*Aegle marmelos correa*) shell as an adsorbent. *J. Hazard. Mater.* 168, 633–640.
- Arslanoglu H. , Altundogan H.S., Tumen F., 2008. Preparation of cation exchanger from lemon and sorption of divalent heavy metals, *Bioresource Technol.* 99, 2699–2705.
- Boparai H.K. ,Joseph M. , Caroll D.M.O., 2011. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. *J.Hazard. Mater.* 186, 458–465.
- Dubinin M.M. ,Radushkevich L.V. , 1947. Equation of the characteristic curve of activated charcoal, *Chem. Zentr.* 1, 870–875.
- Fathy N.A. ,El-Shafey O.I. , Khalil L.B. , 2013. Effectiveness of Alkali-Acid Treatment in Enhancement the Adsorption Capacity for Rice Straw: The Removal of Methylene Blue Dye. *ISRN Phys. Chem.* doi:10.1155/2013/208087
- Freundlich H.M.F. , 1906, *Uber die adsorption in Losungen [Adsorption in solution]*, *Z. Phys. Chem.* 57, 385–470.
- Garcia-Perez J.V. ,Carcel J.A. , Clemente G. , Mulet A. , 2008. Water sorption isotherms for lemon peel at different temperatures and isosteric heats, *LWT Food Sci. Technol.* 41, 18–25.
- Garg V.K , Amita M. , Kumar R. , Gupta R. , 2004. Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste. *Dyes Pigm.* 63, 243-250.
- Gopinath R. , Venugopal N. , 2012. Isotherm studies for adsorption of Cr (VI) using activated carbon, *Ultra Chem.* 8, 333-340.
- Ho Y.S. ,Chiang T.H. ,Hsueh Y.M., 2005. Removal of basic dye from aqueous solution using tree fern as a biosorbent. *Process Biochem.* 40,119–124.
- Husein, D. Z. , 2013, Adsorption and removal of mercury ions from aqueous solution using raw and chemically modified Egyptian mandarin peel, *Desalin. water treat.* 55, 6761-6769. doi. 10.1080/19443994.2013.801793
- Ju D.J. , Byun I.G. , Park J.J. , Lee G.,Ahn H. , Park T.J. ,2008. Biosorption of a reactive dye (Rhodamine-B) from an aqueous solution using dried biomass of activated sludge. *Bioresour. Technol.* 99, 7971–7975
- Kadirvelu K. , Karthika C. , Vennilamani N., Pattabhi S. , 2005. Activated carbon from industrial solid waste as an adsorbent for the removal of Rhodamine-B from aqueous solution: kinetic and equilibrium studies. *Chemosphere* 60, 1009–1017.

- Lagergren S. , 1989. About the theory of so-called adsorption of soluble substances, K. Sven. Vetenskapsakad. Handl. 24, 1–39.
- Langmuir I. , 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. 40, 1361–1403.
- LuD. , CaoQ. ,Li X. ,Cao X. ,ShaoW. , 2009. Kinetics and equilibrium of Cu(II) adsorption onto chemically modified orange peel cellulose biosorbents. Hydrometallurgy. 95, 145–152.
- McKay G. , Ho Y.S. , 1999. Pseudo-second order model for sorption processes, Process Biochem. 34, 451–465.
- Mittal H. ,Mishra B.S., 2014. Gum ghatti and Fe₃O₄ magnetic nanoparticles based nanocomposites for the effective adsorption of rhodamine B, Carbohydr. Polym. 101 1255– 1264.
- Mohanty K. , Jha M. , Meikap B.C. , Biswas M.N., 2005. Removal of chromium(VI) from dilute aqueous solutions by activated carbon developed from Terminalia arjuna nuts activated with zinc chloride. Chem. Eng. Sci. 60, 3049–3059.
- Temkin M.I., Pyzhev V., 1940. Kinetics of ammonia synthesis on promoted iron catalysts, Acta Physicochim. USSR 12. 217–222.
- Taherzadeh M.J. , Karimi K. , 2008. Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: a review. Int. J. Mol. Sci. 9, 1621-1651.
- Vijayakumar G. ,Tamilarasa R. ,Dharmmendirakumar M. , 2012. Adsorption, Kinetic Equilibrium and Thermodynamics studies on the removal of basic dye Rhodamine-B from aqueous solution by the use natural adsorbent perlite. J. Master. Environ. Sci. 3, 157-170.
- Wang S. ,Wang L. ,Kong W. , Ren J. , Liu C., Wang K.,Sun R. , She D., 2013. Preparation, characterization of carboxylated bamboo fibers and their adsorption for lead(II) ions in aqueous solution. Cellulose. 20, 2091-2100.
- Weber W.J. ,Morris J.C. , 1963. Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. Proc. Am. Soc. Civil. Eng. 89, 31–59.
- Zamouche M. , Arris S. , LeHocine M.B., 2014. Removal of Rhodamine B from water by cedar cone: Effect of calcinations and chemical activation. Int. J. Hydrogen Energy. 39 1523-1531.