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Study of Important Operating Parameters for the Adsorption of Acrylic Acid from Wastewater Using Palm Ash

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Abstract: The potential of the agriculture waste residue, palm ash as an adsorbent to remove Acrylic Acid (AA) was investigated in the present study was identified. Palm ash was treated by reflux with sulfuric acid before the adsorption. Batch adsorption study was conducted to study the effect of various operating parameters such as adsorbent dosage, initial concentration of AA, temperature and contact time. The experimental data were correlated to the Langmuir and Freundlich models of adsorption. Isotherm data were fitted well with Freundlich model. The maximum adsorption capacity of AA onto palm ash was obtained as $q_m = 1.98 \text{ mg g}^{-1}$ with an optimum palm ash dosage $w = 200 \text{ g L}^{-1}$ at 303K for $C_0 = 100 \text{ mg L}^{-1}$. The results indicate that palm ash is suitable as adsorbent to remove AA from aqueous solutions.

Key words: Adsorption, waste water, isotherms, palm ash

INTRODUCTION

In a typical acrylic manufacturing unit, the wastewater contains AA concentration in the range of 10-20 mg L^{-1} along with several other toxicants AA family such as acrylonitrile and acetonitrile. Such wastewaters also have very high concentration of dissolved solids, turbidity, very high Chemical Oxygen Demand (COD), highly alkalinity and many heavy metals. This type of wastewaters is concentrated and is almost always incinerated. These treatment methods are suffering from high energy consumption.

In view of the shortcoming of the existing methods, several treatments methods have been developed to remove AA from wastewaters, particularly biological or blend of wet oxidation followed by biological treatment. Adsorption is also a very attractive treatment method for the removal of toxics from wastewaters.

Adsorptive treatment of wastewaters contains AA has been found to be very efficient. Adsorption experiments for AA and the binary mixtures of acrylic-maleic acid copolymer and polyacrylic acid and poly(vinyl) pyrrolidone was done using aluminium (Bournel *et al.*, 1996), alumina (Mao and Fung, 2007; Ishiduki and Esumi, 1997; Santhiya *et al.*, 1999), titanium dioxide (Esumi *et al.*, 1998; Liufu *et al.*, 2005), clay minerals (Blockhaus *et al.*, 1997), carbon nanotubes (Hou *et al.*, 2005) and powdered activated carbon

(Kumar *et al.*, 2010). These studies focused on the determination of adsorption mechanism, surface characteristics, equilibrium sorption isotherm and co-adsorption of behavior of two acids or polyacids. Mao and Fung (2007) and Kumar *et al.* (2010) have performed the study dealing with the adsorption of acrylic acid from aqueous solution. Langmuir isotherm equation is more suitable to be used to explain the adsorption behavior at different pH values of the solution. However, Ahmad *et al.* (2007) and Hameed *et al.* (2007) have proved the equilibrium adsorption data for dye into palm ash was best represented by the Freundlich model.

Previous study showed remarkable efficiency for palm ash as adsorbent for dye removal from aqueous solution (Ahmad *et al.*, 2007; Hameed *et al.*, 2007). Therefore, the objective of this study is to study the utilization of palm ash as adsorbent to remove AA from an aqueous solution. Batch adsorption studies were conducted to study the effect of various operating parameters such as adsorbent dosage, initial concentration of AA, temperature and contact time.

MATERIALS AND METHODS

Adsorbent: palm ash: Palm ash was washed twice with water and dried in the oven at 110°C overnight. Then, the palm ash was sieved through sieve size 150 μm in order to remove any foreign materials and large ash particles. Forty

grams of palm ash is activated by refluxing with 250 mL of 40 wt.% H₂SO₄ at 60°C in a round-bottom flask for 4 h. The suspensions were cooled in air and filtered off. The filter cakes were washed several times with deionized water until the filtrate was neutral. Then, the filtrate was dried in an oven at 110°C for 2 h prior to use.

Adsorbate: Acrylic acids: Laboratory grade of AA was used to prepare synthetic aqueous solutions of various initial concentrations (C₀) in the range of 100 B 500 mg L⁻¹. The required quantity of adsorbate was accurately measured and dissolved in distilled water. Fresh stock solution was prepared everyday and kept under ambient conditions.

Characterization of adsorbent: The Brunauer-Emmett-Teller (BET) surface area, average pore diameter and pore volume were obtained from adsorption of N₂ at 77 K. Prior to measurements, the sample was outgases under vacuum at 200°C for 3 h. SEM micrographs of the palm ash samples were captured using SEM instruments.

Analytical measurements: The concentration of AA in the aqueous solution was determined at 220 nm wave length using High Performance Liquid Chromatography (HPLC). C₈ column size 4.6×150 mm was used for the analysis of AA. A mixture of 3% methanol, 0.1% trifluoroacetic acids and ultrapure water was used as a solvent for AA analysis keeping a flow rate of 1 mL min⁻¹. The calibration curves of AA were plotted as peak area versus concentration.

Batch adsorption studies: Batch adsorption studies were performed to investigate the effect of various operating parameters such as the initial concentration of the solution, C₀, temperature and adsorbent dosage, w. For each experiment, 50 mL of acrylic acid solution of known C₀, temperature and w was poured into 100 mL airtight conical flask with a glass stopper. This mixture was agitated in a temperature-controlled shaking water bath at constant shaking speed at 100 rpm. Samples were withdrawn from the flask at desire time intervals and filtered. The residual acrylic acid concentration of the supernatant was determined using HPLC.

Optimum w value was determined from a number of experiments by contacting 50 mL acrylic acid solution with varying amount of the palm ash until equilibrium was obtained.

The removal of acrylic acid and the adsorptive uptake of acrylic acid, q_t (mg g⁻¹), at any time twas calculated from the following relationships:

$$\text{Acrylic acid removal (\%)} = \frac{100(C_0 - C_t)}{C_0} \quad (1)$$

and:

$$q_t = \frac{(C_0 - C_t)V}{w} \quad (2)$$

where, C₀ and C_t are the acrylic acid concentration (mg L⁻¹). V is the volume of the solution (mL) and w is the mass of the adsorbent (g). At equilibrium, C_t = C_e and q_t = q_e.

RESULTS AND DISCUSSION

Adsorbent characteristics: Figure 1a and b represents the nitrogen sorption isotherm of raw palm ash and activated palm ash. The surface area calculated using Brunauer Emmet Teller (BET) methods shown in Table 1. It is found that surface area of activated palm ash is greater than the surface area of the raw palm ash.

SEM analysis for raw palm ash and activated palm ash are shown in Fig. 2a and b. It is shown that palm ash had a spongy and porous characteristics of the ash particles. This observation was in agreement with an observation reported by Chun *et al.* (2008).

Batch adsorption study

Effect of adsorbent dosage (w): The effect of adsorbent dosage, w on the uptake of AA by activated palm ash was studied. It was found that the removal of AA by activated palm ash increases with an increase in the adsorbent dosage as shown in Fig. 3.

Adsorption of AA is enhanced with an increase in the adsorbent dosage because of the greater surface area and the availability of larger number of adsorption sites. For w, 200 mg L⁻¹, the adsorbent active site is not sufficient to adsorb the AA and thus causing a lower removal efficiency. At w = 200 g L⁻¹, equilibrium condition exists in the adsorbent-adsorbate system. The removal efficiency of AA remains constant at 87% when w = 200 g L⁻¹.

Effect of initial AA concentration and contact time: Based on Fig. 4, the adsorption of AA by activated palm ash

Table 1: The BET results for untreated palm ash, activated palm ash and palm ash after adsorption

Palm ash	Surface area (m ² g ⁻¹)	Average pores diameter (nm)
Raw palm ash	12.702	0.735
Activated palm ash	49.845	0.902

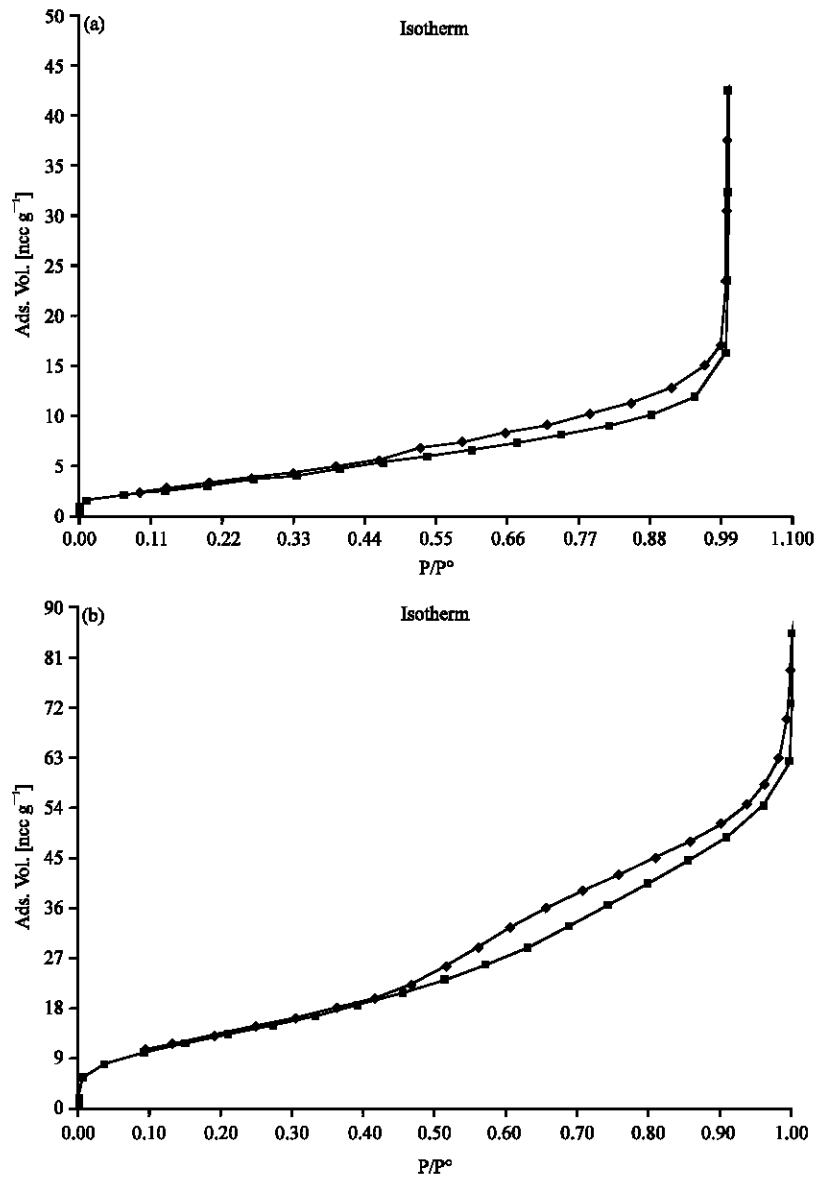


Fig. 1(a-b): N₂ sorption isotherm (a) Raw palm ash and (b) Activated palm ash

increases as the initial AA concentration increases. However, at higher concentration, the sites for adsorption become lesser and hence the removal efficiency of AA is dependent on the initial concentration. The removal of AA increases with increase in contact time. The adsorption capacity is remained nearly constant after the equilibrium time. The time required to-attain the equilibrium state and the amount of AA adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operation conditions.

At the beginning, the AA molecules were adsorbed by the exterior surface of palm ash. The adsorption rate was fast. However, when the adsorption of the exterior

surface reached saturation, the AA molecules entered into the pores of palm ash and were adsorbed by the interior surface of the particles. This phenomenon takes relatively long contact time. These results are in agreement with finding report by Hameed *et al.* (2007) for the adsorption of acid dye using activated palm ash.

Effect of temperature: The adsorption studies were carried out at three different temperatures. The results of these experimental studies are shown in Fig. 5. It shows that the adsorption of AA increases with an increase in temperature. This could be due to the increase of mobility of the AA with increasing temperature. Furthermore,

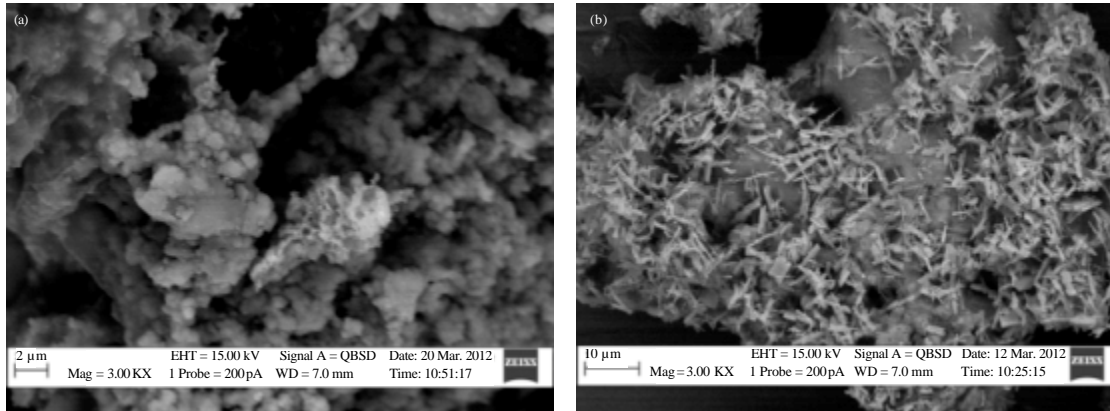


Fig. 2(a-b): SEM of (a) Raw palm ash and (b) Activated palm ash

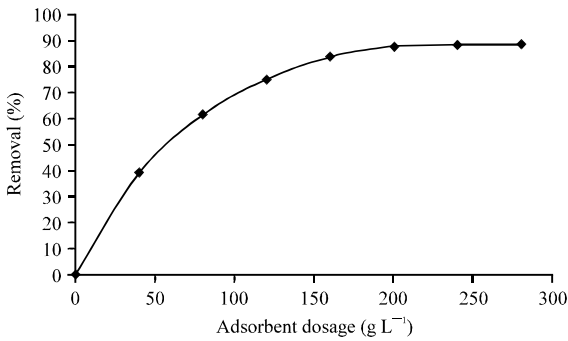


Fig. 3: Effect of adsorbent dosage on the removal of AA by activated palm ash, T: 30°C, t: 6 h and C₀: 100 ppm

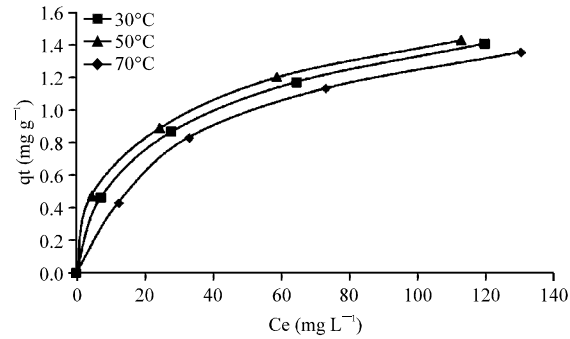


Fig. 5: Equilibrium isotherm for the adsorption of AA onto activated palm ash at different temperature, w: 200 g L⁻¹ and T: 6 h

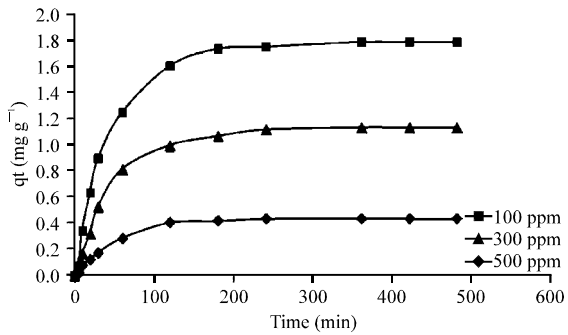


Fig. 4: The variation of adsorption capacity with adsorption time at various initial AA concentrations at T: 30°C

increasing temperature may produce a swelling effect within the internal structure of the activated palm ash enabling larger amount of AA to penetrate further.

Adsorption isotherms: The adsorption isotherms represent the relationship between the amount of a

substance adsorbed at constant temperature and its concentration in the equilibrium solution. Figure 5 shows the adsorption isotherm of the AA at 30, 50 and 75°C.

The following relation can represent the linear form of the Langmuir isotherm model:

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

The constants can be evaluated from the intercepts and the slopes of the linear plots of C_e/q_e versus C_e (Fig. 6). Langmuir parameters calculated from Eq. 3 are listed in Table 2.

The essential characteristics of the Langmuir equation can be expressed in terms of dimensionless separation factor, R_L, defined as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

where, C₀ is the highest initial solute concentration and K_L is the Langmuir's adsorption constant (L mg⁻¹). The R_L

Table 2: Langmuir and Freundlich parameters for adsorption of AA on palm ash at different temperatures

Temperature (°C)	Langmuir isotherm model			Freundlich isotherm model			
	q_{max} (mg g ⁻¹)	K_L (L mg ⁻¹)	R ²	R_L	K_F ((mg g ⁻¹) (L mg ⁻¹) ^{1/n})	n	R ²
30	2.165	0.018	0.912	0.100	0.478	1.929	0.969
40	2.012	0.029	0.932	0.065	0.623	2.341	0.981
75	1.949	0.039	0.927	0.048	0.763	2.680	0.977

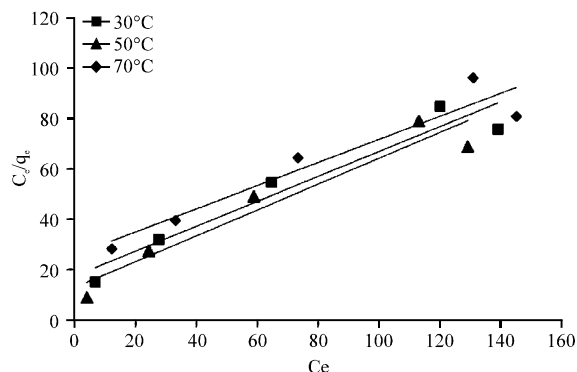


Fig. 6: Langmuir isotherm for AA adsorption onto activated palm ash at different temperatures

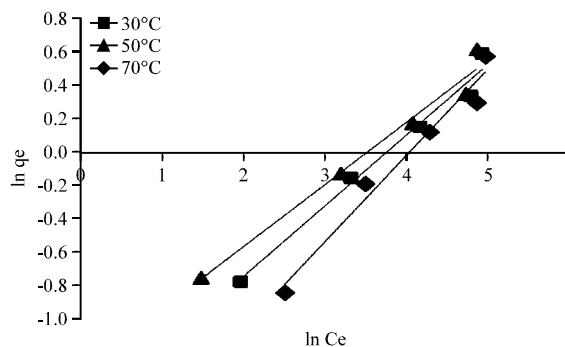


Fig. 7: Linearization Freundlich isotherm for AA adsorption by palm ash at different temperature

value implies the adsorption to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). R_L values for AA adsorption onto palm ash were less than 1 and greater than zero indicating favorable adsorption under conditions used in this study.

The linear form of the Freundlich isotherm model is given by the following equation:

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

where, q_e is the solid phase adsorbate concentration in equilibrium (mg g⁻¹), C_e the equilibrium liquid phase concentration (mg L⁻¹), K_F the Freundlich constant (mg g⁻¹) (L mg⁻¹)^{1/n} and $1/n$ is the heterogeneity factor.

Linear plot of $\ln q_e$ versus $\ln C_e$ shows that the adsorption of AA from an aqueous solution on palm ash also follows the Freundlich isotherm (Fig. 7). The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of the monolayer. The Freundlich equation predicts that the AA concentration on the adsorbent will increase so long as there is an increase in the AA in liquid. Values of K_F and n are calculated from the intercept and slope, respectively and are listed in Table 2. It is shown that n value is greater than 1, $n > 1$ represent favorable adsorption condition. Values of the correlation coefficient (R^2) as shown in Table 2 and it indicates that Freundlich isotherm is best fit model for the adsorption of AA on palm ash.

CONCLUSION

The present study shows that the activated palm ash is an effective adsorbent for the removal of AA from aqueous solution. Optimum adsorbent dosage was 200 g L⁻¹. The equilibrium between AA solution and the adsorbent surface is practically achieved in 6 h. The adsorption capacities were affected by the initial concentration where the uptake increased with the increase in initial AA concentration. The adsorption isotherm data for AA onto palm ash was best represented by the Freundlich models. This agriculture waste residue can be used as adsorbent due to its availability and low cost.

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