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Utilization of Fruits Peel as a Sorbent for Removal of Methylene Blue

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The potential of using fruits skin as a low cost sorbent in the removal of methylene blue from aqueous solution was studied. The sorption behaviour of various fruits skin for methylene blue was carried out as a function of pH, contact time, concentration of methylene blue and sorption isotherms. The sorption process was rapid with high percentage of uptake taking place within the first 1 h, regardless of its initial concentration. Different kinetic models were selected to interpret the experimental data. The sorption process conformed to Langmuir isotherm and maximum sorption capacities for methylene blue were 56.50, 34.97, 50.51, 48.54, 48.31 and 78.74 mg/g for mangosteen's peel, pulasan's peel, pineapple's peel, durian husk, orange's peel and pamelo's peel, respectively. Mathematical models were employed to analyze and explain experimental data obtained. It was found that application of pseudo-second order kinetics provides better correlation of the experimental data than the pseudo-first order model for the different systems studied.

Key Words: Sorption, Methylene blue, Fruits peel, Batch study, Kinetic model.

INTRODUCTION

Dye, a constituent that is widely used in many industries is an easily recognized pollutant. It is estimated that there are more than 100,000 commercially available dyes with over 7×10^5 tonnes of dyestuff being produced annually[1]. A very small amount (10-50 mg/L) of dyes in wastewater is highly visible and will have an inhibitory effect on the food web due to the reduction in light penetration. As such, the removal of dyes from aqueous environment is considered as a challenging problem in the control of environmental pollution as dyes are generally stable to light, oxidizing agent and are resistant to aerobic digestion.

Conventional technologies for colour removal from industrial effluents include biological treatment, coagulation, ozonation, electrochemical processes, nanofiltration and activated carbon adsorption[2]. Amongst all, the sorption process by activated carbon is one of the most efficient techniques but drawback such as high capital and problems with the spent carbon limits its large-scale application. Thus, there is a need to search for economical process to remove dyes from aqueous environment. Materials which are found to possess the quality of efficient sorbents could be processed to replace costly ion exchange and activated carbon problem. These materials, including sugarcane bagasse, castor seed shell, rice hull and spent tea leaves that have the advantage of being inexpensive and readily available[3-6]. In our continued effort to use low-cost materials for the removal of dye, the potential of using various fruits skin as a sorbent for methylene blue removal was attempted under batch experiment condition.

EXPERIMENTAL

Sorbates: The cationic dye methylene blue (C.I. = 52015) was purchased from Sigma-Aldrich Chemical Company and used as received without further purification. Synthetic dye solution of methylene blue with the concentration of 1000 mg/L was prepared as stock solution and subsequently diluted when necessary. The chemical structure of methylene blue is shown in Fig. 1.

Sorbents: The sorbents used in this study were the fruit's peel from mangosteen, pulasan, pineapple, durian, orange and pomelo. The fruit's peels obtained were washed thoroughly with tap water and boiled in water until the filtrate was clear. The materials were then subjected to overnight drying at 60 ºC in the oven. The dried sorbents were ground and sieved to pass through a 1 mm sieve and labeled as mangosteen's peel,

pulasan's peel, pineapple's peel, durian husk, orange peel and pomelo's peel.

Fig. 1. Structure of methylene blue

Batch experiments: Sorption experiments were performed by agitating 0.1 g of sorbent in 20 mL of 50 mg/L dye solution in a centrifuge tube at 150 rpm on an orbital shaker for 4 h at room temperature (25 ± 2 ℃) unless otherwise stated. All experiments were conducted in duplicates and the results stated are the means. Controls without sorbent were simultaneously carried out to ascertain that sorption was due to sorbent and not the wall of the centrifuge tube. The percentage of dye uptake was calculated using the following equation:

$$\% \, \text{Uptake} = \frac{(C_o - C_t)}{C_i} \times 100 \% \qquad (1)$$

where, C_o is the initial concentration and C_t the concentrations at time t.

Effect of pH: A series of 100 mg/L methylene blue dye solutions were prepared. The initial pH of the dye solutions was adjusted to the range of 5-10 by adding dilute HCl or NaOH.

Effect of initial dye concentration and contact time: Contact time experiments were performed using methylene blue dye solutions with concentrations of 50 and 100 mg/L. The samples were withdrawn and analyzed for their dye concentrations at predetermined intervals.

Sorption isotherm: Equilibrium studies were performed by agitating 0.10 g of durian husk with 20 mL of dye solution at various methylene blue concentrations (ranging from 100 to 500 mg/L). The amount of dye adsorbed at equilibrium, can be calculated with the equation:

$$q_e = \frac{C_o - C_e(V)}{W} \qquad (1)$$

where, C_o = Initial dye concentration (mg/L); C_e = Equilibrium dye concentration (mg/L); V = Volume of dye used (mL); W = Weight of sorbent used (g).

Surface morphology: The samples were ground and palletized using a pellet compressor before it was stuck on a stub using double-sided tape. Before the sample was analyzed, the prepared pellet was coated with a thin layer of gold to prevent the occurrence of charging effect.

Techniques: The dye concentrations were analyzed using a Perkin Elmer Lambda 35 UV-VIS spectrophotometer. All measurements were made at the wavelength corresponding to maximum absorption for methylene blue, λ_{max} = 664 nm. Dilutions were carried out when measurement exceeded the linearity of the calibration curve. The surface morphology of all the sorbents was studied using scanning electron microscope (SEM), which is equipped with energy dispersive X-ray spectrometer (SEM-EDX)- JEOL JSM-6400.

RESULTS AND DISCUSSION

Effect of pH: The sorption behaviour of methylene blue by all the sorbents at different pH values was studied and the results obtained are shown in Fig. 2. The optimum pH for the removal of methylene blue by most of the investigated sorbents was found to be in the range of 6-9. Within this pH range, an uptake greater than 93 % was achieved. Lower uptake of methylene blue in the acidic condition was probably due to the presence of H^{+} ion competing with cation groups for the sorption sites. With increasing pH, the number of positively charged sites decreased and the number of negatively charged sites increased. This phenomenon favours the sorption of positively charged dye due to electrostatic attraction[7-9].
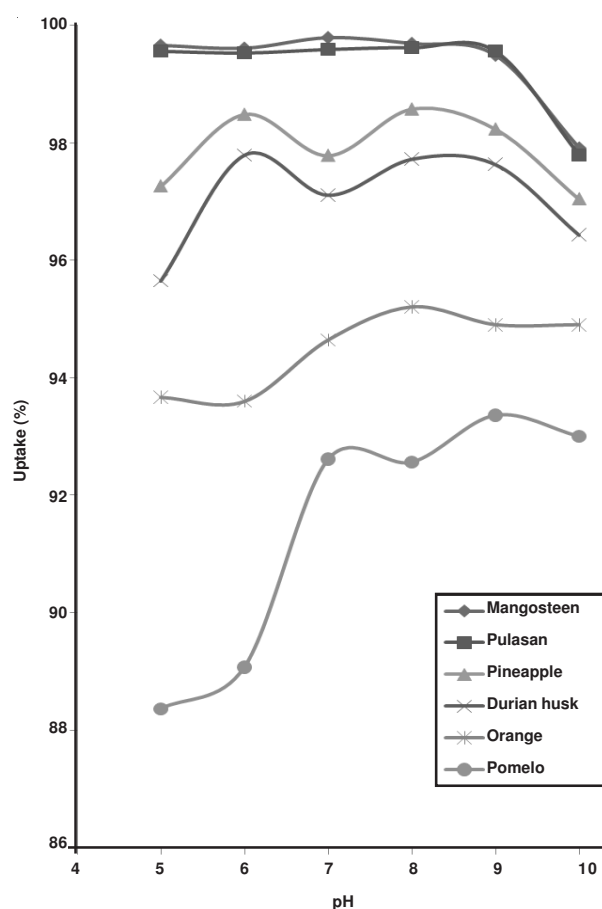
Fig. 2. Effect of pH on the sorption of methylene blue

The previously reported work for the removal of methylene blue onto the garlic peel also showed[10] that the percentage of dye removal increased with increasing pH from 4 to 6. In other study, the sorption of methylene blue became favourable at higher pH and this was attributed by the electrostatic interaction of cationic methylene blue species with the negatively charged hazelnut shell surface[11].

Effect of initial dye concentration and contact time: The rate of methylene blue sorption by various fruits peel at initial dye concentrations of 50 mg/L (Fig. 3) and 100 mg/L (Fig. 4) showed that the uptake was rapid and equilibrium was attained within 1 h. These results agreed well with most of the available sorption studies in literature, whereby the up
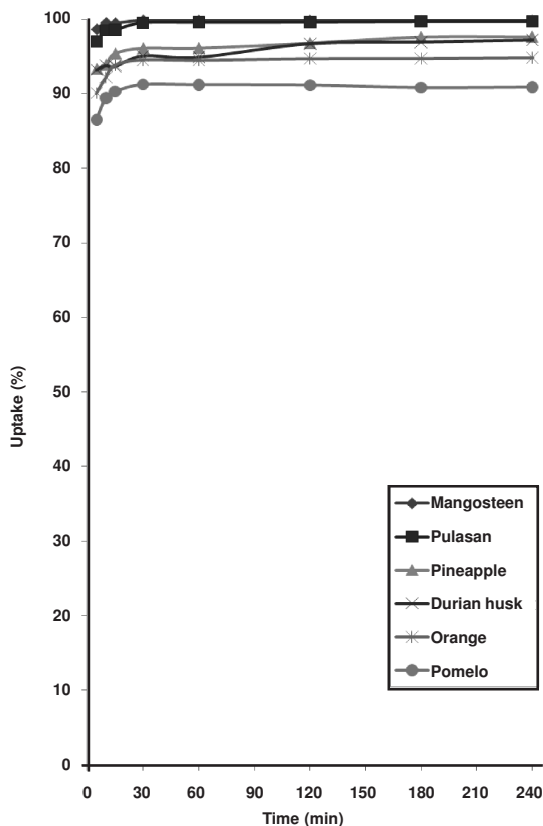
Fig. 3.   Effect of initial dye concentration and contact time on the sorption of methylene blue (50 mg/L)
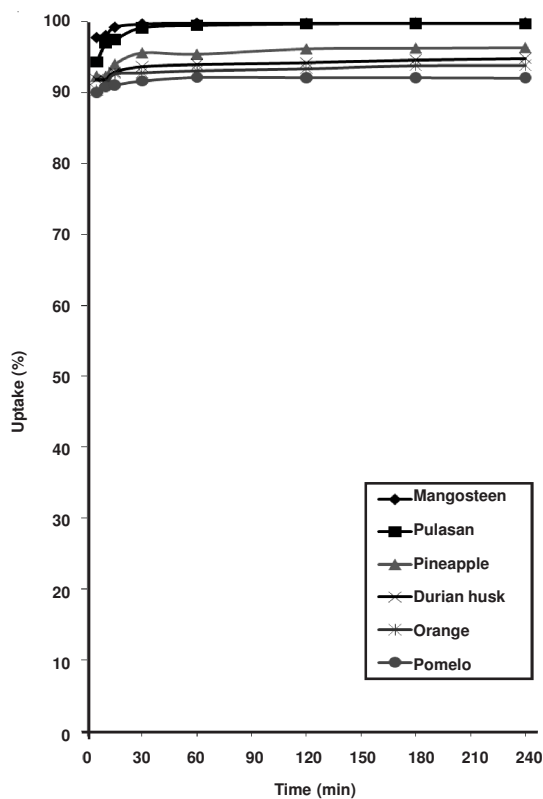

Fig. 4.   Effect of initial dye concentration and contact time on the sorption of methylene blue (100 mg/L)

take of sorbate species is fast at the initial stages of the contact period and thereafter, it becomes slower near the equilibrium. The fast uptake at the beginning may be attributed to the rapid

attachment of the dye molecules to the surface of the sorbent and the following slower sorption due to intraparticle diffusion[12].

The kinetics involved in the sorption of methylene blue onto the sorbents was investigated in order to gather more information about the mechanism of the sorption process. The experimental data were fitted into two kinetics models, namely pseudo-first and pseudo-second order kinetic models. The equations involved can be expressed as follows:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad \text{(pseudo-first order of Lagergren}^{13}) \quad (2)$$

and

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad \text{(pseudo-second order}^{14}) \quad (3)$$

where, q_e = the amount of dyes sorbed at equilibrium (mg/g), q_t = the amount of dyes sorbed at time t (mg/g), k_1 = the rate constant of pseudo-first order sorption (1/min), h ($k_2 q_e^2$) = the initial sorption rate (mg/g min) and k_2 = the rate constant of pseudo-second order kinetics (g/mg min).

In many cases, the kinetics of sorption by biological materials is described by the pseudo-first order kinetics. However, in this study, it was found that the pseudo-first order equation did not fit well for the whole range of concentrations studied and the equilibrium sorption capacities calculated from the first order kinetic model gave unreasonable values compared to those determined experimentally. It thus appears that the system under study is more appropriately described by the pseudo-second order model which was based on the assumption that the rate limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electron between sorbent and sorbate[14]. The plots of t/q_t *versus* t for 50 mg/L methylene blue dye solutions are shown in Fig. 5.
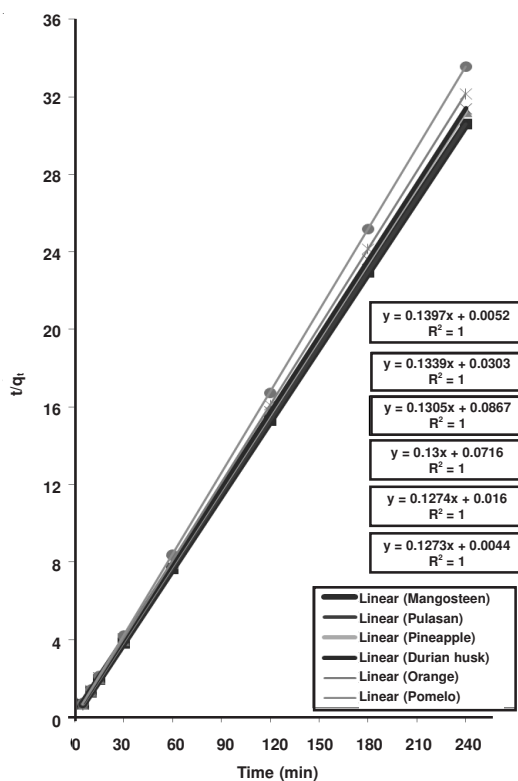

Fig. 5. Pseudo-second order kinetics of methylene blue at 50 mg/L

TABLE-1
LANGMUIR AND FREUNDLICH CONSTANTS FOR THE SORPTION OF METHYLENE BLUE

Sorbent	Langmuir			Freundlich		
	Q_o (mg/g)	K_L (L/mg)	R^2	K_f	n	R^2
Mangosteen's peel	56.50	0.481	0.995	21.53	3.99	0.930
Pulasan's peel	34.97	3.287	0.999	18.11	3.88	0.751
Pineapple's peel	50.51	0.151	0.995	11.40	2.95	0.968
Durian husk	48.54	0.100	0.998	8.43	2.60	0.956
Orange's peel	48.31	0.063	0.983	5.70	1.87	0.980
Pamelo's peel	78.74	0.030	0.997	3.26	1.38	0.977

The values of q_e, k_2 and h against C_0 in the corresponding linear plots of the pseudo-second order equation were regressed to obtain expressions for these values in terms of the initial dye concentration. Thereafter, the generalized predictive models for methylene blue sorbed at any contact time and initial concentration within the given range with relationship of q_e, C_0 and t can be calculated. From all the plots, it is clear that the theoretically generated curves agreed well with the experimental data. The representative plot is as shown in Fig. 6, involving the sorption of methylene blue by mangosteen's peel.
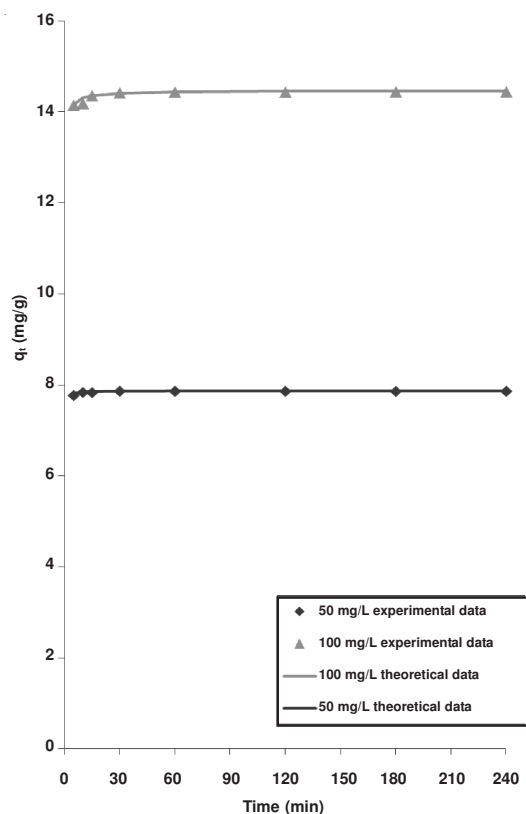

Fig. 6. Comparison between measured and pseudo-second order time profile for methylene blue sorption on mangosteen's peel

Sorption isotherm: The equilibrium data of the sorption of methylene blue was fitted into both Langmuir and Freundlich equations. The linearized Langmuir model is written as:

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \qquad (4)$$

whereas the linear form of Freundlich isotherm model can be represented as:

$$\log q_e = \frac{\log C_e}{n} + \log K_f \qquad (5)$$

where C_e = the equilibrium liquid phase dye concentration (mg/L), q_e = the amount of dye adsorbed at equilibrium (mg/g), Q_o = the maximum adsorption capacity (mg/g), K_L = the adsorption equilibrium constant (L/mg), n = Freundlich constant for intensity and K_f = Freundlich constant for adsorption capacity.

The coefficients for the linearized forms of the isotherm models for the sorption of methylene blue on the investigated sorbents are listed in Table-1. Both Langmuir and Freundlich models appeared to provide reasonable fittings for the sorption data. No doubt these two models are based on different assumptions: Langmuir model implies monolayer coverage and constant sorption energy while the Freundlich model deals with physico-chemical sorption on heterogeneous surfaces, however, the applicability of both isotherms to sorption of dyes by agricultural wastes, activated carbons prepared from wastes and treated spent bleaching earth have been reported previously[5,7,15-16].

Surface morphology: The surface morphology of mangosteen's peel, pulasan's peel, pineapple's peel, durian husk, orange peel and pomelo's peel was examined using scanning electron microscope. Figs. 7-12 showed the SEM micrographs of mangosteen's peel, pulasan's peel, pineapple's peel, durian husk, orange peel and pomelo's peel, respectively. From the SEM micrographs, it is also clear that all the investigated sorbents are non-porous materials, due to the absence of pores and cavities.
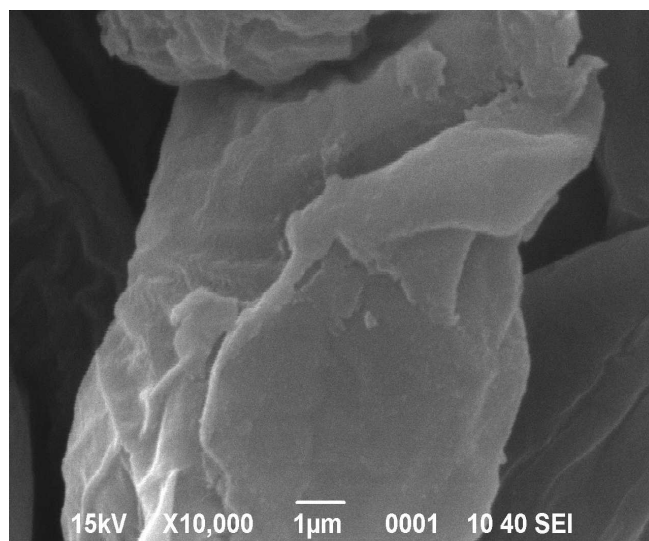

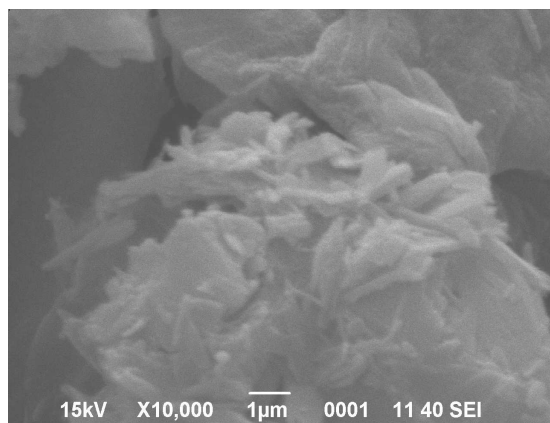Fig. 7. SEM micrograph of mangosteen's peel
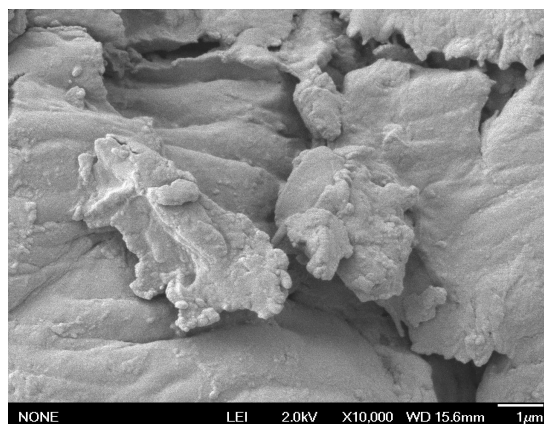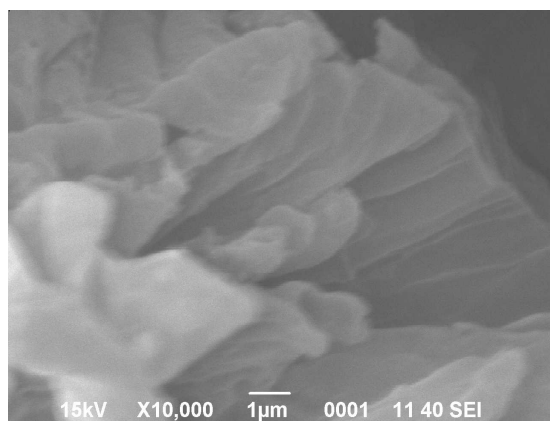
Fig. 8. SEM micrograph of pulasan's peel

Fig. 9. SEM micrograph of pineapple's peel
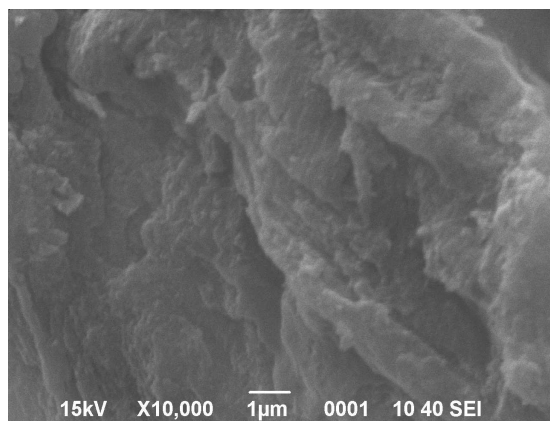

Fig. 10: SEM micrograph of durian husk

Fig. 11. SEM micrograph of orange's peel

Fig. 12. SEM micrograph of pamelo's peel

Conclusion

Based on the experimental results, it revealed that all the six proposed sorbents *i.e.*, mangosteen's peel, pulasan's peel. pineapple's peel, durian husk, orange peel and pomelo's peel, have the potential to be low-cost material for removing methylene blue, a basic dye from aqueous solution. Sorption of me thylene blue was pH dependent and the optimum pH was observed at pH 8-9. The isotherm study showed that equilibrium sorption data of methylene blue on all the investigated sorbents conform to both Langmuir and Freundlich isotherm models. The maximum sorption capacities calculated based on the Langmuir isotherm model was in the range of 35-78 mg/g. From the SEM micrographs, it showed that all the investigated sorbents are non-porous materials, due to the absence of pores and cavities.

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