
DERIVATION OF OIL PALM SHELL-BASED ADSORBENT USING H₂SO₄ TREATMENT FOR REMOVAL OF ATRAZINE FROM AQUEOUS SOLUTIONS

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Abstract: Activated carbon is a prominent material for adsorption of atrazine, however its usage is restricted due to the high cost. Thus, alternative adsorbent derived from agricultural waste has been investigated. This study was conducted to investigate the feasibility of oil palm shell-based adsorbent to remove atrazine from aqueous solutions. Oil palm shell-based adsorbent was prepared using H₂SO₄ treatment. The adsorbent was characterized for the surface morphology and surface chemistry via scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy. SEM micrographs confirmed that the H₂SO₄ treatment developed porosity on the surface of the adsorbent. The FTIR spectrum obtained for the adsorbent before and after the treatment was almost similar. Batch adsorption experiments were conducted to determine the effects of initial atrazine concentration (5 - 30 mg/L), contact time, adsorbent dosage (0.2 - 2.0 g) and solution pH (pH 2 - 12) on the adsorption uptake of the adsorbent for atrazine. The adsorption uptake of atrazine increased with increasing initial concentration. The percentage of removal of atrazine increased with increasing adsorbent dosage, but it decreased as the solution pH increased. The equilibrium data were well described by the Freundlich isotherm model. Kinetic studies showed that the adsorption of atrazine on the adsorbent followed the pseudo-second-order kinetic model. Based on the experimental results, it was evident that the oil palm shell-based adsorbent derived in this work might be employed as a low cost adsorbent for removal of atrazine from aqueous solutions.

Keywords: Adsorption, atrazine, isotherm, kinetic, oil palm shell

1.0 Introduction

Atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) is a chlorinated s-triazine group of herbicide and is extensively used over the world (Ligy and Pranab,

2006). Atrazine is used extensively as a pre- and post-emergent treatment to control broadleaf and grassy weeds on both agricultural and non-agricultural land (Jamil *et al.*, 2011; Mudhoo and Garg, 2011). However, agricultural use of pesticides negatively impacts water quality and poses environmental pollution, even though its use is in a limited amount of compound (Aydinalp and Porca, 2004). Adsorption technique is favourable for atrazine removal due to its simplicity as well as the availability of a wide range of adsorbents. Commercial activated carbon has high adsorption capacity for removal of atrazine. However, the major drawback is its high cost of production, making its usage in removal of atrazine less attractive. Thus, there is a demand for alternative adsorbents, which are of inexpensive materials such as agricultural wastes. Since oil palm shell is abundant in Malaysia, therefore this study aims to investigate the feasibility of oil palm shell-based low cost adsorbent for removal of atrazine from aqueous solutions.

2.0 Materials and Methods

2.1 Materials

Analytical grade standard of atrazine was used for preparation of stock solution. Analytical grade standard of methanol was used for UV-Visible spectrophotometry analysis of atrazine concentration. Double distilled water was used for purifying adsorbent material and preparing solution samples. Oil palm shell obtained from FELCRA, Kota Samarahan division was selected as raw material to prepare the adsorbent. Oil palm shell granular activated carbon (6 x 12 mesh size) obtained from Bravo Green Sdn. Bhd. was used for comparison with the adsorbent developed for the adsorption studies.

2.2 Preparation of Adsorbent

The oil palm shell was washed with double distilled water to remove foreign impurities and the sample was then dried in oven at 50 °C for 48 h. The washed and dried material was ground and sieved to particle size of 0.15 - 0.30 mm. The fibres attached to the surface of oil palm shell were then removed. 300 g of the sieved oil palm shell was soaked in 400 mL of n-hexane to remove oil from the surface of the oil palm shell. The sample was then washed thoroughly with double distilled water and dried in oven at 110 °C for 12 h. The sample was then soaked in 400 mL of 0.1 M sulphuric acid (H₂SO₄) for 4 h at 30 °C. After the H₂SO₄ treatment, the adsorbent was washed with hot double distilled water until pH 7 to remove residue H₂SO₄ and was then dried in oven at 110 °C for 12 h. The dried adsorbents were cooled to room temperature and were stored in air-tight container for further characterization and adsorption studies.

2.3 Characterisation of Adsorbent

The surface morphology of the oil palm shell and oil palm shell-based adsorbent were analyzed by using a scanning electron microscope (Model JEOL JSM-6390LA). The Fourier transform infrared (FTIR) spectroscopy analysis was conducted using FTIR spectrophotometer (Model Shimadzu IRAffinity-1) in the range of 400-4000 cm^{-1} wavelength with 4 cm^{-1} resolution. FTIR characterization was used to determine the functional groups present on the surface of the samples.

2.4 Batch Adsorption Studies

Stock solution of atrazine of 30 mg/L was prepared by dissolving 30 mg of atrazine in 10 mL of methanol initially in 1000 mL volumetric flask. The solutions were then made up to the volume with double distilled water. Stock solution of atrazine was initially dissolved in a small quantity of methanol in order to accelerate its dissolution in water. The stock solution was then diluted using double distilled water to the desired concentration in the range of 5-30 mg/L. Adsorption studies of atrazine on the oil palm shell-derived adsorbent were carried out in batch mode. Adsorption experiments to study the effect of initial concentration were carried out by contacting 0.2 g of adsorbent with 200 mL of atrazine solution of different concentrations: 5, 10, 15, 20, 25 and 30 mg/L at constant temperature (30 °C) in 250 mL Erlenmeyer flasks. The effect of initial concentration was then evaluated on activated carbon for comparison. The effect of adsorbent dosage on the adsorption of atrazine on oil palm shell-based adsorbent was studied by contacting 200 mL of atrazine solution at fixed concentration of 30 mg/L with various adsorbent dosages of 0.2, 0.4, 0.8, 1.2, 1.6 and 2.0 g at 30 oC in 250 mL Erlenmeyer flasks. Meanwhile, the effect of pH on atrazine adsorption was investigated by contacting 0.2 g of adsorbent with 200 mL of atrazine solution with fixed concentration (5 mg/L) at varying initial solution pH (2-12) at 30 °C.

The absorbance of atrazine at maximum wavelength of 222 nm was plotted against atrazine concentration to obtain a calibration curve for determination of atrazine concentration in this study. The adsorption uptake at time t, q_t (mg/g), was expressed by Eq. 1:

$$q_t = (C_o - C_t)V/W \quad (1)$$

where q_t is the amount of atrazine adsorbed by adsorbent (mg/g), C_o is the initial liquid-phase concentrations of atrazine (mg/L), C_t is the liquid-phase concentration of atrazine at any time t (mg/L), V is the solution volume (L), and W is the mass of adsorbent used (g).

2.5 Adsorption Isotherms

Langmuir and Freundlich isotherm models were employed to fit the equilibrium data to evaluate the equilibrium between adsorbate and adsorbent of the adsorption process. Langmuir isotherm is mainly employed to monolayer adsorption on perfectly smooth and homogeneous surface. The linear form of the Langmuir (Langmuir, 1918) adsorption isotherm equation (Eq. 2) can be expressed as:

$$C_e/q_e = 1/Q_m K_L + (1/Q_m) C_e \quad (2)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q_m and K_L are Langmuir constants related to adsorption capacity (mg/g) and rate of adsorption (L/mg), respectively. The plot of C_e/q_e against C_e would give the value of Q_m and K_L .

Freundlich isotherm is extensively applied for adsorption surfaces with non-uniform energy distribution. The linear form of the Freundlich (Freundlich, 1906) adsorption isotherm equation (Eq. 3) can be expressed as:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (3)$$

where K_F and n are Freundlich constants which K_F is the adsorption capacity of the adsorbent (mg/g)(L/mg)^{1/n} and n is a measure of favourability of the adsorption process. The plot of $\ln q_e$ against $\ln C_e$ would give the value of K_F and n .

2.6 Adsorption Kinetics

The kinetics data obtained were fitted to pseudo-first-order and pseudo-second-order kinetic models to determine the adsorption mechanism. The pseudo-first-order (Eq. 4) (Kannan and Sundaram, 2001) and pseudo-second-order (Eq. 5) (Yang and Al-Duri, 2005) equations can be expressed as:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

where q_e and q_t are the amounts of adsorbate adsorbed (mg/g) at equilibrium and at time t , respectively, and k_1 is the adsorption rate constant (min⁻¹). Constant k_1 and q_e could be calculated from the plot of $\ln (q_e - q_t)$ versus time t .

$$t/q_t = 1/k_2 q_e^2 + (1/q_e) t \quad (5)$$

where k_2 is the rate constant of second-order adsorption (g/mg min). The plot of t/q_t against t would give the value of k_2 and q_e .

3.0 Results and Discussion

3.1 Characterisation of Adsorbent

The SEM micrographs of the raw oil palm shell, oil palm shell-based adsorbent treated with H_2SO_4 , activated carbon and oil palm shell-based adsorbent after adsorption of atrazine are presented in Figures 1(a), (b), (c) and (d), respectively. From Figure 1(a), the SEM micrograph shows dirt-covered and unclear pores on the surface of raw oil palm shell. There were very small pores present on the surface of the raw oil palm shell. Chemical activation with H_2SO_4 on the oil palm shell-based adsorbent resulted in the development of pores, as shown in Figure 1(b). However, the pores developed were not deep enough for high adsorption of atrazine. Meanwhile, the pores found on the surface of the activated carbon were relatively larger. It could be seen that the external surface of activated carbon was full of clear and deep pores, as illustrated in Figure 1(c). Owing to these well-developed pores, the activated carbon possessed higher surface area and adsorptive capacity (Guo and Lua, 1998). From Figure 1(d), it could be observed that there were some atrazine molecules adsorbed on the surface of the oil palm shell-based adsorbent. However, the pores developed on the surface of the adsorbent were slightly being occupied by the atrazine molecules.

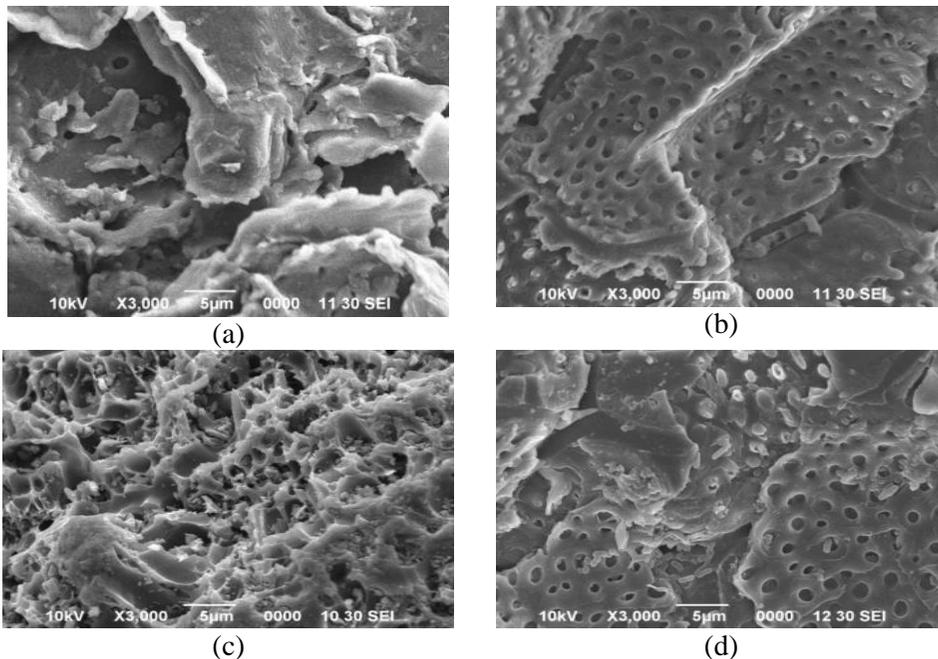


Figure 1: SEM micrographs (3000 x magnification) of (a) Raw oil palm shell, (b) Oil palm shell-based adsorbent treated with H_2SO_4 , (c) Activated carbon and (d) Oil palm shell-based adsorbent after adsorption of atrazine

From the FTIR spectrum obtained (data not shown), the presence of chemisorbed water and surface hydroxylic groups in raw oil palm shell was indicated by the absorbance peak of O-H stretching vibration between 3450 and 4000 cm^{-1} (Yacob *et al.*, 2008). A weak absorbance peak was observed at 2885.51 cm^{-1} corresponding to the C-H sp^3 stretching (Yacob *et al.*, 2008). The C=C stretching vibration of alkynes group was indicated by the absorbance peak between 2200 – 1950 cm^{-1} , indicating the presence of ketones (Guo and Lua, 2002). The strong broad absorbance peak between 1780 – 1640 cm^{-1} represented the C=O stretching vibration which indicated the presence of quinones (Guo and Lua, 2002). The very strong absorbance peaks at 1525.69 cm^{-1} and 1024.20 cm^{-1} were attributed to C=C stretching vibration of aromatic rings and O-H deformation vibration, respectively (Guo and Lua, 2002). The absorbance peak at 1247.94 cm^{-1} represented the stretching vibration of C-O functional group, indicating the presence of carboxylic acids (Guo and Lua, 1998; Yacob *et al.*, 2008). Although the adsorbent was prepared through chemical treatment, it exhibited similarity in the FTIR spectrum with that of raw oil palm shell. This indicated that the chemical treatment with H_2SO_4 increased the porosity of adsorbent without changing the surface chemistry. However, the absorbance peaks at 1247.94 cm^{-1} and 1024.20 cm^{-1} which were assigned to C-O carboxylic acid had been eliminated due to that the sample was washed thoroughly with hot double distilled water to remove any remaining H_2SO_4 . Lower intensity observed at the absorbance peaks between 2200 – 1950 cm^{-1} could be attributed to the reaction between the sulfuric acid and the oil palm shell. Moreover, the FTIR spectrum of activated carbon also exhibited similar trend as the oil palm shell-based adsorbent.

3.2 Effect of Contact Time and Initial Atrazine Concentration

The effect of contact time and initial atrazine concentration on adsorption of atrazine on oil palm shell-based adsorbent and activated carbon are shown in Figures 2 and 3, respectively. Batch adsorption experiments were carried out for 24 h to attain equilibrium. Figure 2 shows that the contact time necessary for adsorption of atrazine on oil palm shell-based adsorbent to reach equilibrium ranged between 150 to 240 min. However, for adsorption of atrazine on activated carbon, longer contact time of 24 h was required to achieve adsorption equilibrium, as shown in Figure 3. It could be seen that the adsorption rate at different concentrations was rapid in the first 15 min and steadily decreased with time until it gradually approached a plateau. The initial rapid uptake could be attributed to the availability of the number of free adsorption sites on the adsorbent and the higher concentration gradient created at the beginning of the adsorption process (Alam *et al.*, 2004). As the atrazine loading on the adsorbent increased, the concentration gradient reduced and gave way to a much slower uptake. Furthermore, the atrazine uptake, q_t increased with increasing in initial atrazine concentration. The amount of atrazine uptake at equilibrium, q_e increased from 0.168 to 3.378 mg/g for oil palm shell-based adsorbent and from 5.392 to 30.734 mg/g for activated carbon, with the increase in the initial atrazine concentrations from 5 to 30 mg/L. The initial concentration provided an important driving force to overcome all

mass transfer resistances of the atrazine between the aqueous and solid phases. Hence, a higher initial concentration of atrazine would enhance the adsorption process. Furthermore, the adsorption of atrazine could be described by three consecutive mass transport steps (Alam *et al.*, 2007). Firstly, the adsorbate transferred through the solution to the adsorbent exterior surface, followed by adsorbate diffusion into the pores of adsorbent. Finally, the adsorbate was adsorbed into the active sites at the interior of the adsorbent particle. Thus, activated carbon showed a much better adsorption performance than oil palm shell-based adsorbent, which could be attributed to the higher porosity in activated carbon.

3.3 Effect of Adsorbent Dosage

Figure 4 shows the removal percentage of atrazine as a function of adsorbent dosage. The removal percentage of atrazine increased from 9.35 to 14.34 % with increasing adsorbent dosage from 0.2 to 2.0 g. This was due to the increase in the number of adsorption sites (Selvaraj *et al.*, 1997; Sharma and Forster, 1993). Gupta *et al.* (2011) reported similar trend in the study of pesticides (methoxychlor, atrazine and methyl parathion) removal from waste water on activated carbon prepared from waster rubber tire. It was reported that the increase in adsorbent dosage from 0.2 to 1.6 g resulted in a significant increase in removal percentage of atrazine probably due to a stronger driving force and larger surface area (Gupta *et al.*, 2011). Any further increment of the adsorbent did not pose any noticeable change in the removal percentage, which might be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles (Namasivayam *et al.*, 1998).

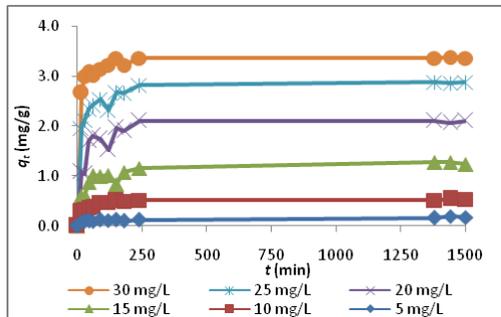


Figure 2: Time variation of adsorption of atrazine on oil palm shell-based adsorbent at various initial concentrations

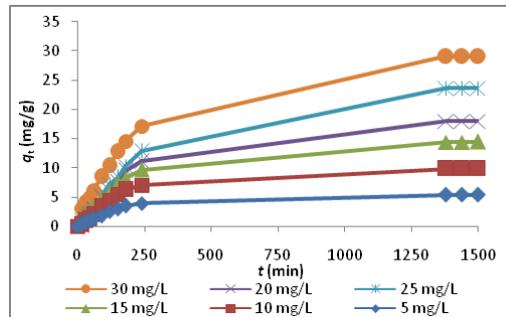


Figure 3: Time variation of adsorption of atrazine on activated carbon at various initial concentrations

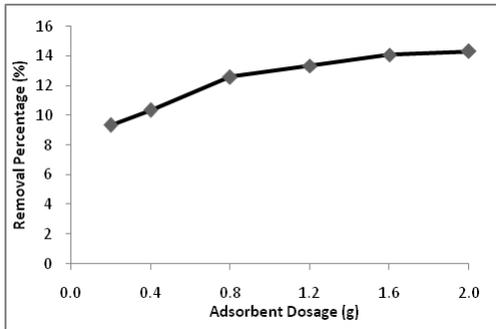


Figure 4: Removal percentage of atrazine on oil palm shell-based adsorbent at different adsorbent dosage

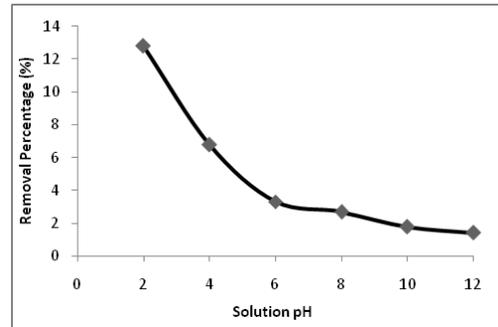


Figure 5: Removal percentage of atrazine on oil palm shell-based adsorbent at different solution pH

3.4 Effect of Solution pH

Figure 5 shows the effect of solution pH on the removal percentage of atrazine on the oil palm shell-based adsorbent. The removal percentage of atrazine decreased from 12.79 to 1.41 % with an increase in the solution pH from 2 to 12. Similar trends had been reported for the adsorption of atrazine (Rafique and Nasreen, 2011), prometryn (Topp *et al.*, 1997), imazaquin and imazethapyr (Barriuso *et al.*, 1992). As the solution pH increased, the functional groups especially carbonyl and hydroxyl groups became deprotonated, thus leading to development of negative charge at the surface of adsorbent (Gupta *et al.*, 2011). At higher pH, a more negatively charged surface of the adsorbent posed stronger electrostatic repulsion for atrazine molecules and thereby decreased the adsorption of atrazine. However, with a decrease in solution pH, the adsorption of atrazine on oil palm shell-based adsorbent increased due to weaker electrostatic repulsion as a result of the reduction in degree of deprotonation (Gupta and Imran, 2008). Besides, atrazine is a weak basic herbicide with pK_a value of 1.68. Atrazine could be adsorbed on adsorbent as both protonated and neutral species, depending on the solution pH (Weber, 1970). As the pH values were close to pK_a value, atrazine experienced protonization in acidic solutions which favoured hydrogen bond formation or proton transfer, thus resulting in the increase of removal percentage of atrazine (Rafique and Nasreen, 2011). However, atrazine is found as neutral molecule in the environment ($pH \approx 5$ to 8) (Colombini *et al.*, 1998). Meanwhile, with the increasing of solution pH, weakly basic atrazine became molecular species (Jamil *et al.*, 2011). At higher solution pH, a more negative charge developed at the surface of adsorbent and posed a stronger electrostatic repulsion for atrazine molecules, thus resulted in decrease in adsorption of atrazine (Gupta *et al.*, 2011).

3.5 Adsorption Isotherms

The Langmuir equation is applicable to homogeneous adsorption where the adsorption of each adsorbate molecule on to the surface has equal adsorption activation energy. When C_e/q_e was plotted against C_e , a straight line with slope of $1/Q_m$ was obtained. The values of Q_m and K_L were determined from the Langmuir plots and are presented in Table 1. The adsorption data of atrazine on both oil palm shell-based adsorbent and activated carbon were not fitted well into Langmuir isotherm as the correlation coefficients, R^2 obtained were relatively low. Furthermore, the negative values of Langmuir constants for oil palm shell-based adsorbent indicated the inadequacy of Langmuir isotherm to describe the adsorption of atrazine on the adsorbent (Uçar *et al.*, 2011). Unlike Langmuir isotherm model, Freundlich model occupies heterogeneous adsorption surface and active sites with different energy (Djebbar *et al.*, 2012). The Freundlich equation is suitable for a highly heterogeneous surface and an adsorption isotherm lacking a plateau, indicating a multi-layer adsorption (Daifullah *et al.*, 2004). The Freundlich constants K_F and intensity n could be calculated from the slope and intercept of the linear plot of $\ln q_e$ versus $\ln C_e$ and the values are presented in Table 1. The correlation coefficient, R^2 of Freundlich isotherm for oil palm shell-based adsorbent and activated carbon were 0.995 and 0.888, respectively, indicating that the equilibrium data were better fitted to Freundlich isotherm. Thus, the Freundlich isotherm model was used to estimate the adsorption capacity of the adsorbent for atrazine. The adsorption capacity, K_F and intensity n for adsorption of atrazine on oil palm shell-based adsorbent were $0.007 \text{ (mg/g)(L/mg)}^{1/n}$ and 0.531, respectively. Furthermore, the value of n was less than one, indicating that the adsorption of atrazine on oil palm shell-based adsorbent was less favorable as compared to activated carbon.

Table 1: Langmuir and Freundlich constants for the adsorption of atrazine on oil palm shell-based adsorbent and activated carbon

Adsorbents	Langmuir			Freundlich		
	Q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)(L/mg) ^{1/n}	n	R^2
Oil palm shell-based adsorbent	-1.065	-0.034	0.713	0.007	0.531	0.995
Activated carbon	62.058	1.196	0.626	46.462	1.321	0.888

3.6 Adsorption Kinetics

The adsorption kinetics data were fitted to the pseudo-first-order and pseudo-second-order kinetic models to evaluate the adsorption mechanism of the adsorption process. Constants k_1 and q_e for the pseudo-first-order kinetic model could be calculated from the plot of $\ln (q_e - q_t)$ versus time t , and are presented in Table 2. The correlation coefficient, R^2 values for the pseudo-first-order kinetic model were lower than those for pseudo-second-order kinetic model at all initial atrazine concentrations. In addition, the pseudo-first-order model gave a relatively large deviation between the calculated and

experimental values of q_e , indicating that pseudo-first-order model did not appropriately describe the adsorption process of atrazine on oil palm shell-based adsorbent. The pseudo-second-order kinetic model predicted the adsorption behaviour based on the agreement with chemisorption being the rate limiting step (Ho and McKay, 1998). The linear plots of t/q_t versus t were plotted. The constants k_2 and q_e could be calculated from the plots and are shown in Table 2. The pseudo-second-order kinetic model yielded a better fit than the pseudo-first-order kinetic model as the correlation coefficient, R^2 values were between 0.951 and 0.999, indicating the applicability of the pseudo-second-order kinetic model to depict the adsorption process of atrazine on oil palm shell-based adsorbent. It could be concluded that the mechanism of adsorption was pseudo-second-order reaction. A better fit to the pseudo-second-order kinetic model suggested that the adsorption rate was dependent more on the availability of the adsorption sites rather than the atrazine concentration (Salman *et al.*, 2011).

However, for adsorption of atrazine on activated carbon, the experimental data were better fitted into the pseudo-first-order kinetic model than the pseudo-second-order kinetic model, reflected by the correlation coefficient, R^2 values as listed in Table 2. Besides, the q_e values predicted by the pseudo-first-order kinetic model agreed well with the experimental q_e values, further confirming that the adsorption of atrazine on activated carbon followed the pseudo-first-order kinetic model. Table 2 illustrates that the rate constant k_1 decreased with increasing initial atrazine concentrations, which indicated that it was faster for the adsorption of atrazine on activated carbon at lower initial concentrations to achieve equilibrium.

Table 2: Pseudo-first-order and pseudo-second-order constants for adsorption of atrazine on oil palm shell-based adsorbent and activated carbon

Adsorbents	Initial Conc. (mg/L)	Exp. q_e (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
			k_1 (min^{-1})	Calc. q_e (mg/g)	R^2	k_2 (g/mg/min)	Calc. q_e (mg/g)	R^2
Oil palm shell-based adsorbent	5	0.168	0.001	0.193	0.502	0.502	0.130	0.977
	10	0.519	0.002	0.924	0.675	0.675	0.753	0.951
	15	1.275	0.001	2.160	0.662	0.662	1.188	0.956
	20	2.101	0.002	2.269	0.508	0.508	2.005	0.980
	25	2.874	0.001	2.326	0.650	0.650	2.697	0.995
	30	3.378	0.001	3.468	0.708	0.708	3.396	0.999
Activated carbon	5	5.209	0.005	5.618	0.992	2.037×10^{-4}	11.364	0.787
	10	10.027	0.005	10.740	0.992	0.837×10^{-4}	24.390	0.794
	15	14.777	0.004	14.397	0.996	3.831×10^{-4}	16.667	0.917
	20	18.385	0.004	19.240	0.995	0.563×10^{-4}	37.037	0.937
	25	24.101	0.004	24.484	0.992	1.477×10^{-4}	27.027	0.748
	30	29.696	0.003	28.078	0.996	2.987×10^{-4}	27.027	0.892

4.0 Conclusions

The present study showed that oil palm shell could be used as a potential precursor for the preparation of low cost adsorbent for removal of atrazine from aqueous solutions. SEM micrographs illustrated that chemical treatment with H_2SO_4 developed porosity on the surface of the adsorbent. The FTIR spectrum obtained for the adsorbent before and after the treatment was almost similar. Over the range of initial concentrations studied, the time for the adsorption of atrazine on the oil palm shell-based adsorbent to attain equilibrium ranged from 150 to 240 min. The adsorption uptake increased with increasing in initial atrazine concentration, with maximum atrazine uptake of 3.86 mg/g at concentration of 30 mg/L. The removal percentage of atrazine increased from 9.35 to 14.34 % with increasing adsorbent dosage from 0.20 to 1.20 g. The removal percentage of atrazine showed a decreasing trend from 12.79 to 1.41 % as the solution pH increased from 2 to 12. The negative values of Langmuir constants indicated that the Langmuir isotherm model was inadequate to describe the adsorption process. The adsorption equilibrium was well described by the Freundlich isotherm model, with correlation coefficient R^2 of 0.995, giving adsorption capacity K_F of $0.007 (mg/g)(L/mg)^{1/n}$ at 30 °C. It was found that the adsorption kinetics followed the pseudo-second-order kinetic model. The experimental results revealed that the oil palm shell-based adsorbent developed could be employed as an inexpensive adsorbent for the removal of atrazine from aqueous solutions.

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