



Removal of Basic Blue 159 from Aqueous Solution Using Banana Peel as a Low-Cost Adsorbent

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Received 30 Jun. 2013; Final version received 12 Aug. 2013

Abstract

In this paper, the adsorption of Basic Blue 159 (BB159) onto banana peel as a low-cost material was studied. At first, the banana peel was sieved. Later, banana peel particles were characterized by field emission scanning electron microscopy (FESEM), energy dispersive x-ray spectroscopy (EDXS) and Fourier Transform Infrared (FTIR) techniques. Batch adsorption experiments were carried out as a function of pH, contact time, initial dye concentration, the mass of adsorbent and mixing speed. Batch adsorption models, based on the assumption of the Pseudo-first-order, Pseudo-second-order, Elovich and Intraparticle diffusion mechanism, showed that kinetic data follow closely the pseudo-second-order model. Results indicate that banana peel could be used as an adsorbent to remove the cationic dyes from contaminated watercourses.

Key words: *Banana peel, Kinetic, Low-Cost material, Basic dye, Banana peel.*

Introduction

Textile industries have shown a significant increase in the use of synthetic complex organic dyes as coloring materials [1]. Adsorption has been used extensively in industrial process for separation and purification. The removal of colored and colorless organic pollutants from industrial wastewater

is considered as an important application of adsorption processes [2]. Treatment of dye wastewater involves physico-chemical methods such as coagulation, precipitation, adsorption by activated coal, oxidation by ozone, ionizing radiation and ultra filtration. These methods are costly, less efficient, has limited application but

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also generate wastes which are difficult to dispose off [3].

The search for alternative sources of nutrients, such as agricultural residues, has a double advantage: they add value to this waste while lowering the costs of producing enzymes. Another interesting feature of lignocelluloses residues is the physical–chemical properties of the functional groups available on their surface. These groups are responsible for the adsorption capacity of some specific solutes through ionic interactions. Natural sorbents have been obtained from agricultural waste, such as corn cobs, coconut shell, sugar cane bagasse and fruit peel like orange and banana [4]. Banana, which belongs to the Musaceae family, is native to the Indonesian Malaysian region of Asia. Banana peel is a solid waste with high carbohydrate content, around 60% of dry matter. It is thus possible that it supports fungal growth [5]. The production of bananas and plantains in the world exceeded 94 million tons by 2008, with Africa, Latin America and the Caribbean being the major exporters [6]. At the time of harvest, a banana plants estimated to have a weight of 100 kg, of which 15 kg correspond to leaves, 50 kg to pseudo-stalks, 33 kg to fruits and 2 kg to rachis [7].

The banana peel has been used as bioadsorbent of soluble contaminants, such as dyes [4], metal, and phenolic compounds. Different processes for color removal typically include physical, chemical

and biological schemes. Some processes, such as electrochemical techniques and ion pair extraction, are relatively new for textile waste treatment, while others have been used in the industry for a long time. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, use of operation and insensitivity to toxic substances [8].

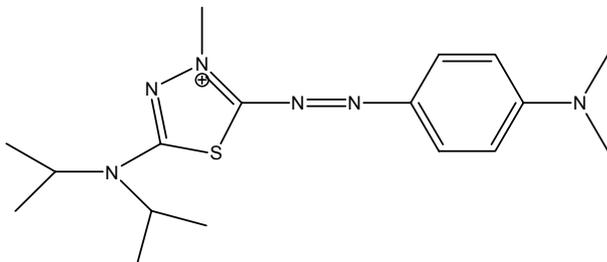
The aim of this work was to study the adsorption of BB159 from aqueous solution onto banana peel as a low cost adsorbent. Basic Blue159 (BB 159) was chosen as a model dye. The banana peel was characterized by FESEM, EDXA and FTIR. The effect of pH solution, contact time, initial dye concentration, the mass of adsorbent and mixing speed on adsorption of banana peel were studied. The Pseudo-first-order, Pseudo-second-order, Elovich and Intraparticle diffusion were used to study of adsorption kinetic of BB159 on banana peel. Results indicate that banana peel could be used as adsorbent to remove the cationic dyes from contaminated watercourses.

Experimental

Materials

Basic Blue159 was purchased from BEZEMA Company and used without further purification. Table 1 illustrates some characteristics of BB159. All other chemicals were provided from Merck chemical company. All other chemicals were provided from Merck chemical company.

Table 1. Characteristics of Basic Blue 159.

Name and color index(C.I)	structure	commercial name	λ_{\max} (nm)	CAS Number
Basic Blue 159		Astrazon Blue FBL	700nm	105953-73-9

Instrumentation

A Unico 4802 UV-Visible spectrophotometer was employed for absorbance measurements using quartz cell of 1 cm path length. A pH meter (Metrohm 691, Metrohm, and Riverview, FL, USA) was chosen to measure the pH values of sorption process.

Methods

Preparation and characterization of adsorbent

The banana peel was obtained from fruit purchased at a local market. It was dried in sunlight for 7 days. The dried banana peel was ground and sieved with planetary mill (Planetary Ballmill/ PM100). Field emission scanning electron microscopy (FESEM-S-4160) analysis was carried out to study its surface texture.

Preparation of dye stock solution

The stock solution was prepared by dissolving accurately weighted dye in distilled water to the concentration of 1000 mg l^{-1}

Adsorption process

The adsorption experiments were carried out in batch processes. In each experiment 100 mL of the dye solution was mixed with 0.4 gr of banana peel in a glass tub. After a predetermined time interval the mixture was centrifuged and filtered and quantity of dye not adsorbed, i.e. that remaining in solution, was measured by spectrophotometer at 700 nm. The same experiment was repeated using different parameters: initial dye concentration (50–400 mg l^{-1}) contact time (5-120 min), the mass of adsorbent (0.2-0.8g), pH of solution (3-10) and mixing speed (100-400 rpm).

Kinetic studies

0.4gram of adsorbent was used for adsorption of BB159 at different times (5-120min, pH 9, mixing speed 200 rpm and initial dye concentrations (50-400 mg l^{-1}). The amount of equilibrium adsorption q_e (mgg $^{-1}$) was calculated using the equation 1:

$$q_t = (C_0 - C_e)V/W \quad (1)$$

Where q_t is the quantity of dye adsorbed on the adsorbent (mgg^{-1}) at any time, C_0 and C_t are the initial and dye concentrations (mg l^{-1}) after adsorption time t , respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent (g).

The percentage of removed dye in solution for each treatment can be given by:

$$\text{Removal percentage} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where C_0 and C_e (mg l^{-1}) are initial dye concentration and dye concentration after sorption procedure.

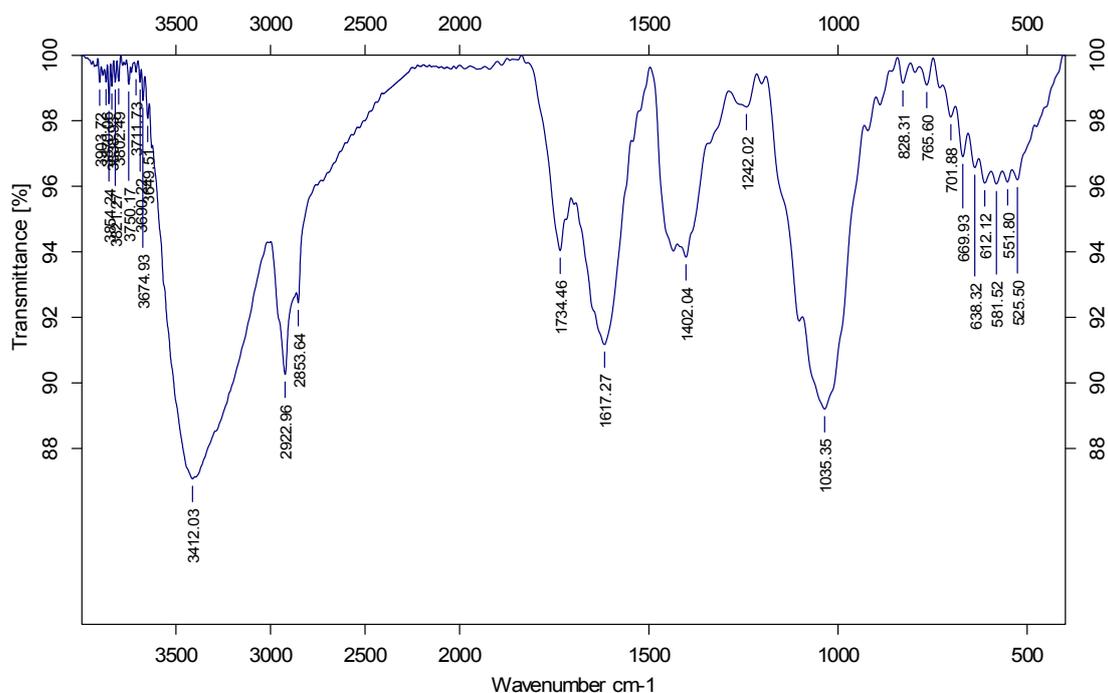
The BB159 concentrations graph for standard solution versus absorbance at 700 nm wavelength, at where the maximum absorbance was reached, was prepared and used to determine the concentration of an unknown solution. For each adsorption process, the absorbance of dye solution

was monitored. Then, the BB159 concentrations in the residual solution and the dye adsorbed by banana peel were calculated using the standard graph. Subsequently, the adsorption rate of BB159 on banana peel was plotted.

Results and discussion

Characterization of adsorbent

FTIR were used to analyze functional group distributions in the banana peel. Figure 1 shows the FTIR of banana peel particles. In Figure 1, the peaks around 3444.64 cm^{-1} , 2923.34 cm^{-1} , 1733.88 cm^{-1} and 1037.36 cm^{-1} resulted from O-H stretch, C-H stretch, C=O stretch and C-O stretch, respectively. It can be found that banana peel has hydroxyl and carbonyl groups. These groups have negative charge where can be good sites for adsorption of Basic Blue 159.



Field emission scanning electron microscopy (FESEM) has been a main tool for characterizing the surface morphology and fundamental physical properties of the adsorbent surface. It is useful for establishing the particle shape, porosity and appropriate size distribution of the adsorbent. The FESEM of banana peel was recorded and is shown in Figure 2. In the FESEM micrograph 2(a) the

bright spots show the rough and porous surface of the adsorbent, which one of the factors increasing adsorption capacity. The loaded FESEM images show the adsorption of Basic Blue 159 on the banana peel. In Figure 2(b) depicting the surfaces of particle after adsorption, it is clearly seen that the caves, pores and surfaces of adsorbent were covered by dye.

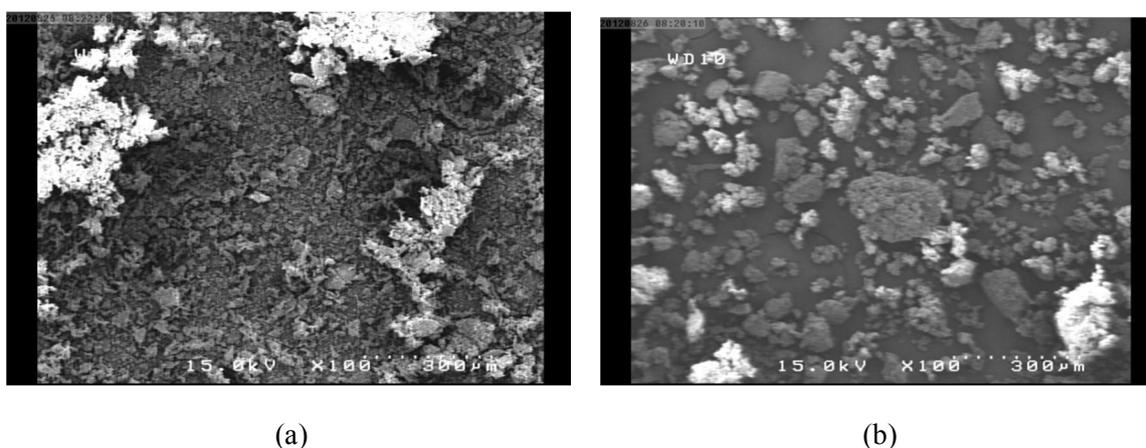


Figure 2. Field emission scanning electron microscope of (a) banana peel and (b) dye adsorbed banana peel.

The energy dispersive X-ray spectrometry (EDXS) analysis was employed to determine the composition of banana peel. Energy dispersive X-Ray spectrum (EDXS) of banana peel is shown in Table 2. It shows peaks corresponding to K (Potassium), C (Carbon), O (Oxygen), Mg (Magnesium) and Cl (Chlorine), no trace amount

of other impurities could be seen in the detection limit of the EDXS. The results show that oxygen is the most elements in banana peel. It is indicated that hydroxyl, carbonyl groups where have been shown in FTIR are the most important groups in banana peel

Table 2. The Energy dispersive X-Ray spectrum (EDXS) of banana peel.

Elements	Norm. C (wt. %)
Carbon	33.24
Oxygen	56.27
Magnesium	0.29
Silicon	0.69
Chlorine	1.83
Potassium	7.68
Total: 100 %	

Effect of the mass of adsorbent

The removal of BB159 by banana peel were studied by changing the quantities of sorbents (0.2, 0.4, 0.6 and 0.8g) for the initial dye concentration of 100 mgL^{-1} at room temperature, pH 9 and mixing speed 200 rpm for 60 min. The residual dye concentration was measured by spectrophotometer after centrifuged and filtration. In Figure 3 the

dye removal percentage by different masses of adsorbent is shown. The results indicated that increase in mass of adsorbent to 0.4 g leads to increasing in BB159 removal percentage. The results show that the more masses of adsorbent have a different effect and leads to decrease of dye adsorption. It seems that aggregation of adsorbent occur when mass of adsorbent is high [9].

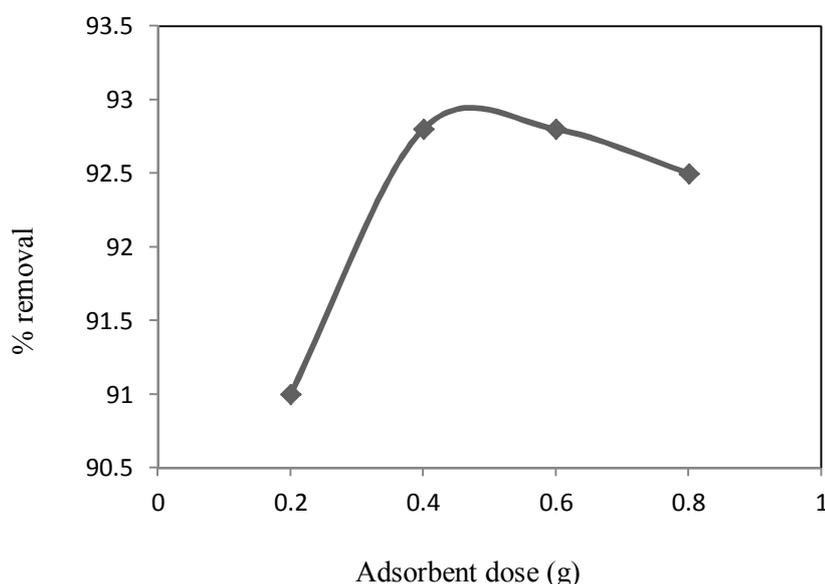


Figure 3. Effect of adsorbent dose on the adsorption of BB159 on banana peel.

Effect of pH

The pH of the dye solution is one of the most important parameters which controlled the adsorption process, particularly the adsorption capacity. The pH of the solution changed due to, (1) the surface charge of the adsorbent, (2) the degree of ionization of the adsorptive molecule and (3) extent of dissociation of functional groups on the active sites of the adsorbent [10]. Figure 4 shows the effect of pH on removal percentage

of BB159 by banana peel. It was revealed that the decolonization efficiency increased with the increase of pH and reached a maximum level at the pH of 9.0. Carolyn Palma and et al [12] have shown that if the pH of a solution is higher than the value of pH pzc, the surface of the adsorbent has a negative net charge since the acid groups are de-protonated and could preferably interact with cationic species. In solutions with a lower pH than pH pzc, the net charge of solid surface is

positive since the basic groups have the ability to share electrons, i.e., they are proton acceptors, and could do with those negatively charged, According to these results, banana peel could be a low-cost bioadsorbent to uptake Basic dyes from industrial wastewater [11].

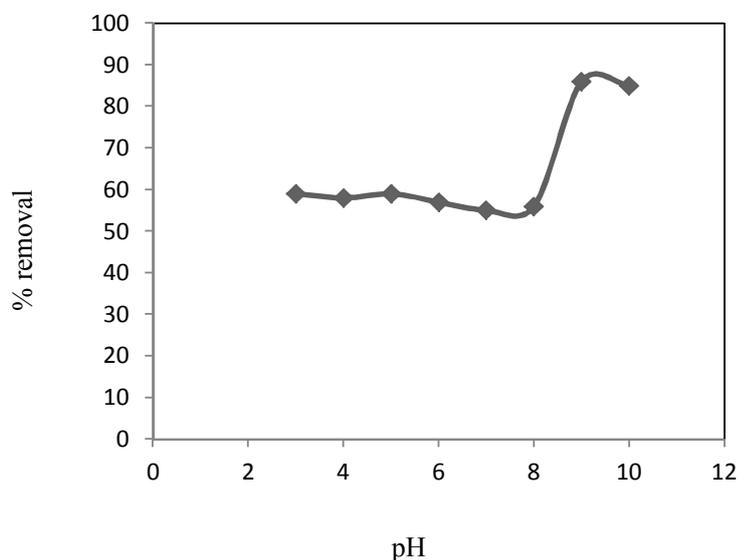


Figure 4. Effect of pH on the adsorption of BB159 by banana peel.

Effect of mixing speed

The contact of dye molecules to adsorbent particles is very important in adsorption process. The mixing speed leads to increase in contact of dye molecules to adsorbent particles. The effect of mixing speeds on dye adsorption has shown in Figure 5. According to Figure 5, increase of the mixing speed from 100

rpm to 200 rpm leads to increasing in dye removal percentage. The experimental data shows that higher mixing speed (300 and 400 rpm) causes to decrease of the dye removal percentage. It seems that increase in mixing speed leads to increase in turbulence and decrease in contact of dye molecules to adsorbent particles.

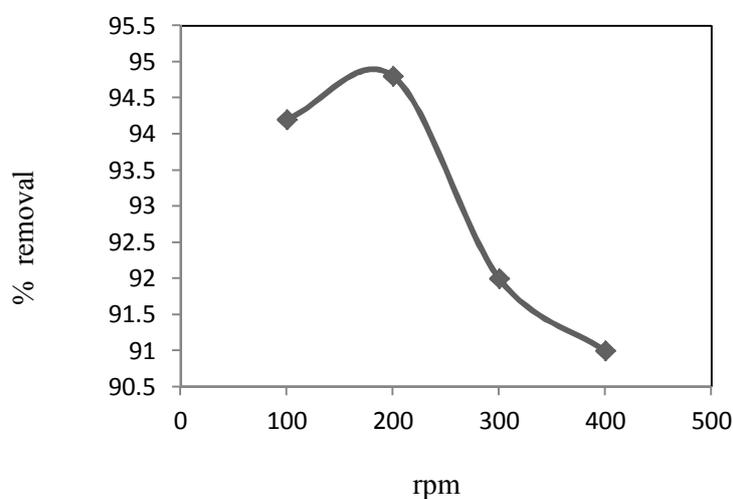


Figure 5. Effect of mixing speed on the adsorption of BB159 by banana peel.

Effect of contact time and initial dye concentration

Determining of equilibrium time is another important parameter in adsorption which represents the adsorption of BB159 on banana peel. In Figure 6, the effect of contact time and initial dye concentration on adsorption of BB159 by banana peel is shown. According to Figure 6, the dye adsorption increases with increasing of time to 60 min for all initial dye concentrations. Longer time has no influence on dye adsorption.

This means that the dye adsorption reaches to equilibrium for different concentrations. Also, the results show that increasing of dye concentration leads to increase in BB159 adsorbed on banana peel. The maximum adsorption of BB159 on banana peel reaches at 400 mgL⁻¹. Increasing of initial dye concentration improved number of collisions between dye molecules and banana peel particles. Hence a higher initial concentration of dye will enhance the adsorption process [12].

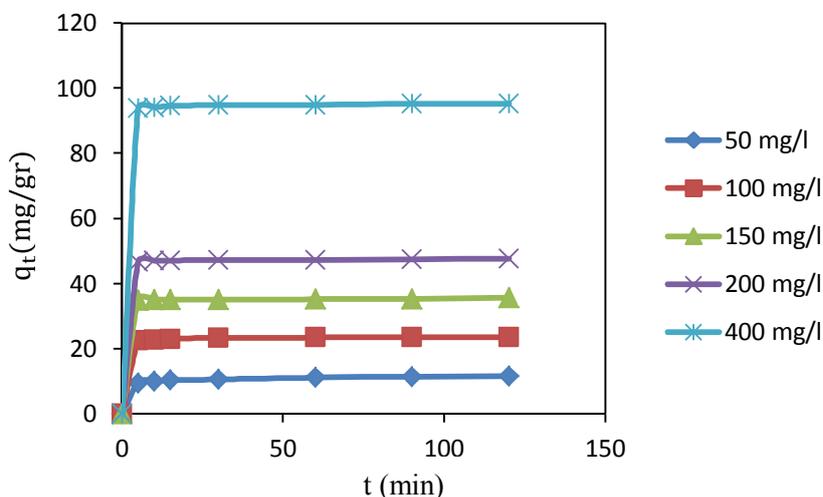


Figure 6. Effect of the contact time and initial dye concentration on BB159 adsorption by banana peel.

Adsorption kinetics

Adsorption kinetics has been proposed to elucidate the adsorption mechanism. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transport process. In order to investigate the mechanism of BB159 adsorption on the banana peel and examine the potential rate-controlling step, i.e., mass transfer or chemical reaction. The capability of Pseudo-first-order, Pseudo-second-order, Elovich kinetic and Intraparticle diffusion models was examined in this study.

Pseudo first order

This model assumed that the rate of solute uptake with time was directly proportional to difference in saturation concentration and the adsorbed amount [13, 14]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

Where k_1 is the rate constant of Pseudo first order, q_e and q_t are the amount of dye adsorbed (mg/g) at contact time t (min), respectively. After Integrating with the boundary conditions at $t=0$, $q_t=0$ and at

$t=t$, $q_t=q_t$ and rearranging equation (4), the rate law for a Pseudo-first-order reaction became:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

The k_1 and q_e values calculated from the slope and intercept of the plot of $\ln(q_e - q_t)$ against t (Figure 7). The k_1, q_e and R^2 values are listed in Table 3.

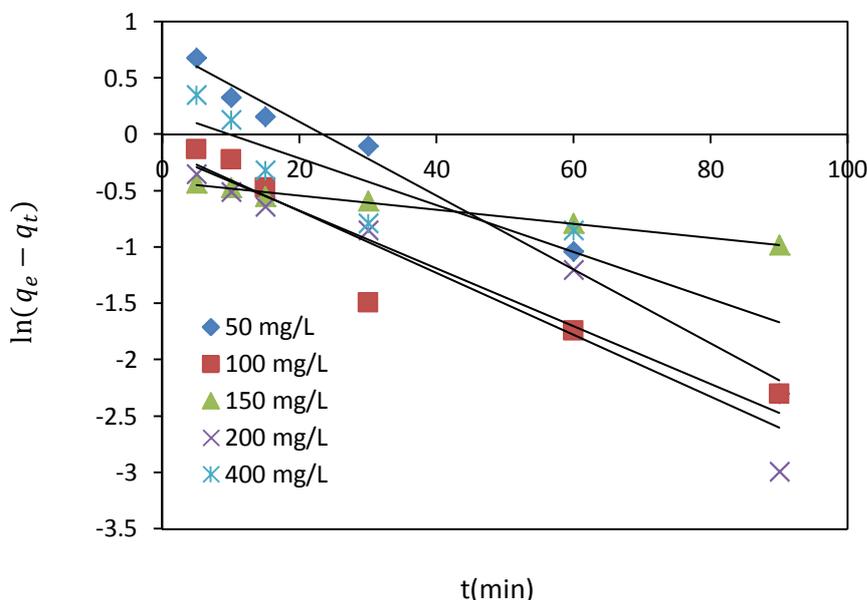


Figure 7. Pseudo first order kinetics for BB159 adsorption on banana peel.

Pseudo second order

Ho [15] proposed a second order model for the sorption of divalent metal ions onto peat particles based on the adsorption capacity of the adsorbents with the goal of differentiating the kinetics of a second-order rate expression based on the adsorbent concentration from models which are based on the solute concentration and represent a pseudo-second-order rate expression.

The linearized form of the Pseudo-second-order model as given by Ho [15]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

Where k_2 (mggmin^{-1}) is the rate constant of pseudo second order adsorption, q_e is the amount of dye adsorbed on the adsorbent at equilibrium (mgg^{-1}) and q_t is the amount of dye adsorbed on

the adsorbent at any time, t (mgg^{-1}). Integrating equation (6) and applying the initial conditions:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

and The initial adsorption rates h (mggmin^{-1}) can be calculated from the pseudo second order model by the following equation:

$$h_i = k_2 q_e^2 \quad (7)$$

Where h_i is the initial dye adsorption rate. k_2 (mggmin^{-1}) can be calculated from the slope and intercept of the plot of t/q_t against t (Figure 8). The values of k_2, h_i, q_e and R_2 are listed in Table 3.

Similar phenomenon has been observed in the adsorption of methylene blue by hazelnut shells and wood sawdust [16], activated carbon prepared

from rattan sawdust [18] and bamboo based activated carbon.

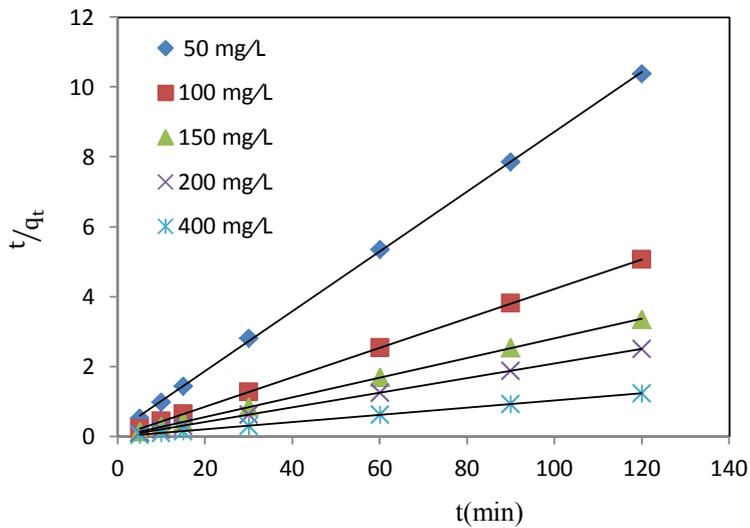


Figure 8. Pseudo second order kinetics for BB159 adsorption on banana peel.

Elovich

The Elovich equation is given as follows [17]:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (8)$$

Where α is the initial sorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is the desorption constant (g mg^{-1}). To simplify

the Elovich equation, it is presumed that $\alpha\beta t \gg 1$ and by applying the boundary conditions $q_t = 0$ at $t = 0$, this equation becomes [17].

$$q_t = \beta \ln(\alpha\beta) + \beta \ln t \quad (9)$$

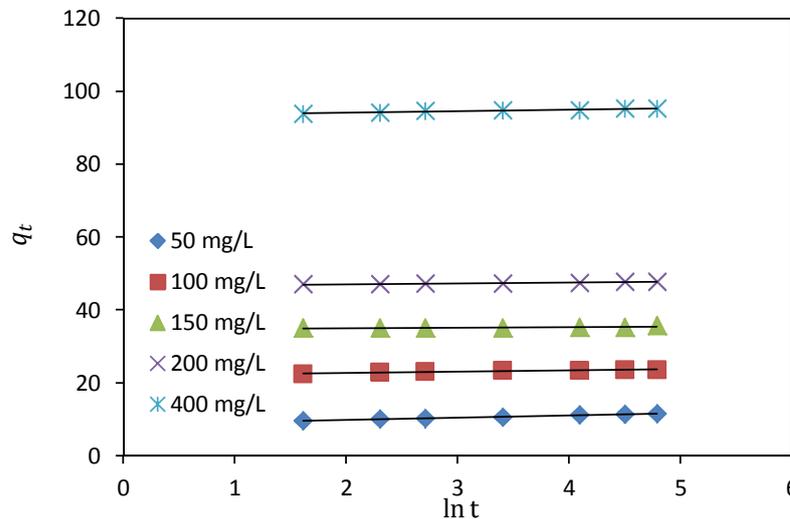


Figure 9. Elovich kinetics for BB159 adsorption on banana peel.

Intra-particle diffusion

Any adsorption process consists of different steps, the surface diffusion followed by Intra-particle diffusion. In general, the adsorption was governed

by the liquid phase mass transport. The mass transfer rate can be expressed as a function of the square root of time (t). The intra-particle diffusion model was expressed by [18]:

$$q_t = kt^{\frac{1}{2}} + C \quad (10)$$

Where q_t is the amount of dye adsorbed on banana peel at time t , and k is the intra-particle diffusion

rate constant. The values of R^2 are listed in Table 3. The results show that experimental data did not fit well into the Intra particle diffusion equation.

The R^2 values calculated from the slope and intercept of the plot of q_t against \sqrt{t} (Figure 10).

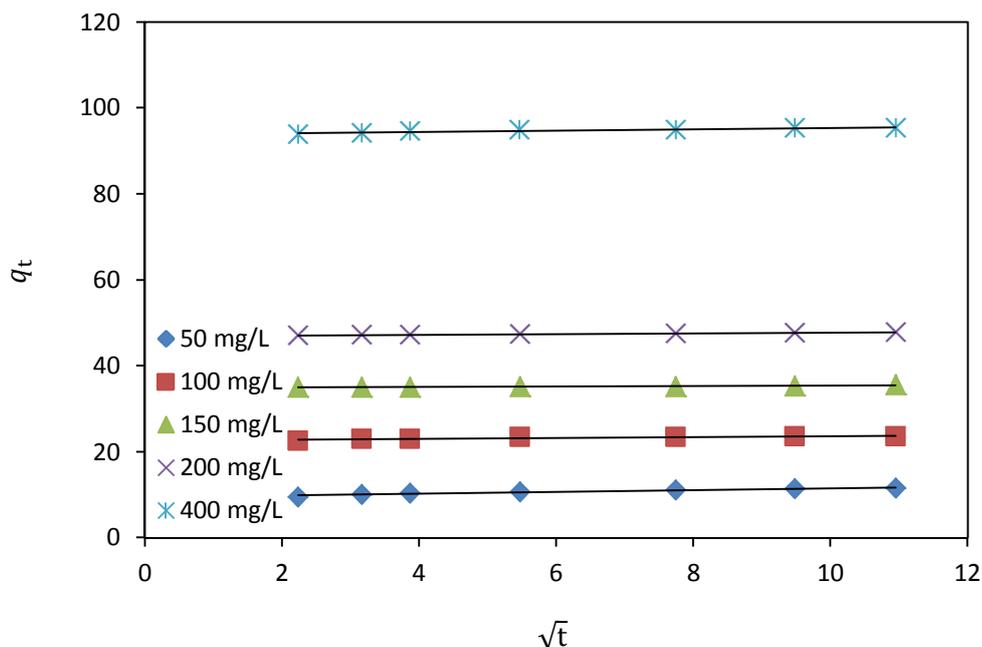


figure 10. Intra particle kinetics for BB159 adsorption on banana peel.

Table 3. The values of Pseudo first order, Pseudo second order, Elovich and Intra-particle diffusion models for the adsorption of BB159 on banana peel.

		50mg/l	100mg/l	150mg/l	200mg/l	400mg/l
Pseudo first order	K_1	0.0328	0.0257	0.0063	0.0275	0.0208
	$q_{e\text{ cal}}$	2.1591	0.852	0.6597	0.88	1.22
	R^2	0.9865	0.8992	0.9902	0.8903	0.7393
Pseudo second order	K	0.045	0.075	0.097	0.041	0.025
	$q_{e\text{ cal}}$	11.68	23.86	35.58	48.309	96.15
	R^2	0.9998	0.9999	0.9999	0.9998	0.9999
	h_i	6.139	42.69	122.79	65.68	231.12
Elovich	R^2	0.9915	0.9465	0.6963	0.9456	0.952
Intra-particle Diffusion	R^2	0.943	0.849	0.8184	0.9828	0.8841

Conclusion

In this research the removal of Basic blue 159 (BB159) from aqueous by banana peel was studied. Banana peel was characterized by FESEM, FTIR analysis and EDXS. The adsorption was highly dependent on various operating parameters, like: the mass of adsorbent, initial dye concentration, contact time, pH and mixing speed (rpm). The results show that the best removal percentage observed at 60 min, 0.4 g adsorbent, 200 rpm and pH9. The kinetic of BB159 adsorption onto banana peel was examined using the pseudo-first-order, pseudo-second-order, Elovich and Intra-particle diffusion models. The adsorption kinetic followed the pseudo-second-order kinetic model. The results indicate that banana peel could be used as adsorbent to remove the cationic dyes from contaminated watercourses.

References

- [1] A.M. Talarposhti, T. Donnelly, *Water Research*, 35 (2), 425 (2001).
- [2] Z. Al-Qodah, *Water Research*, 34 (17), 4295 (2000).
- [3] K.C. Chen, W.T. Wu, J.Y. Huang, J.Y. Hwang, *J. Ind. Microbiol. Biotechnol.*, 23, 686 (1990).
- [4] V. K. Gupta, *J. Environ. Manag.*, 90, 8, 2313 (2009).
- [5] J. P. Essien, E. J. Akpan, E. P. Essien, *Bioresour.*, 96, 1451 (2005).
- [6] FAO (Food and Agriculture Organization of the United Nations): Faostat Statistics Database (last updated December 2009), Agriculture, Rome, Italy (2008).
- [7] M. Bao, S. Delgado, M. Garcí'a, M. Torres, *Rev. Agroquim. Tecnol. Aliment.*, 27, 24 (1987).
- [8] V. Meshko, L. Markovska, M. Minchev, A. E. Rodrigues, *Water Research*, 35 (14), 3357 (2001).
- [9] H.B. Senturk, D. Ozdes, C. Duran, *Desalination*, 252, 81 (2010).
- [10] B. K. Nandi, A. Goswami, M. K. Purkait, *Applied Clay Science*, 42, 583 (2009).
- [11] C. Palma, E. Contreras, J. Urrea, *Waste Biomass Valor*, 2, 77 (2011).
- [12] B. H. Hameed, D. K. Mahmoud, A. L. Ahmad, *J. Hazard. Mater.*, 158, 65 (2008).
- [13] S. Lagergren, *Handlinger.*, 24, 1 (1998).
- [14] Y. Zhou, Q. Jin, T. Zhu, Q. Zhang, T. Ma, *Cellulose Chemistry and Technology*, 46 (5-6), 319 (2012).
- [15] Y. S. Ho, Thesis, Univ. Birmingham, Birmingham, U. K. (1995).
- [16] F. Ferrero, *J. Hazard. Mater.*, 142, 144 (2007).
- [17] K. Farizadeh, M. E. Yazdanshenas, M. Montazer, A. Rashidi, R. M. A. Malek, *J. Textile Research*, 33, 443 (2009).
- [18] J. W. J. Weber, J. C. Morriss, *J. Sanit. Eng. Div. Am. Soc. Civil Eng.*, 89, 31 (1963).