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Chitosan Beads as an Adsorbent for the Removal of Colour from Natural Rubber Wastewater

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Abstract: Natural rubber processing wastewater contains high concentration of organic compound, colour, nitrogen, and other contaminants. This study evaluated a chitosan bead as an adsorbent in adsorption process for natural rubber wastewater treatment. The effects of adsorbent dosage, pH, shaking speed and contact time and adsorption isotherm on colour adsorption onto chitosan beads were evaluated using batch experiments. Meanwhile, Langmuir and Freundlich isotherm models were used to validate the experimental data. Maximum removal of 71.5%, for colour was observed for an adsorbent dosage 4.5 g, pH 7, and shaking speed 150 rpm. Equilibrium was achieved in 120 min. The equilibrium data were fitted to Langmuir isotherm model when compared with Freundlich isotherm models.

Keywords: Wastewater, natural rubber, chitosan, colour, adsorption

1. Introduction

The industry of rubber is one of the most important industries in Malaysia and plays a vital role in the nation's economy [1]. However, rubber processing industry usually generates large quantities of wastewater containing a high concentration of organic matter, colour, suspended solids and nitrogen [2]. Their toxic effluents are a major source of aquatic pollution and will cause considerable damage to the receiving waters if discharged untreated [3–5]. Colour is the first contaminant to be recognized in wastewater and the presence of very small amounts in water is highly visible and undesirable. Discharge of coloured substances into water bodies not only can aesthetically cause issues but also it is harmful to biological organisms and ecology [6,7].

Among various treatment approaches, biological methods especially aerobic, anaerobic and facultative ponds are widely used for the treatment of rubber wastewater in Malaysia. However, these systems are inexpensive and have a high efficiency for organic load reduction, but required large areas to implement [1]. The adsorption process is one of the effective methods to remove colour from water and wastewater [8 - 15]. The application of activated carbon as the most widely used adsorbent has become limited because of its high cost and the need for regeneration [16].

Chitosan is an abundantly available low-cost bio-polymer for dye removal that can be obtained from natural resources. As compared with other commercial adsorbents, it has received a lot of focus due to its specific properties such as cationic, high adsorption capacity, macromolecular structure, abundance and low price [6]. Chitosan is derived by deacetylation of the naturally occurring biopolymer (chitin) which is the second most abundant polysaccharide in the world after cellulose. This natural polymer possesses several intrinsic characteristics that make it an effective adsorbent for the removal of colour. [17]. Conversion of raw chitosan flakes into beads has been reported to be an essential way to improve the adsorption capability by enhancing the porosity and surface area. This conversion has been performed by dropping acid-dissolved chitosan into an alkali solution such as NaOH or methanol-NaOH, followed by drying [6]. The aim of this study was to explore the removal efficiency of the colour of natural rubber wastewater by an adsorbent chitosan bead. The efficiency of the adsorption process was analyzed based on the effect of adsorbent dosage, pH, shaking speed and contact time. Adsorption isotherm models, namely, Langmuir and Freundlich, were used to analyze the experimental data.

2. Material and Methods

2.1 Preparation of Adsorbent

The preparation of chitosan bead according to Thilagan et al., [18], 2 g of Chitosan were dissolved in

200ml of 1% acetic acid and stirred for 5 hours to make a chitosan gel. The mix was added and stirred for 1 hour for uniform mixing. Then the Chitosan gel was injected through a syringe (without needle) over the surface of 1M NaOH solution in a wide glass tray. Then the beads were carefully separated from NaOH solution, cautiously washed several times with distilled water and allowed to be dried for 48 hours at room temperature. The surface morphology of chitosan beads was analyzed using scanning electron micrographs.

2.2 Wastewater

Natural rubber wastewater was collected from a rubber industry in Kluang, Johor Malaysia. To prevent the wastewater from undergoing biodegradation due to microbial action, the wastewater sample was preserved at a temperature less than 4˚C. Colour concentration of the sample solutions was detected by a UV-vis spectrophotometer (DR6000, Hach).

2.3 Batch Experiment

Optimization of important process parameters such as adsorbent dose, pH, shaking speed and contact time for the maximum removal of colour from natural rubber wastewater was carried out by using the classical approach. The 250-mL conical flasks containing 100 mL of natural rubber wastewater with known adsorbent dose were shaken in an orbital shaker at 150 rpm in 90 min contact time.

2.3.1 Effect of Adsorbent Dosage

Effect of the adsorbent dose was investigated by using different adsorbent doses (0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5 and 6 g) at 150 rpm shaking speed and 90 min contact time.

2.3.2 Effect of pH

The effect of pH on the rate of colour removal was analyzed in the pH range at 3 to 12 at 150 rpm, 90 min contact time and 100 mL of natural rubber wastewater at optimum dosage. The pH was adjusted using 0.1 N NaOH and 0.1 N HCl solutions by using an Orion 920A pH-meter with a combined pH electrode.

2.3.3 Effect of Shaking Speed

Effect of shaking speed was investigated by conducting experiments at different shaking speeds (50, 75, 100, 125, 150 and 175 rpm) at 90 min contact time and under optimum pH and adsorbent dosage.

2.3.4 Effect of Contact time

In order to examine the effect of contact time on colour removal efficiency, the time of shaking was varied from 5 to 300 min and others were fixed according to optimum dosage, pH and shaking speed.

2.4 Isotherm

250 ml Erlenmeyer flasks with 100 ml of natural rubber wastewater were arranged. All samples were adjusted to the optimum pH. The conical flasks were agitated at optimum shaking speed, contact time and adsorbent dosage. Then the flask was removed and allowed to settle a bit before the supernatant was withdrawn for analysis of colour [19].

3. Results and Discussion

3.1 Characterization of chitosan beads

Fig. 1 show a surface morphology of the chitosan beads. From these figures indicated the present of micro-pores. The present of micro-pores on spherical-shaped chitosan beads can act as active sites for adsorption and increase the surface to volume ratio of the adsorbent [20].

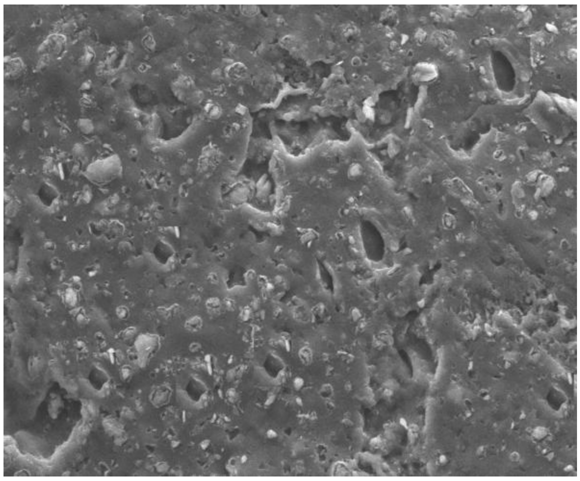

Fig. 1 SEM micrographs of a surface chitosan bead

3.2 Adsorption Study

3.2.1 Effect of Adsorbent Dosage on Colour Adsorption

Fig. 2 show the effect of chitosan beads dosage to the removal of colour in natural rubber wastewater. Results indicated that by increasing the adsorbent dose of chitosan beads from 0.5 g to 4.5 g, the colour removal also increased. The increase in adsorption of colour by increase in adsorbent dose can be attributed due to the fact that at higher adsorbent doses, the surface area and hence the binding sites available for the attachment of colour molecules increase which results in the more efficient adsorption process [21,22]. Fig. 2 shows that the maximum colour removal was found at 4.5g and no significance colour removal after that. This is due to aggregation of adsorbent at higher doses which leads to the blockage of binding sites on the surface of adsorbent and hence no further removal of colour molecules was achieved even at higher adsorbent doses [23].

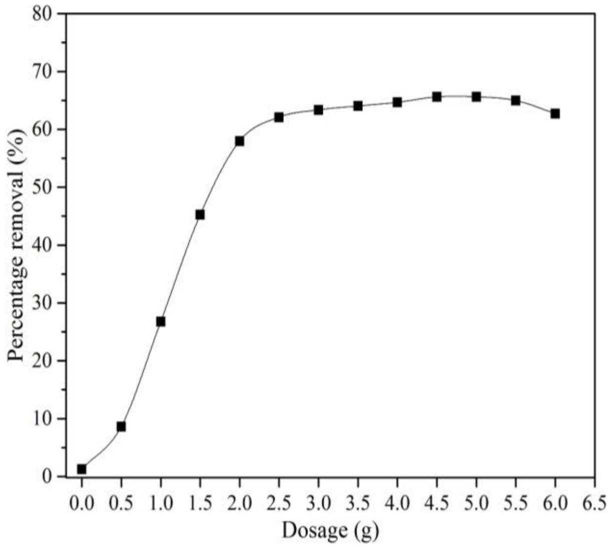

Fig. 2 Effect of chitosan bead dosage on adsorption of colour

3.2.2 Effect of pH on Colour Adsorption

The removal pattern of colour using chitosan bead as the adsorbent is shown in Fig.3. Generally, the removal of colour increases as the pH increases from 6 to 8 and slowly reduces after pH 8 to 12. The removal pattern was observed 76.2% using chitosan bead. The maximum removal of colour occurs at pH 7.0. Sajab *et al.,* ., [23] conclude that the increase in colour removal as pH increases could be explained on the basis of a reduction in competition between hydronium ions and colour species for the surface sites and likewise by the decrease in positive surface charge on the adsorbent, which ensued in a lower electrostatic repulsion between the surface and the ions and hence uptake of ions increased.

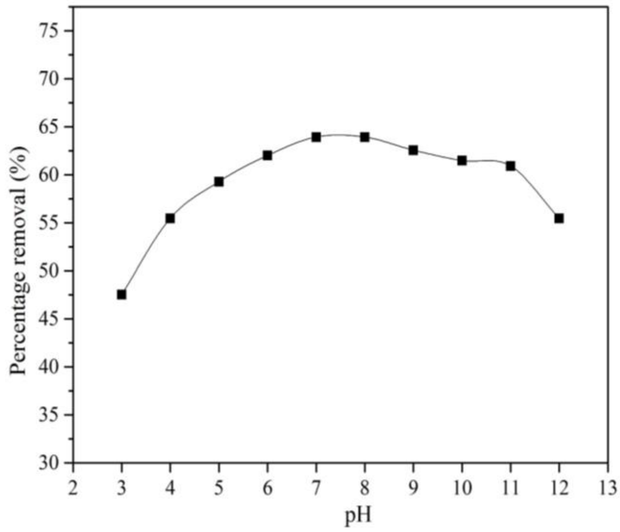

Fig. 3 Effect of pH on adsorption of colour

3.2.3 Effect of Shaking Speed on Colour Adsorption

The shaking speed is among one of the mass transfer parameters which influence the adsorption process [16]. The effect of shaking speed on the removal of colour from natural rubber wastewater containing wastewater was explored by changing the shaking speed from 50, 75, 100, 125, 150 and 175 rpm and the results are presented in Fig. 4. Generally, increasing the shaking speed improved colour removal uniformly. It was observed that the highest removal of colour was obtained when the shaking speed was fixed at 150 rpm with 78.5 using chitosan bead.

Kamaruddin et al., [24] explained, in theoretically, inducing dynamic movement towards the adsorbent in batch test increases the reactivity of water molecules. This process enhanced the diffusion of colour molecules towards the surface of the adsorbent. However, further increasing the shaking speed was found to reduce the adsorption capacities of the adsorbent. This was due to the fact that excessive contact between the wall of the adsorbent and water molecules caused attrition of the adsorbent and deteriorated its outer surface severely.

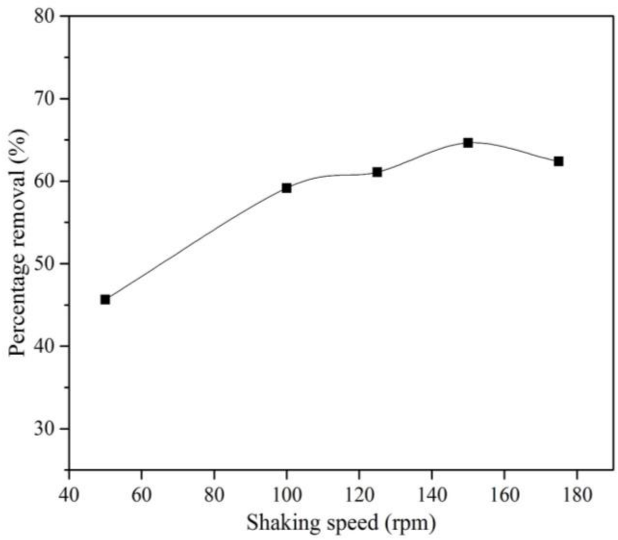

Fig. 4 Effect of shaking speed on adsorption of colour

3.2.4 Effect of Contact Time on Colour Adsorption

The effect of contact time on the percentage removal of colour unto chitosan bead is presented in Fig. 5. It is observed that the rate of removal of colour from natural rubber wastewater was initially rapid and then diminished gradually until an equilibrium time beyond which there was no significant increase in the removal rate. Equilibrium removal was achieved around 90 min and increased slightly up to 120 min for colour adsorption. However, a further increase in contact time recorded a slight decrease in the percentage removal. This is due to the fact that, at the initial stage of adsorption, a large number of vacant surface sites are available for adsorption, and once equilibrium is attained the remaining vacant sites are difficult to be occupied due to the repulsive forces between the molecules on the adsorbents and the bulk phase [25]. Hence, a contact time of 120 min was chosen to ensure optimum removal of colour using chitosan bead.

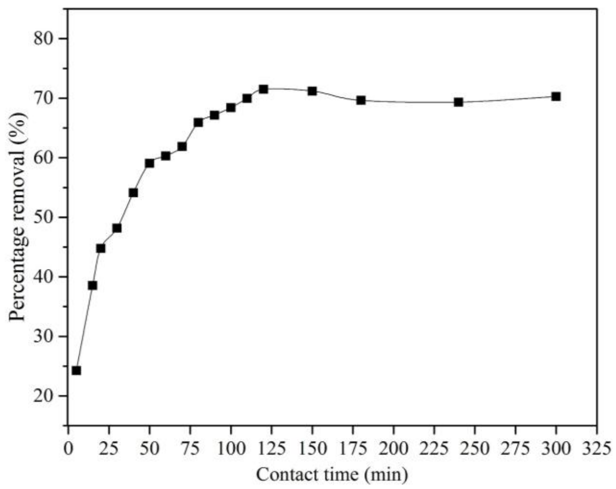

Fig. 5 Effect of contact time on adsorption of colour

3.3 Adsorption Isotherm

There are a number of formulas used to analyse isotherm equilibrium absorption experiments. Langmuir and Freundlich isotherm models are the most commonly used [20]. The linear form of the Langmuir model is:

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

where C_e sorbate in solution (mg/L), q_e is the amount adsorbed per unit mass of adsorbent (mg/g) and K_L is Langmuir constant (L/mg) [26]. The linear form of the Freundlich model is:

$$\log q_e = \log K_F + 1/n \log C_e \quad (2)$$

where q_e is adsorbed per unit mass of adsorbent (mg/L), K_F is adsorption capacity $[(mg/g)(mg/L)^n]$ and $1/n$ is adsorption intensity [26-33]. Fig. 6 and Fig. 7 show the Langmuir and Freundlich isotherm for adsorption of colour onto chitosan bead respectively.

Meanwhile, Table 1 summarizes the values of qm and kl for Langmuir isotherm and kf and n (Freundlich isotherm and the correlation coefficients for both isotherms. The result indicated that Langmuir isotherm is well fitted to this adsorption process by the high correlation coefficients (R2=0.9900). Thus, this adsorption process belongs to a monolayer adsorption model. Furthermore, the value of separation factor RL = 0.1690 for the adsorption system studied is between 0 and 1, which confirms that the ongoing adsorption is favourable [25].

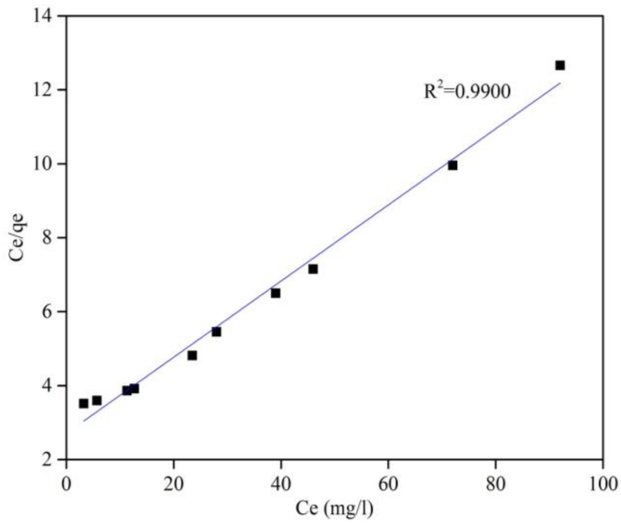

Fig. 6 Langmuir isotherm for adsorption of colour onto chitosan beads

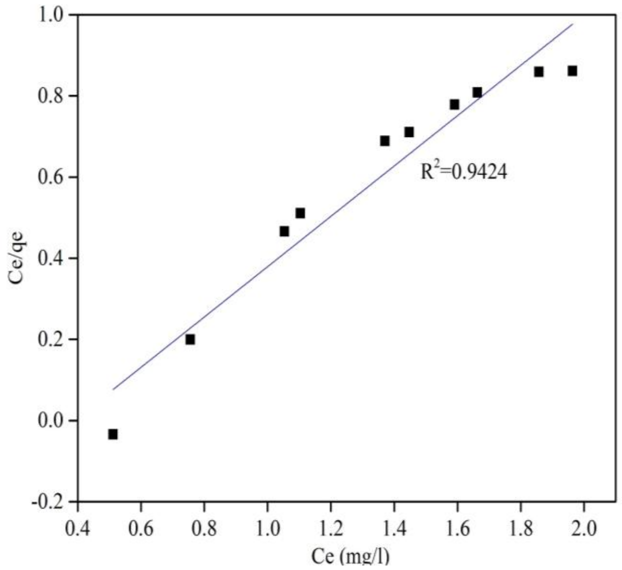

Fig. 7 Freundlich isotherm for adsorption of colour onto chitosan beads

Table 1. The adsorption isotherm parameters of colour adsorption

Isotherm parameter	Chitosan bead
Langmuir	
R_L	0.1690
q_m	9.7087
K_L	0.0380
R^2	0.9900
Freundlich	
K_F	1.7418
n	1.6123
R^2	0.9424

4. Summary

The adsorption of colour from natural rubber wastewater using chitosan bead was an investigation. The results indicated that the adsorption process of the chitosan bead was considerably affected by adsorbent dosage, pH, shaking speed and contact time. The result shows that chitosan is a good adsorbent to remove colour from natural rubber wastewater. Meanwhile, the results showed that the experimental data were correlated reasonably well by Langmuir adsorption isotherm. It can be concluded that chitosan bead is a good alternative low-cost adsorbent in wastewater treatment.

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