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Removal of Acid Blue 158 from Solution by Sunflower Seed Hull

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The removal of Acid Blue 158, acid dye for textile dyeing, from aqueous solution by sunflower seed hull was studied. The extent of adsorption capacity was studied as a function of heating temperature, sulphuric acid treatment, adsorbent size and pH of the solution. Sunflower seed hull was heated at 200, 300 and 400°C in oxygen deficient conditioned furnace. As the results, the sunflower seed hull heated at 200°C was the best absorbent for the dye removal with the maximum value of 30.84% at pH 4. Furthermore, removal ratio of Acid Blue 158 increased when the adsorbent was treated with 2M sulphuric acid. Particle sizes examined in this study were 250-355, 710-2000 and over 2000 micrometer. It was showed that the size of adsorbent affected on the removal capacity, i.e. the removal capacity increased along with the decrease of the size of absorbent. pH of the solution was studied between 1 and 6, and it was found that the optimum pH was pH 2. At the optimum condition, the modified adsorbent showed the removal ability of about 50%. The results obtained under the conditions of pH 4, 2M H_2SO_4 treatment of sunflower seed hull and the size of 500-710 micrometer at room temperature, the adsorption isotherm was fitted to Langmuir adsorption model, and the maximum adsorption capacity, q_m, of 18.52 mg/g and Langmuir adsorption constant, K_l, of 5.25×10^{-3} L/mg were obtained.

Keywords: Acid Blue 158 removal, Sunflower seed hull, Adsorption isotherm

INTRODUCTION

The textile industry uses large volumes of water in wet processing operation and thereby, generates substantial quantities of wastewater containing large amount of dissolved dyestuff and other products such as dispersing agent, dyebath carriers, salts, emulsifiers, leveling agent and heavy metals. It is nowadays well known that there is the need of treating textile wastewater by not only concerning primary and secondary treatment of organic matter and suspended solid removal but also a tertiary treatment mostly for residual colour removal. The textile industry is always looking for persistent and bright colours, in order to please the consumers. So, the dyestuffs are becoming progressive more and more and resistant to the traditional process of treating wastewater. The removal of remaining dye from textile industry wastewater is currently of great importance in recent years. Acid dyes are used by several industries, such as textile, paper and colouring products. Many acid dyes, Acid Violet 17 (Thinakaran *et al*. 2008), Acid Blue 15 (Foo and Hameed 2011), Acid Red 97, Acid Orange 61, Acid Brown 425 (Gomez *et al*. 2007), were studied with agricultural waste-adsorbent, sunflower seed hull, in order to investigate the dye removal capacity. Although many conventional methods such as precipitation, ion exchange, solvent extraction, electrochemical treatment, biosorption, filtration and adsorption are used for dye removal from aqueous solution, these methods are either expensive or incomplete for removal of high concentration of contaminants and high energy consumption. Dyestuffs have complex chemical structures, and are hard to degrade biologically. Adsorption is a commonly used method for dyestuff removal from wastewater and discharges high water quality effluents without dyestuffs. Powdered activated carbon (PAC) has been the most widely used adsorbent for dyestuffs removal from wastewater. However, PAC is expensive and its use usually requires regeneration and reactivation procedure. Development and use of low cost adsorbents has been investigated by many researchers for effective removal of dyestuffs from wastewater. In Thailand, there are a large amount of sunflower seed hulls from unpeel company as well as rice husk as agricultural waste. Although they can be used as organic fertilizer or solid fuel, for another benefit for using these materials, they can be used as the adsorbents in rural areas or small communities to conserve their environments. Sunflower seed hull and rice husk were studied for dye removal (Srisorrachatr *et al*. 2007, Srisorrachatr 2011) as well as metal ions by S. Srisorrachatr *et al*. and they showed the high ability of adsorption/removal. In this study, we attempt to investigate the adsorption capacity of sunflower seed hull for dye removal, which is agricultural waste in the community. The dye used in this study is Acid Blue 158, which is one of dyestuff often used by the textile industry.

EXPERIMENT

Chemicals

Acid Blue 158 (Abb. = AB158), Neolan Blue 2G; $C_{20}H_{12}CrN_2Na_2O_8S_2$ (MW = 518.433) was kindly obtained from Thongthai Textile Co., Ltd., Bangkok, Thailand, and was used without any purification. The structure of Acid Blue 158 is shown in figure 1. All the chemicals used are analytical reagent grade and all the

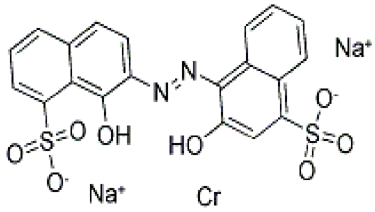

Fig. 1: Chemical structure of Acid Blue 158 (www.chemicalbook.com)

standards and reagent solutions were prepared with distilled water. Sodium hydroxide (NaOH) was purchased from VWR International Limited, England. Sulphuric acid (H_2SO_4) used for sunflower seed hull activation was purchased from J.K.T Baker, USA. Sunflower seed hulls were collected from a dehulling unit of Flower Food Products Co., Ltd. (Thailand). Bangkok, Thailand.

Preparation of adsorbents

The raw sunflower seed hulls were repeatedly washed with distilled water to remove dirt, dust and other impurities. The washed hulls were then sundried for 24 hours and also dried overnight (SSH) in an oven around 100°C. The dried hulls were divided into 2 portions for further treatment; heat and sulphuric acid treatment.

Heat treatment

The heat treated sunflower seed hulls were prepared by carbonizing at 200°C, 300°C or 400°C for 1 hour in oxygen deficient conditioned furnace (Fisher Scientific Isotemp Muffle Furnce, England). The result hulls were sieved and kept in desiccator.

Sulphuric acid treatment

The SSHS1 was prepared by refluxing 12 grams of dried sunflower seed hulls with 100 mL of 1.0 M H_2SO_4 for 30 minutes and then soaked them for 1 hour, and SSHS2 was also prepared by using 2.0M H_2SO_4 for activation. After treatment, the hulls were washed by distilled water until the filtrate reached to neutral pH. After that, the resulting hulls were dried in the oven at 105 °C (Oven: Lenton model WF 120(P),Thermal Designs England). The treated hulls were powdered and sieved by sieve-shaker (Retsch, model Rheinische str 36, Germany).

Batch adsorption experiments

All experiments in this study were examined as batch adsorption at room temperature. The parameters affecting on the removal capacity were investigated, such as modified adsorbents, acid treatment and heat treatment, pH of the solution and adsorbent size. A stock solution, 1000 mg/L Acid Blue 158 (AB158), was prepared, and then diluted to 100 mg/L for initial concentration. The actual dye concentration was calculated from the calibration curve using spectrophotometrical method (UV-visible spectrophotometer model T80, PG Instruments, China) at 588 nanometers. The pH of the dye solution was adjusted to desired value by addition of dilute H_2SO_4 or NaOH solutions. For batch study, 2.0 grams of adsorbent was mixed with 200 mL of 100 mg/L AB158 in erlenmeyer flask. The mixture was shaked on orbital shaker (Gallenkamp orbital shaker, England) with constant speed of 150 rpm at room temperature. The dye solutions were then withdrawn at determined time interval periodically and separated from the adsorbents by micro-syringe filtration. The resulting dye concentration was determined spectophotometrically and the removal capacity then was examined. The effect of heating temperature of sunflower seed hulls on dye removal was studied in the range of 100°C- 400°C and compared with control, unheated one. The effect of pH on dye removal was also studied over pH range of 2-6. The sizes of adsorbent used for study were between 250-335, 710-

2000, over 2000 micrometer. The dye removal percentage and the amount of adsorbed dye were calculated by Eq. (1) and (2) respectively.

$$Percentage\ Removal = \frac{C_i - C_f}{C_i} x100 \quad (1)$$

$$Amount\ adsorbed\ at\ equilibrium (q_e), \quad (2)$$

$$q_e = \frac{C_i - C_f}{W} xV$$

where C_i and C_f are the initial and final concentrations(mg/L) of dye, W is the mass(g) of adsorbent and V is the volume of dye solution(mL). The adsorption isotherm experiment was carried out by mixing 1 gram of adsorbent and 100 mL of dye solution of various concentration; 350, 400, 450, 500 and 550 mg/L with pH 4, shaking at 150 rpm.

RESULTS AND DISCUSSION

Effect of heat treatment

Removal of AB158 by sunflower seed hulls (SSH) with different conditions of heat treatment was investigated under the conditions of pH 4 and particle size of 500-710µm. It was shown that unheated as well as 200°C treated sunflower seed hulls has higher affinity for adsorption. Whereas the over 200°C treated hulls resulted in the less removal of AB158 as shown in figure 2. Percentage of dye removals by 200°C treated, untreated, 300°C treated and 400°C treated SSH were 30.84, 28.02, 21.17 and 12.11 respectively .This treatment may make the surface of the hull cleaner due to the heating temperature of 200°C, but when heated at the temperature higher than 200°C, it may destroy the hull surface and active site, and OH^- functional group on cellulose structure was also eliminated and so the adsorption property was decreased.

Effect of acid treatment

Removal of AB158 by sunflower seed hulls treated with 1.0 M and 2.0 M H_2SO_4 was examined and compared to the untreated one. It was found that H_2SO_4 treated sunflower seed hull gave higher removal capacity than untreated one. This may be due to the more positive charge of

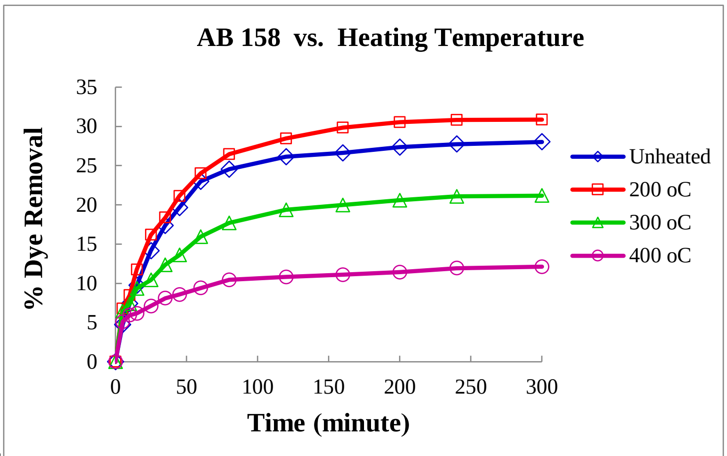

Fig. 2: Effect of heating temperature of SSH on percentage removal of Acid Blue158 from the solution of pH 4 at various times.

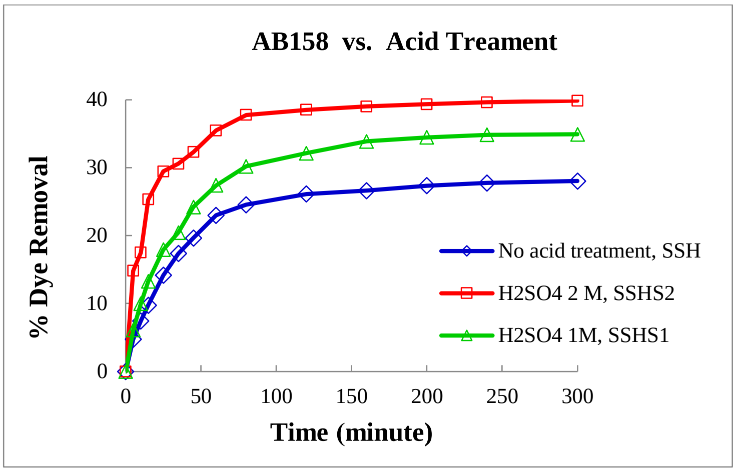

Fig. 3: Effect of H_2SO_4 treated SSH on percentage removal of Acid Blue 158 from the solution of pH 4 at various time

the hull surface. Since the dye in solution posses the negative charge, the charge interaction is occurred during adsorption process. Furthermore, by treatment with higher concentration of H_2SO_4, the dye removal capacity of SSHS2 was also became greater. The removal percentage were 28.02, 35.84 and 39.84% for SSH, SSHS1 and SSHS2 respectively as shown in figure 3. For further investigation, SSHS2 was used as the adsorbent.

Effect of pH

The effect of pH on the removal of AB158 by SSHS2 was studied by varying pH of dye solution from 1.0 to 6.0 at an initial concentration of 100 mg/L. The dye removal percentages at the different pH were plotted in figure 4. The maximum removal occurs at pH 2 and the removal percentage was lowered as pH increased. The lower dye removal at higher pH may be due to the present of excess OH^- ions competing with the dye ions at the adsorption site. At acidic pH, a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and negatively charged ionic dye (Kadirvelu *et al.* 2005) and also similar to the adsorption of acid red14 by soy meal hull (Arami *et al.* 2006).

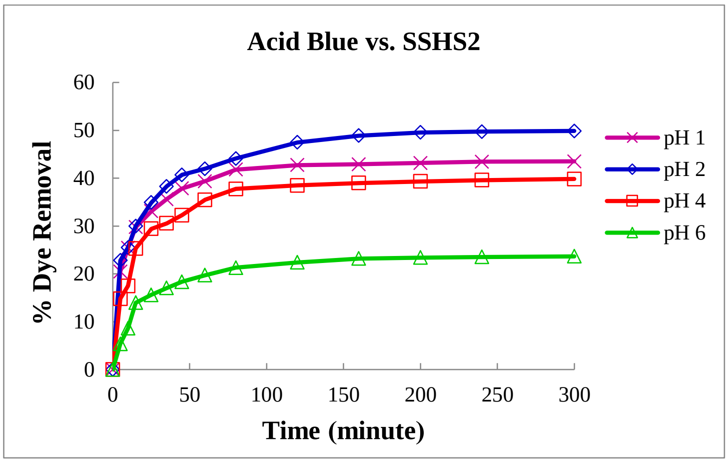

Fig. 4: Effect of pH for Acid Blue 158 removal by SSHS2 of 500-710 μm at various times.

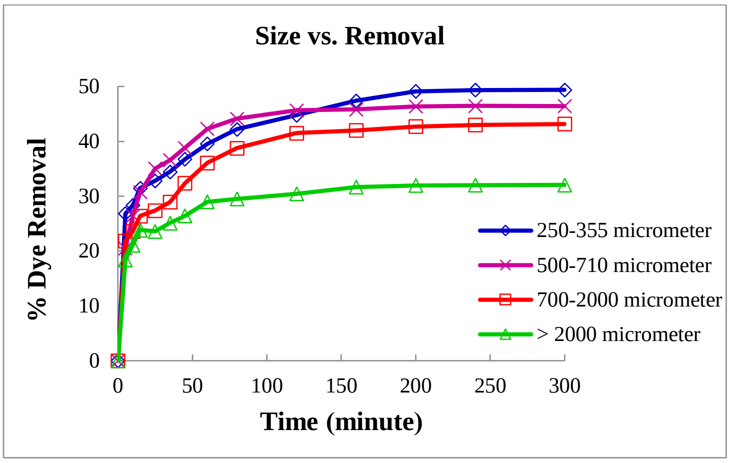

Fig. 5: Effect of adsorbent sizes on AB158 removal by SSHS2 at various times.

Effect of adsorbent size

The size of adsorbent was varied in order to examine the effect of particle size on removal capacity. From the experiment at pH 2, it was found that the smaller size showed the higher removal capacity because of the larger specific surface of the smaller size. The experimental results were showed in figure 5.

Adsorption Isotherm

Adsorption isotherm describes the interaction between adsorbate and adsorbent materials. The experiment was carried out at pH 4 with 100 mL solution of adsorbate concentration of 350, 400, 450, 500 and 550 mg/L using 1.0 g of treated adsorbent. As shown in figure 6, the experimental data fitted to Langmuir's adsorption model (Eq. (3)) with R^2 = 0.97 and also fitted to Freundlich's adsorption model (Eq. (4)) with R^2 = 0.91.

$$\frac{C}{q} = \frac{1}{K_l q_m} + \frac{C}{q_m} \tag{3}$$

and

$$\log q = \log K_f + \frac{1}{n} \log C \tag{4}$$

where C is equilibrium concentration

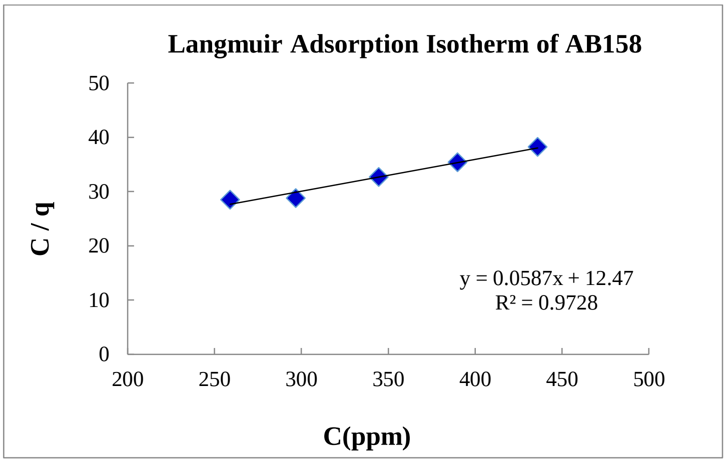

Fig. 6: Plot of Langmuir adsorption isotherm for Aid Blue158 with SSHS2, 500-710μm, pH 4

(mg/L), q is adsorption capacity(mg/g), q_m is maximum adsorption capacity (mg/g), K_l is Langmuir adsorption constant and K_f is Freundlich adsorption constant. The plot of C/q versus C for Langmuir's adsorption model will give the straight line with slope of $1/q_m$ and intercept of $1/(K_l\ q_m)$. For Freundlich's adsorption model, plot of log q against log C also will be linear relationship. The experimental data for Langmuir adsorption model was showed in figure 6. For data, the value of maximum adsorption capacity, q_m, was 18.52 mg/g and Langmuir adsorption constant, K_l, was $5.25x10^{-3}$ L/mg. Whereas the Freundlich adsorption model give n= 2.86 and K_f = 1.53 mg/g. It can be interpreted that the interaction between the hull and AB158 was ionic interaction with monolayer adsorption. The adsorption behaviors of AB158 quite similar to that of AB14 (Srisorrachatr *et al*. 2012).

CONCLUSIONS

The removal of Acid Blue 158 by various activation sunflower seed hulls such as heating temperatures and H_2SO_4 treatment, were investigated under various conditions. Acidic pH, H_2SO_4 treatment as well as 200°C treated sun flower seed hull are more favourable for Acid Blue158 removal, and the optimum condition in this study was 2.0 M H_2SO_4 treatment, particle size of 500-710 µm and pH 2. At optimum condition, the modified adsorbent showed removal capacity about 49.40%. The adsorption isotherm was fitted to Langmuir model and adsorption capacity was found to be 18.52 mg/g and Langmuir adsorption constant, K_l, of $5.25x10^{-3}$ L/mg.

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