2011 International Conference on Environment Science and Engineering
IPCBEE vol.8 (2011) © (2011) IACSIT Press, Singapore

Effect of cationic and anionic dye adsorption from aqueous solution by using chemically modified papaya seed

N. Nasuha, H.Z. Zurainan, H.I. Maarof, N.A. Zubir, N. Amri
Faculty of Chemical Engineering
Universiti Teknologi Mara (UiTM)
Permatang Pauh, 13500 Pulau Pinang, Malaysia
e-mail: norhaslinda342@ppinang.uitm.edu.my

Abstract— **Papaya seed (PS) was modified using chemically esterification of carboxyl group to improve performance in adsorption capacity for removal cationic and anionic dye from aquoues solution. The operation parameters investigated included initial concentrations, (50-500 mg/L) and various adsorbent (NPS and EPS). The experimental data were analyzed by using Langmuir and Freundlich models of adsorption. The adsorption isotherm data for MB were best fitted to the Langmuir isotherm and the maximum monolayer adsorption capacity was found to be 250.00 mg/g and 200.00 mg/g at 30°C for EPS and NPS respectively, while for CR for both adsorbents (NPS and EPS) the best fit experimental data were Freundlich isotherm. The adsorption kinetics can be predicted by the pseudo-first order and pseudo-second order.The experiment data were obeys pseudo-second order with higher coefficient of correlation $R^2 \geq 0.99$. The result revealed that NPS can be act as good adsorbent for removal anionic dye (CR) and EPS can be remarkable as excellent adsorbent modified of PS for cationic dye removal.**

Keywords-adsorption; methelyne blue; congo red; esterification, isotherm; kinetics

I. INTRODUCTION

Most of the industries such as textile, paper, printing, leather, food, cosmetics, etc. use dyes to colour their final product also consume substantial volume of water. As a result, they generate a considerable amount of coloured wastewater. Wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light [1]. The presence of dyes even in very low concentration is highly visible and causes damage to the environment as they are toxic to aquatic life [2, 3].

Methylene blue and congo red can be considered as hazardous chemical because it content highly toxic due to the large number of metal complex dye [4]. Methylene blue (MB) is the most commonly used substance for dying cotton, wood and silk. It can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [5]. Congo red (CR) is a benzidine-based anionic bisazo dye known to metabolize to benzidine, a known human carcinogen [6]. CR is toxic to animals and plants and thus its introduction to water stream is of potential health, environmental, and ecological concern. Therefore, CR and MB containing effluents have to be sufficiently treated before they are discharged into the water bodies.

Various methods have been identified for the dye removal from industrial effluent includes ion exchange, activated carbon adsorption, membrane technology and coagulation [7]. Adsorption techniques used activated carbon has been found as most efficient method used for removal dyes. However, it's used is still limited because higher the quality of activated carbon, the greater it operation costs. The need for regeneration and difficulty of separation from the wastewater after use are also major concerns associated with activated carbon [8]. Today, researchers have come out with study that has been focused on the low-cost adsorbents that are mainly obtained from agriculture waste and industrial by product since they required little processing and abundant in nature. Plant wastes are inexpensive as they have no or very low economic value.

Papaya seed is one of the agricultural wastes in Malaysia that can be used has an alternative low cost adsorbent in order to remove dyes from aqueous solution. The seeds are often times discarded as waste. The fruits have tremendous nutritional value and contain 1.5% protein, 0.1% fat, 7.1% carbohydrates, and 35.0 calories per 100 g edible fruit. They also contain high levels of calcium, iron, sodium, potassium, carotene, vitamin B2, niacin, and vitamin C [9].

Previously, some low cost plant waste had directly been used as adsorbent for dye adsorption from wastewater treatment. However, the application of untreated plant waste adsorbent can also bring several problems such as lower adsorption capacity, higher chemical oxygen demand (COD) and biological chemical demand (BOD) as well as total organic carbon (TOC) due to the released of soluble organic compound contained in the plant material [10]. Therefore, there are needs to modified agriculture waste product in order to increase its adsorption performance.

This study has been focusing on the modification method of adsorbent using chemical modification of esterification The comparison on adsorption capacity of cationic and anionic dye onto these modified adsorbents was studied since surface modification alone would substantially decrease the adsorbent preparation cost [11].

II. EXPERIMENTAL

A. Adsorbent

Papaya seeds (PS) used in this study was obtained from food factory waste, Simpang Ampat, Pulau Pinang. The seeds were washed with distilled water and boiled with water for 40 min. Then, the seeds were filtered out before been dried in an oven at 60 ^{0}C for 24 h in order to eliminate its moisture content. The dried materials were grinded and sieved into 125–250 μm to reduce it size into form of powder. The prepared papaya seed sample was stored in air-tight container and referred as NPS.

B. Adsorbate

Stock solution was prepared by dissolving 1.0 g of (MB) in 1 L distilled water. It was soaked slowly to make sure all MB powder has been dissolved in distilled water. This stock solution was stored for further used. This entire step has been repeated with CR instead of MB. The maximum wavelength for MB is 668 nm whereas CR is 500 nm.

C. Preparation of Treated Papaya Seed

Esterification was carried out by suspended 9.0 g of papaya seed into 633 ml of 99.9% pure methanol and 5.4 ml of 0.1 M HCl solution in a conical flask. The mixture was stirred for 3 hours. Then the esterified papaya seed was thoroughly washed with distilled water until reached pH 7, before been filtered and dried with 60 ^{0}C in an oven for 24 hours. It is then been stored for further used. The sample was referred as EPS.

D. Equilibrium studies

This experiment was carried out by adding 0.5 g of adsorbent into a six number of 250 ml conical flask containing specific volume 200ml at different initial concentration (50-500 mg/L) of dye solution of MB and CR without changing pH and temperature. The flask was placed in an orbital shaker and agitation was provided at 150 rpm for 180 min to make sure equilibrium was reached. The samples were taken for every 5 minutes in first 30 min, after that every 10 min in 60 min and the rest for every 15 min in 90 min. Final concentration of dye solution were analyzed using UV-vis spectrophotometer. The amount of equilibrium uptake of dyes is calculated by using:

$$q_e = \frac{(C_o - C_e)V}{W} \times 100 \quad (1)$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V (L) is the volume of the solution and W (g) is the mass of PS used. The percentage removal dye is defined as the ratio of difference in dye concentration before and after adsorption (C_o–C_e) to the initial concentration of dye in the aqueous solution (C_o) and was calculated using the equation:

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

III. RESULT AND DISCUSSIONS

A. Effect of dye adsorption by chemical modification on (MB) and (CR)

Fig. 1 shows the influence of chemical modification on adsorption percentages of cationic dyes. EPS obtained highest percentage removal between 96.29 to 86.55% compared to NPS that resulted 91.79% to 69.75% with initial concentration increased from 50 to 500 mg/g. It indicates that carboxyl group bearing negative charge inhibited the adsorption of anionic dyes. In order to remove negative charge from carboxyl group by esterification, the dye uptakes of CR were visibly increased [12].

Fig.2 shows the effects of chemical modification on the percentage removal of anionic dyes. From the result obtained, it shows that NPS had highest percentage in removal CR compared to EPS. At equilibrium time, the %removal of NPS is between 76.30% to 25.99%compared to EPS that resulted 57.71% to 26.86% for increasing in initial concentration of dye solution from 50 to 500 mg/L. This experimental result proved that carboxyl group was major functional group in the adsorption of cationic dyes.

B. Effect of initial concentration and contact time

The effect on initial concentration (50-500 mg/L) of MB adsorption onto EPS are presented in fig. 3. A rapid increased is observed for the first 15 min and it then proceeds slowly until reached equilibrium. This may due to the increased in the number of vacant surface sites available at initial stage. The equilibrium adsorption of MB is increased from 17.61 to 118.65 mg/g as increasing concentration of MB from 50 to 500 mg/g. It was significant different with percentage removal that decreased from 88.08 to 59.32% as initial concentration increased. The adsorption of MB at low concentration 50 and 100 mg/g achieve equilibrium in less than 20 min while in high concentration the time necessary to achieve equilibrium was 120 min.

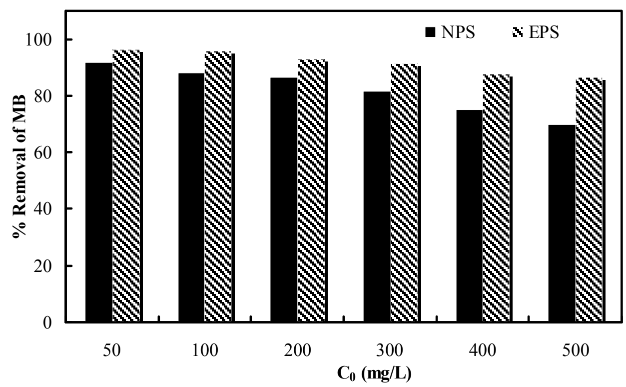

Fig. 1. Influence of chemical modification on adsorption of MB by papaya seed

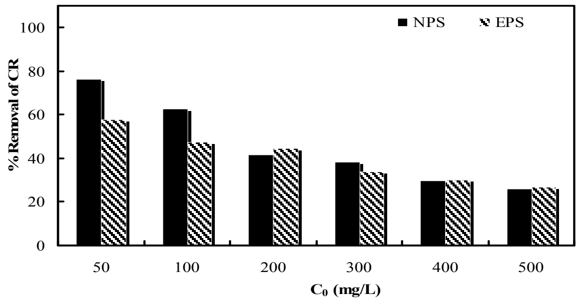

Fig. 2. Influence of chemical modification on adsorption of CR by papaya seed

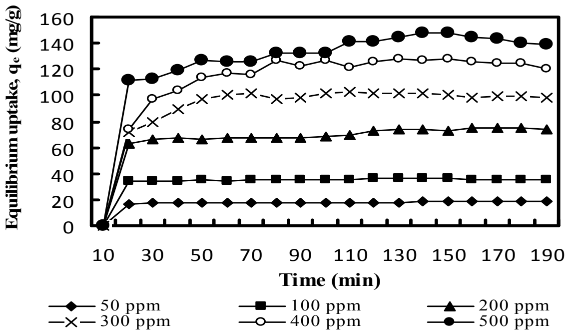

Fig. 3. Effect of contact time and initial concentration on the adsorption of MB on EPS

Fig. 4 shows the effect on initial concentration of CR adsorption onto EPS. Equilibrium adsorption of CR onto EPS increased from 10.78 to 50.69 mg/g and percentage removal is decreased from 53.9 to 25.33% as initial concentration increased. After 15 min, adsorption of methylene blue was proceed slowly until it reached equilibrium saturated. Data was collected until 180 min to ensure equilibrium adsorption has been achieved.

C. Adsorption isotherms

The adsorption isotherm represents the relationship between the amount adsorbed by a unit weight of solid adsorbent and the amount of adsorbate remained in the solution at equilibrium time [13]. Langmuir and Freundlich isotherms are commonly used to describe the equilibrium characteristic of adsorption. This experimental data were fitted to both isotherm models. Linear regressions were used to determine the best fit model and least squares has been widely used for obtaining the isotherm constant.

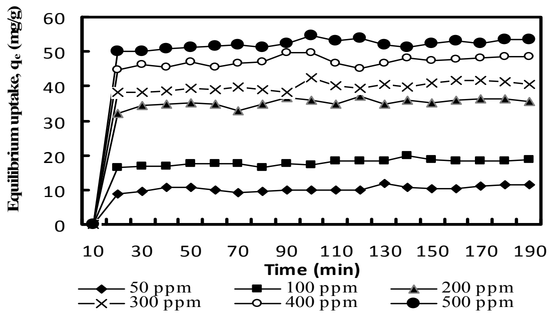

Fig. 4. Effect of contact time and initial concentration on the adsorption of CR on EPS

Langmuir isotherm [14] refers to homogeneous adsorption, which adsorption can only occur at a fixed number of definite localized sites, with no transmigration of the adsorbate in the plane of the surface. The Langmuir model can be given as

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{1}{q_{\max}} C_e \quad (3)$$

where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), and q_{max} (mg/g) and K_L are the Langmuir isotherm constants related to free energy. The above equation can be linearized to get the maximum capacity, q_{max} by plotting a graph of C_e/q_e vs. C_e.

The linear form of the Freundlich isotherm [15] model is derived assuming a heterogeneous surface of adsorption capacity and adsorption intensity with a non-uniform distribution of heat of adsorption. The Freundlich model can be given as:

$$q_e = K_F C_e^{\,1/2} \quad (4)$$

Rearranging eq. 3,

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where K_F and 1/n are Freundlich isotherm constant (mg/g) $(dm^3/g)^n$ related to adsorption capacity. A plot of log q_e vs log C_e yields a straight line, with a slope of 1/n and intercept of ln K_F.

The Langmuir and Freundlich isotherm parameters along with their regression coefficients for MB and CR are listed in Tables 1. Tables 1 show that the Langmuir isotherms appear to fit the experimental data of MB better than the Freundlich isotherms, as reflected by correlation coefficients (R^2). This indicates that the adsorption of MB on NPS and EPS is homogeneous distribution of active sites in adsorption affinity. As shown in results (Table 1), the EPS was performed better than NPS for removing MB. Esterification brings negative charge of ion which is different with positive ion carried by metyhlene blue. This condition has lead to the decreasing in removal dye of MB due to the increasing repulsive force between surface functional group of papaya seed and MB that mainly exists was a cation form. Adsorption on CR on NPS shows that both Freundlich and Langmuir isotherms was fit to the experimental data. Physical interactions can be considered as the most effective in MB adsorption. Besides the physical interactions, some of MB ions would be adsorbed via ion-exchange.

Freundlich isotherm fit the experimental data of CR for EPS and NPS better than Langmuir isotherms. It shows that the Freundlich isotherm can be used for non-ideal sorption that involves heterogeneous surface energy systems. The heterogeneity is caused by presence of different functional group on the surface, and also by various mechanism of adsorbent-adsorbate interaction. As a result, it is allowing multi-layer adsorption. The larger value of K_F indicates the higher value of adsorption. The more heterogeneous the surface will bring the 1/n value closer to zero [16]. The magnitude of the exponent 'n' gives indication of the favorability and K_F the capacity of the adsorbent or adsorbate system.

D. *Kinetic Study*

The kinetic adsorption data were processed to study the dynamics of the adsorption process in expressions of the order of rate constant.

The specific rate constants, k_1, for the adsorption of MB and CR on NPS and EPS were commonly obtained pseudo-first and pseudo-second-order kinetic models

Kinetic data were analyzed with the pseudo-second-order kinetic models. The pseudo-second-order kinetic can be presented by equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_e} t \tag{6}$$

The linear plots of t/qt versus t (Figure not shown) experimental data are fit with the pseudo second-order-kinetic model for the both cationic and anionic dyes. The R_2 values for pseudo second- order model were ≥0.98, which is higher than the R_2 values obtained for the pseudo-first-order model. The calculated q_e and k_2 for all cases are represented in Table 2. From the Table 2 and Table 3, it shows that the experimental data and the correlation coefficients for the second-order kinetic model are better represented the adsorption kinetics, suggesting that the adsorption process was controlled by chemisorption [18, 19].

TABLE I. ISOTHERM CONSTANTS FOR THE ADSORPTION OF MB AND CR BY NPS AND EPS

		CR		MB	
Isotherm	**Parameter**	***NPS***	***EPS***	***NPS***	***EPS***
Langmuir	q_{max}	71.43	58.8	200	250
	K_L	0.07	0.02	0.022	0.038
	R^2	0.942	0.98	0.952	0.967
Freundlich	K_F	1.43	2.26	2.59	3.25
	n	1.02	2.84	1.75	1.703
	R^2	0.97	0.99	0.989	0.989

TABLE II. PSEUDO-SECOND-ORDER KINETIC PARAMETERS FOR REMOVAL OF CR BY NPS AND EPS AT 30 ^{0}C

C_o (mg/g)	EPS			NPS		
	q_e	K_2 (1/min)	R^2	q_e	K_2 (1/min)	R^2
50	18.18	0.014	0.99	19.22	0.054	0.99
100	30.30	0.005	0.99	37.03	0.045	0.99
200	37.04	0.004	0.99	76.92	0.013	0.99
300	38.46	0.005	0.99	111.4	0.009	0.99
400	43.48	0.009	0.99	142.5	0.007	0.99
500	50.00	0.010	0.99	200.6	0.005	0.99

TABLE III. PSEUDO-SECOND-ORDER KINETIC PARAMETERS FOR REMOVAL OF MB BY NPS AND EPS AT 30 ^{0}C

C_o (mg/g)	NPS			EPS		
	q_e	K_2 (1/min)	R^2	q_e	K_2 (1/min)	R^2
50	18.18	0.101	0.98	10.86	0.009	0.98
100	37.03	0.035	0.99	18.51	0.002	0.99
200	76.92	0.006	0.99	76.92	0.002	0.99
300	111.1	0.003	0.97	41.66	0.001	0.99
400	142.8	0.002	0.99	47.61	0.001	0.99
500	166.6	0.001	0.99	55.55	0.001	0.99

IV. CONCLUSIONS

Present studies shows that the chemical modification esterification of carboxyl group could increased the performance adsorption capacity of papaya seed in removal cationic dye from aqueous solution compared to anionic dye. It shows that carboxyl group was major functional group in cationic dye. The adsorption isotherm data for MB were best fitted to the Langmuir isotherm and the maximum monolayer adsorption capacity was found to be 250.00 mg/g and 200.00 mg/g at 30 ^{0}C for EPS and NPS respectively. Meanwhile for CR, the best fit isotherm model was Freundlich isotherm. The adsorption kinetics can be predicted by the pseudo-second order model. The results would be useful for the designing of wastewater treatment plants for the removal of various types of dye especially cationic dyes. Since the raw material papaya seed abundantly in large quantities the treatment method seems to be economical.

ACKNOWLEDGMENT

The authors acknowledge the research grant provided by Universiti Teknologi Mara under the Research Management Institute (RMI) Scheme. (Project: 600-RMI/ST/FRGS 5/3/Fst (129/2010).

REFERENCES

[1] V.K. Garg, R. Gupta, A.Yadav, R. Kumar, "Dye removal from aqueous solution by adsorption on treated sawdust", Bioresour. Technol., vol. 89, 2003, pp.121–124.

[2] T. Robinson, G. McMullan, R. Marchant, P. Nigam, "Remediation of dyes in textiles effluent: a critical review on current treatment technologies with a proposed alternative", Biresour. Technol., vol. 77, 2001, pp. 247–255.

[3] M. Rafatullah, O. Sulaiman , R. Hashim, A. Ahmad, "Adsorption on methyhlene blue on low cost adsorbent : A review," J.Hazard. Meter., vol. 177, 2010, pp.70–80.

[4] I.M. Banat, P. Nigam, D. Singh, R. Marchant, "Microbial decolourization of textile-dye-containing effluents: a review", Bioresour. Technol., vol. 58, 1996, pp.217–227.

[5] I.D. Mall, V.C. Srivastava, N.R. Agarwa, I.M. Mishra, "Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses," Chemosphere vol. 61, 2005, pp. 492–501.

[6] R. Ahmad, R. Kumar, "Adsorption studies of hazardous malachite green onto treated ginger waste", Appl. Surf. Sci., vol. 91 (4), 2010, pp.1032-1038.
[7] S. T. Ong, C. K. Lee,Z. Zainal, "Removal of basic dye and reactive dyes using ethylenediamine modified rice hull", Bioresour. Technol., vol. 98, 2006, pp.2972–2799.
[8] C.H. Weng, Y.T. Lin, T.W . Tzeng, "Removal of methylene blue from aqueous solution by adsorption onto pineapple leaf powder", J.Hazard. Meter., vol. 170, 2009, pp. 417–424.
[9] E.K. Marfo, O.L Oke, O.A. Afolabi, "Chemical composition of papaya (Carica papaya) seeds", Food Chemistry, vol. 22, 1986, pp.259–266.
[10] W.S. Wan Ngah, M.A.K.M. Hanafiah, "Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review", Bioresour.Technol., vol. 99 , 2008, pp.3935–48.
[11] M.H. Kalavathy, L.R. Miranda, "Comparison of copper adsorption from aqueous solution using modified and unmodified Hevea brasiliens saw dust", Desalination, vol. 255, 2010, pp.165–174.
[12] R.Gong, Y.Suna,J.Chen, H.Liu and C.Yang, "Effect of chemical modification on dye adsorption capacity of peanut hull", Dyes and Pigments, vol. 67, 2005, pp.175–181.
[13] Z.Hu, H.Chen, S.Yuan, "Removal of Congo Red from aqueous Solution by cattail root", J.Hazard.Meter., vol. 173, 2010, pp.292–297.
[14] I. Langmuir, "The constitution and fundamental properties of solids and liquids," J. Am. Chem. Soc., vol.38 (11), 1916, pp. 2221–2295.
[15] H.M.F. Freundlich, "Over the adsorption in solution", J. Phys. Chem., vol.57, 1906, pp.385–47.
[16] I.D.Mall, V.C.Srivasta, N.K.Agarwal, I.M.Minshra, "Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: Kinetic study and equilibrium isotherm analyses", Chemosphere, vol. 61, 2005, pp.492–501.
[17] S. Azira, T.N. Wong, Y.Robiah, T.G.Chuah, "Adsorption of methylene blue onto palm kernel shell activated carbon", E. Proceeding Regional Conference For Young Chemists 2004. University Sains Malaysia, Penang, Malaysia.
[18] B.H.Hameed, "Spent tea leaves: A new non-conventional and low-cost adsorbent for removal", J. Hazard. Meter., vol.161, 2009, pp.753–759.
[19] N. Nasuha, B.H.Hameed, A.T. Mohd Din, "Rejected tea as a potential low cost adsorbent for the removal of methylene blue", J. Hazard. Meter, vol. 175, 2010, pp.126–132.
[20] A. Kumar, S. Kumar, "Adsorption of resorcinol and catechol on granular activated carbon: equilibrium and kinetics", Carbon, vol. 41, 2003, pp.3015–3025.
[21] D .Mohan, K.P. Singh, S. Sinha, D. Gosh, "Removal of pyridine from aqueous solution using low cost activated carbons derived from gricultural waste materials", Carbon, vol. 42, 2004, pp.2409–2421.