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Adsorption of Dyes From Aqueous Solution by Pummelo (*Citrus grandis* (L.) Osbeck) Peel

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Laboratory investigations of the potential use of powdered pummelo peel as a sorbent for removal of the methylene blue, neutral red and congo red from aqueous solutions were conducted. The effects of various experimental parameters (*e.g.*, initial pH, sorbent dose, initial dye concentration and contact time) were tested and optimal experimental conditions were ascertained. The isothermal data of methylene blue and neutral red fit the Langmuir model well and the processes of adsorption follow first order rate kinetics. As to the anionic dye congo red, the adsorption basically obeys Langmuir isotherm, but the uptake rate is rather lower than those of methylene blue and neutral red. The results in this study indicate that pummelo peel is a promising candidate for removing cationic dyes methylene blue and neutral red from the dye wastewater.

Key Words: Adsorption, Dye, Kinetics, Pummelo peel, Waste materials.

INTRODUCTION

Dyes are used widely in modern industrial society. Most of them are inert and difficult to biodegrade when discharged into waste streams due to their synthetic origin and complex aromatic molecular structures. Even small quantities of dyes can colour large water bodies. As a result, it not only affects aesthetic merit but also reduces sunlight penetration and photosynthesis. In addition, some dyes or their metabolites are either toxic or mutagenic and carcinogenic[1,2].

Many biological, physical or chemical methods have been used for dye wastewater treatment[3-7]. Adsorption techniques are proved to be an effective and attractive process for removal of non-biodegradable pollutants (including dyes) from wastewater[8,9].

Many efforts have been made to investigate the use of various low cost organic sorbents due to higher cost of activated carbon. These sorbents should be cheap, easily available and disposable without regeneration. These materials are derived from natural resources, plant wastes or industrial by-products. Most of them are cellulose-based and can be used without any previous thermal or chemical treatment. Adsorption of dyes has been studied using sorbents such as peanut hull[10], rice husk[11], water hyacinth roots[12], guava seeds[13], algae *Sargassum muticum*[14], *etc.*

Pummelo (*Citrus grandis* (L.) Osbeck) is giant citrus and parent of many citrus fruits. Pummelos are native to Southeast Asia and grown mainly in eastern countries including China, Japan, India, Fiji, Malaysia and Thailand[15]. They are featured by very thick and soft peel. However, Pummelo peel is usually thrown away as waste in many places of China.

In this work, batch experiments were performed on pummelo peel towards aqueous solutions of methylene blue (MB), neutral red (NR) and congo red (CR). The equilibrium and kinetic data of the adsorption were then examined in order to better understand the adsorption.

EXPERIMENTAL

The pummelo peel used in this study was obtained from a local fruit market of Nanjing, China. The collected biomaterial was rinsed with distilled water, cut into small pieces and then dried in an oven at 60 ºC for 48 h. Dry biomass was crushed into granules, sieved to different particle sizes and then 60-100 mesh particles were preserved in desiccators for use.

The three dyes (Table-1) were purchased from Sanaisi reagent Ltd. (Shanghai, China) and used without further purification. Their chemical structures are shown in Fig. 1. The dye stock solutions were prepared by dissolving accurately weighted dyes in distilled water to the concentration of 1000 mg L^{-1}. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations.

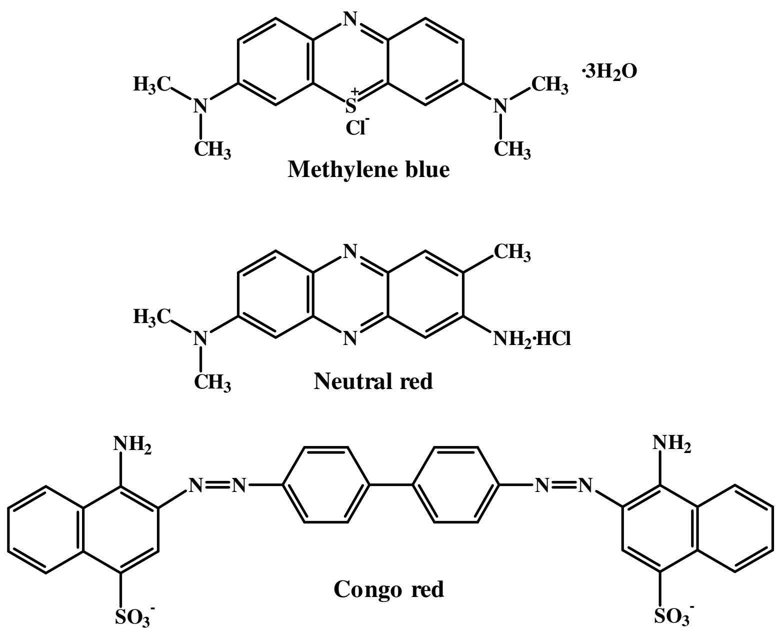


Fig. 1. Chemical structures of the three dyes

TABLE-1
GENERAL DATA OF THE THREE DYES USED IN THE PRESENT WORK

Trade name	C.I. no	FW	λ_{max} (nm)
Methylene blue (MB)	52015	373.9	663
Neutral red (NR)	50040	288.8	530
Congo red (CR)	22120	696.7	500

General procedure: Adsorption experiments were carried out in a rotary shaker at 150 rpm and 30 ºC using 100 mL flasks containing 40 mL of dye solutions with different concentrations and initial pH values. The initial pH values of the solutions were previously adjusted with 0.1 M HNO_3 or NaOH. Different doses of sorbent were added to each flask and then the flasks were sealed to prevent change in volume of the solution during the experiments. After shaking for predetermined time intervals, the samples were taken out from the flasks and the dye solutions were separated from the sorbent by filtration with a 200 mesh stainless steel sieve and then centrifuged (BECKMAN J2-MC, USA). Dye concentrations in the supernatant solutions were estimated by measuring the absorbance at the selected maximum wavelengths using a spectrophotometer (VIS-7220, Beijing, China). The amount of dyes sorbed by the biomaterial was calculated using the following equation:

$$q = (C_0\text{-}C_e)\ V/W$$

where q (mg g^{-1}) is the amount of dye sorbed by biomass, C_0 and C_e (mg L^{-1}) are the initial and equilibrium liquid-phase concentrations of the dye, respectively. V (L), the initial volume of dye solution and W (g), the weight of the pummelo peel.

The experiments were conducted in triplicate and the negative controls (with no sorbent) were simultaneously carried out to ensure that sorption was by pummelo peel and not by the container.

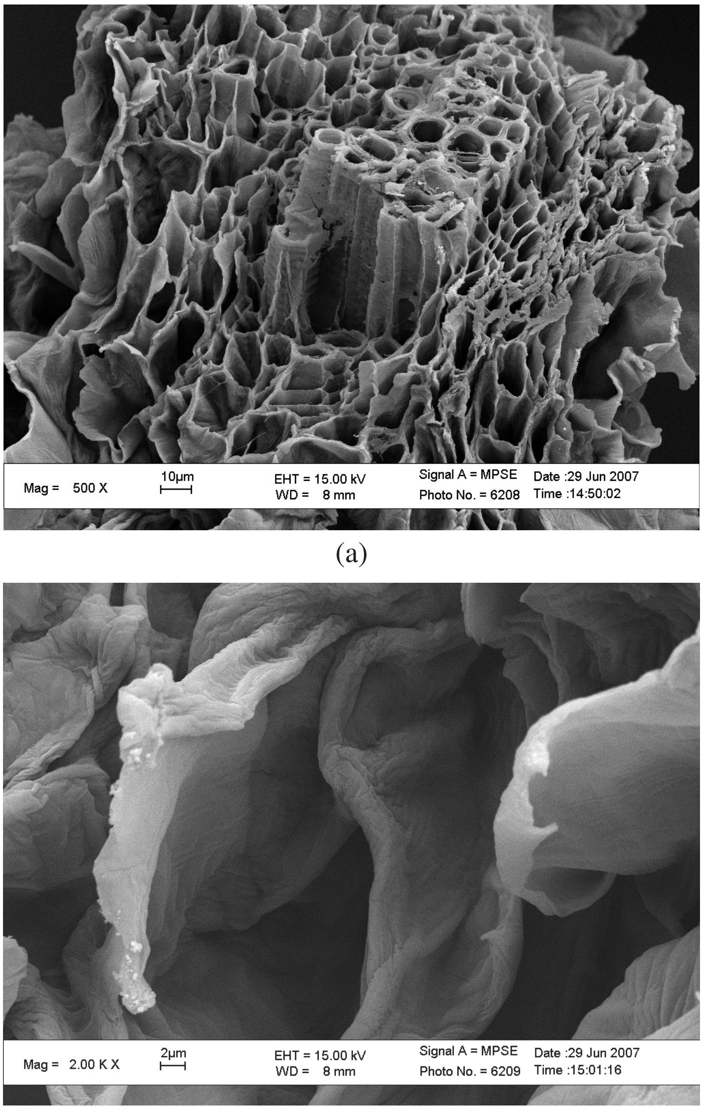
Detection method: The IR spectra of pummelo peel were obtained using a Fourier transform infrared spectrometer (VECTOR 22, Bruker) and the surface and cross section of pummelo peel were observed by scanning electron microscopy (SEM, JSM6300).

RESULTS AND DISCUSSION

IR and SEM studies: The infrared spectrum showed the following bands (ν_{max}, cm^{-1}): 3424 (-OH or N-H), 2925 (C-H), 1741(C=O), 1627 (C=C), 1051(C-O-H).

Based on analysis of the images (Fig. 2) taken by SEM before the adsorption process. It is observed that the highly heterogeneous pores with diameters about 10 or 2 μm are distributed in pummelo peel particles.

Effect of initial pH: The pH value of the solution was an important controlling parameter in the adsorption process and the initial pH value of the solution has more influence than the final pH. The pH ranges selected for MB, NR and CR were 3-11, 4-7 and 4-9, respectively. To avoid dye precipitation, the selected pH ranges



(a)

(b)

Fig. 2. SEM images for: (a) original pummelo peel (500 ×) and (b) original pummelo peel (2000 ×)

for NR and CR are narrower than that of MB. Effects of initial pH on adsorption percentages of the 3 dyes are shown in Fig. 3. According to these results, pH values 8, 5 and 7 are chosen for the experiments of MB, NR and CR, respectively. Moreover, the dye removal ratios under the optimal pH values could be also realized from Fig. 3. The ratio of CR sorbed by pummelo peel is rather poor (*ca.* 40 %), but the removal ratios of the other 2 dyes are more promising (over 90 %). Present results are consistent with other studies[16].

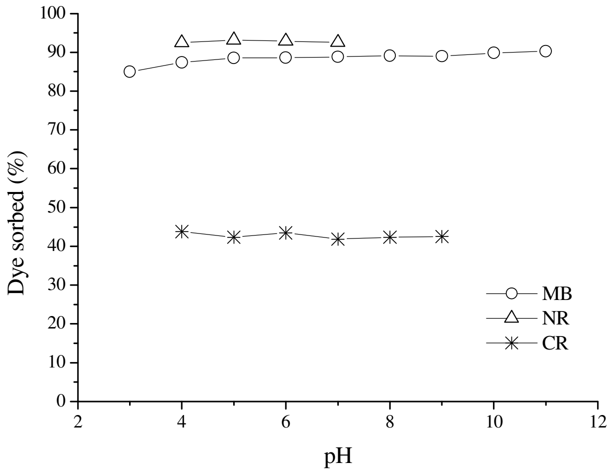


Fig. 3. Influence of initial pH on adsorption of MB, NR and CR by pummelo peel.

Effect of sorbent dose: The effects of sorbent dose on the removal ratios of the three dyes are depicted in Fig. 4. The percentage of dye sorbed increase as the sorbent dose increase over the range 0.5-2.0 g L^{-1}. As for MB and NR, the removal ratios show no significant difference ($p > 0.05$) when the sorbent dose increase from 2.0 to 7.0 g L^{-1}, while the ratio of the CR sorbed kept increasing following the adding of the sorbent. Therefore, the dose of 2.0 g L^{-1} is determined for the further experiments of MB and NR and 5.0 g L^{-1} for CR.

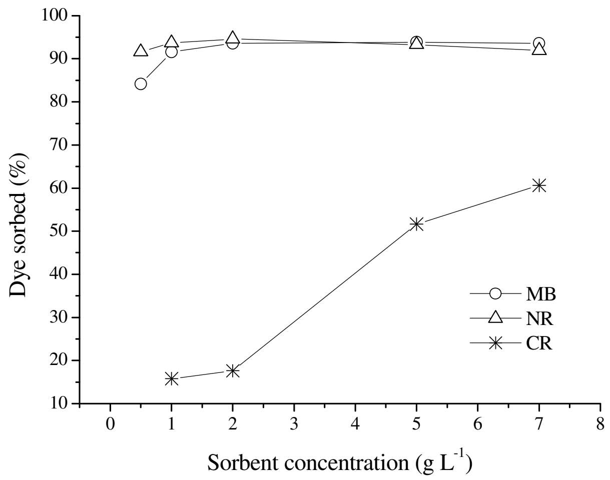


Fig. 4. Effect of adsorbent dose on adsorption of MB, NR and CR by pummelo peel

Adsorption kinetics: The effect of contact time on the adsorption of three different dyes on the pummelo peel is shown in Fig. 5. The removal rates of three dyes are rapid during the initial stages of the sorption processes and then slowly decline with lapse of time. The adsorptions of dyes reach equilibrium in 30, 20 and 300 min for MB, NR and CR, respectively. Fig. 5 also indicates that removal rate of anionic CR by pummelo peel is rather lower than that of the other two cationic dyes. The removal *versus* time curve is single, smooth and continuous leading to saturation, suggesting the possibility of monolayer coverage of methylene blue on the outer surface of the sorbent[17]. The rapid uptake of dye indicates that the sorption process could be ion-exchange in nature where the cationic dye molecules bind with the various negatively charged organic functional groups present on the surface of the aquatic plant[12,17].

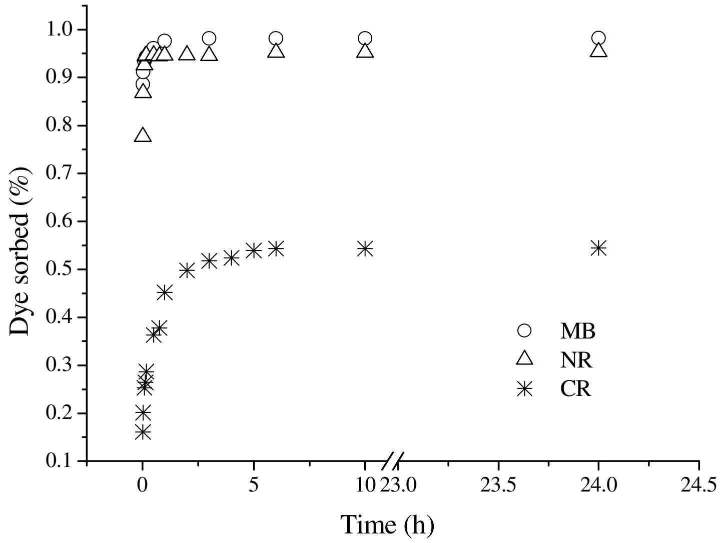


Fig. 5. Biosorption kinetics of MB, NR and CR by pummelo peel

The kinetic data were treated with the following Lagergren's pseudo-first order rate equation (eqn. 1)[18]:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \quad (1)$$

where q_e and q_t (mg g^{-1}) refer to the amount of dye sorbed at equilibrium and time t (min), respectively and k_{ad} is the rate constant (min^{-1}). Linear plots of log (q_e–q_t) *versus* t were obtained for different dyes (Fig. 6). The k_{ad} values calculated from the slope of the linear plots of MB, NR and CR adsorption were 0.0444, 0.388 and 0.0181, respectively.

Effect of initial dye concentration: As seen from Fig. 7, equilibrium uptake increases with the increasing of initial MB concentrations (C_0) at the range of experimental concentration (20-600 mg L^{-1}). A higher initial concentration could provide an important driving force to overcome all mass transfer resistance of the dye between the aqueous and solid phases, thus increases the uptake. Moreover,

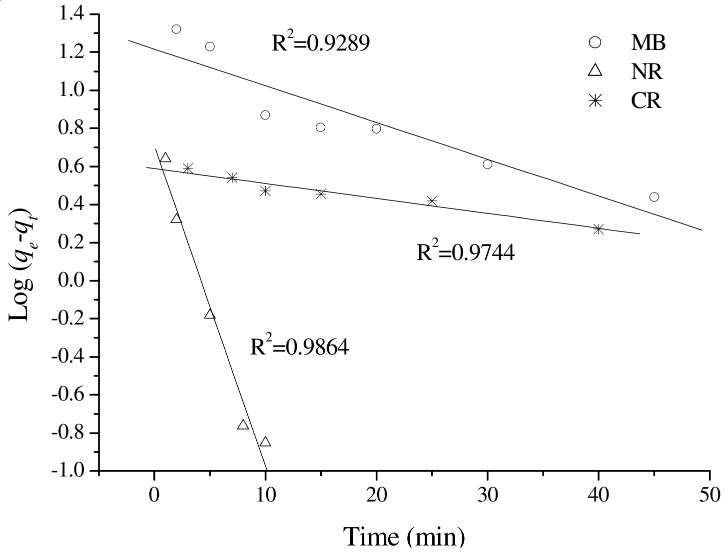


Fig. 6. Lagergren plots for the adsorption of MB, NR and CR by Pummelo peel

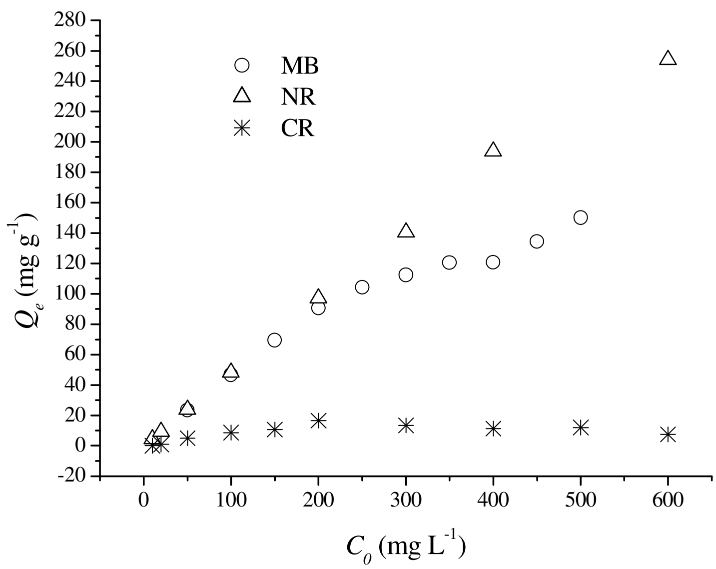


Fig. 7. Equilibrium adsorption quantities of methylene blue (MB), neutral red (NR) and congo red (CR) at different initial dye concentrations

increasing initial dye concentration increases the number of collisions between dye cations and the sorbent particles, which enhances the adsorption process. So the values of q_e increased with the increasing of initial methylene blue concentrations.

Langmuir and Freundlich equations are the most frequently employed models to describe the experimental data of adsorption isotherms[19]. In this work, both models were used to describe the relationship between the amount of dye adsorbed and its equilibrium concentration.

Langmuir isotherm equation has been widely applied to describe experimental adsorption data based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the sorbent surface.

The equation represents the Langmuir isotherm is shown here (eqn. 2)

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (2)$$

where K_a is the Langmuir constant related to the energy of adsorption and q_m (mg g^{-1}) is the maximum amount of adsorption corresponding to complete monolayer coverage on the surface. q_e (mg g^{-1}) is the amount of dye adsorbed on the sorbent at equilibrium, C_e (mg L^{-1}) is the equilibrium concentration of dye solution.

The constants K_a and q_m can be determined from the following linearized form of eqn. 3:

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{C_e}{q_m} \quad (3)$$

Freundlich isotherm is the earliest known relationship describing the sorption equation. This fairly satisfactory empirical isotherm can be used for non-ideal sorption that involves heterogeneous surface energy systems and is expressed by the eqn. 4:

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

where K_F is roughly an indicator of adsorption capacity and 1/n is the adsorption intensity.

In general, as K_F increases the adsorption capacity of a sorbent for a given adsorbate increases. The magnitude of the exponent 1/n gives an indication of the favourability of adsorption.

Eqn. 4 may be linearized by taking logarithms:

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

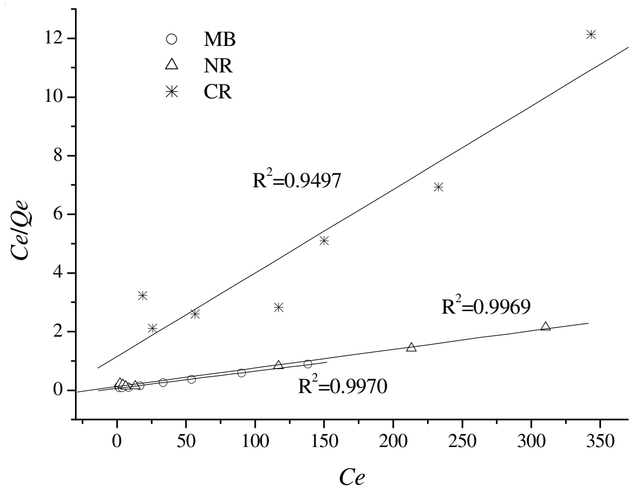
Langmuir and Freundlich isotherms are shown in Fig. 8. The adsorption isotherm parameters along with the correlation coefficients are summarized in Table-2. It reveals that, over the range of MB and NR concentrations studied, all experimental data are fitted well by the Langmuir isotherms with the regression coefficients (R^2) 0.9970 and 0.9969, respectively. At the same time, sorption of CR basically fits the Langmuir model and does not fit the Freundlich model.

The maximum sorption capacities (q_m) of the sorbent for MB and NR were 167.5 and 152.7 mg g^{-1}, respectively. It appears that pummelo peel shows great

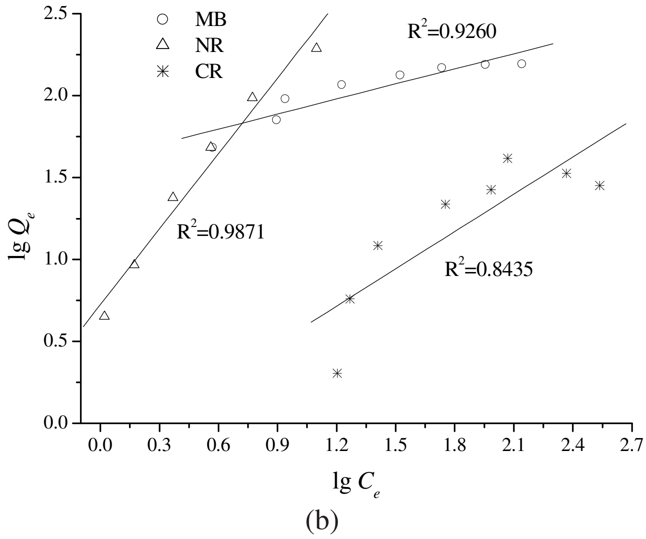
TABLE-2
VALUES OF PARAMETERS AND CORRELATION COEFFICIENTS OF LANGMUIR AND FREUNDLICH EQUATIONS

Dye	Langmuir isotherm			Freundlich isotherm		
	q_m (mg g^{-1})	K_a	R^2	1/n	K_F	R^2
Methylene blue	167.5	0.0523	0.9970	0.3063	40.85	0.9260
Neutral red	152.7	0.0689	0.9969	1.5350	46.88	0.9871
Congo red	33.1	0.0304	0.9497	0.6545	1.08	0.8435*

*R^2 = 0.8435 << 1, the Freundlich model was not fitted.



(a)



(b)

Fig. 8. Linearized Langmuir isotherms (A) and Freundlich isotherms (B) for methylene blue (MB), neutral red (NR) and congo red (CR) adsorption by pummelo peel

potential as a sorbent for these two dyes. While the q_m of the peel for congo red adsorption was only 33.1 mg g^{-1}. Since this biomaterial is readily available in the environment, it is a low-cost sorbent with high adsorption capacity. In addition, regeneration is not necessary and it can be burnt with the sorbed dyes as a source of energy.

Conclusion

Pummelo peel was investigated for its ability to perform as a suitable sorbent for cationic dye methylene blue and neutral red and anionic dye congo red from aqueous solution. The effects of pH and sorbent dose were investigated using a batch sorption study. The suitable pH values chosen for adsorption of methylene blue, neutral red and congo red are 8, 5 and 7, respectively. Maximum sorption capacities of pummelo peel for methylene blue, neutral red and congo red are 167.5, 152.7 and 33.1 mg g^{-1}, respectively. The isotherm data of methylene blue and neutral red are closely fitted to the Langmuir equation and the processes of uptake follow first order rate kinetics. However, the adsorption capability of the pummelo peel for anionic dye congo red is rather low than the other two cationic dyes. The results reveal the potential of pummelo peel as a low-cost sorbent for the cationic dyes methylene blue and neutral red.

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