Removal of Atrazine from Aqueous Solutions Using HNO$_3$ Treated Oil Palm Shell-Based Adsorbent

I.A.W. Tan, L.L.P. Lim, and K.T. Lim

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 focused on the feasibility of developing low-cost adsorbent from oil palm shell for removal of atrazine from aqueous solutions. The adsorbent was derived from oil palm shell using HNO$_3$ treatment. The derived adsorbent was characterized for the surface morphology and surface chemistry using SEM and FTIR, respectively. Adsorption equilibrium experiments were carried out in batch mode to investigate the effects of adsorbent dosage, initial concentration, contact time and solution pH on the adsorption uptake of atrazine on the adsorbent. The Freundlich isotherm model showed a better correlation compared to Langmuir isotherm model to fit the equilibrium data, giving the adsorption capacity of 0.046 mg/g(l/mg)$^{1/n}$ at 30 $^{\circ}$C. Atrazine solutions with pH 2 showed the highest adsorption uptake of 17.68%. The highest percentage removal was found to be 6.06% with adsorbent dosage of 2 g/200 ml. The adsorption process was found to follow the pseudo-second-order kinetic model more than the pseudo-first-order kinetic model as the correlation coefficients, R^2 for the pseudo-second-order kinetic model were relatively higher for all atrazine concentrations, ranging from 0.878-0.999. The adsorbent derived was proven to be feasible in removing atrazine from aqueous solutions.**

Keywords: Oil Palm Shell, Atrazine, Adsorption, Isotherm, Kinetic

I. INTRODUCTION

I NTOXICATIONS ascribed to pesticides have been estimated to be as high as 3 million cases of acute and severe poisoning annually. Hence, the importance of alternatives to prevent many of the pesticides poisonings, contaminations and remove pesticides from the aqueous solutions that exist today is of major concern [1]. Atrazine,2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine, is an organic compound consisting of an s-triazine-ring which is widely used as herbicide. Atrazine is used to stop pre- and post-emergence broadleaf and grassy weeds in major crops [2] – [3]. The compound is both effective and inexpensive, and thus is well-suited to production systems with very narrow profit margins, as is often the case with maize. The wide use of atrazine however negatively impacts the water quality and poses environmental pollution, even though its use is in a limited amount of compound despite its use is within the permitted dosage. 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 made of inexpensive materials such as agricultural wastes. Since oil palm shell is abundant in Malaysia, therefore this study aims to investigate the feasibility of using oil palm shell-based low-cost adsorbent for removal of atrazine from aqueous solutions.

II. MATERIALS AND METHODS

2.1 Materials and apparatus

In this research, oil palm shell was selected as raw material to prepare the lowcost adsorbent. The oil palm shell was collected from Federal Land Consolidation and Rehabilitation (Felcra) palm oil mill, Sarawak and the granular activated carbon of 6x12 mesh size was provided by Bravo Green Sdn Bhd. Analytical grade of atrazine was used for the preparation of stock solution. Distilled water was used in the preparation of all solutions and adsorbent sample purification. Volumetric flask of 1000 ml was used to prepare stock solution. Conical flasks of 500 ml were used in batch adsorption experiments.

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Plastic pipettes of 3 ml were used in the experiment for addition of sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH) to adjust the solution pH and to extract the sample. The concentrations of atrazine were analyzed by using a UV-visible spectrophotometer (Shimadzu UV mini 1240).

2.2 Preparation of adsorbent

The oil palm shell was washed with double distilled water to remove foreign impurities. The sample was dried in an oven at 110 ^{o}C for 24 h. The sample was then cooled to room temperature, crushed and sieved in stainless steel mesh sieve to obtain particles sized within the range of 0.15 - 0.30 mm. The sample was washed again thoroughly with double distilled water to remove the fibers and fine particles, then dried at 45 ^{o}C for 4 h in an oven. 50 g of the sample was soaked in 200 ml of n-hexane to remove residue oil from the oil palm shell surface. Then, the sample was chemically treated with 200 ml of 0.1 M nitric acid for 1 h, followed by soaking in 200 ml of methanol for 1 h to remove inorganic and organic matters from the surface of the adsorbent [4]. The adsorbent sample was washed with hot water until the solution pH reached 7, then subjected to thermal treatment in an oven at temperature of 200 ^{o}C for 6 h to increase the surface area. The chemically and thermally treated adsorbent was stored in a sample bottle for further characterization and analysis.

2.3 Characterization of adsorbent

The oil palm shell-based adsorbent was characterized using scanning electron microscope (SEM) (JEOL JSM-6390LA) to study the surface morphology of the adsorbent before and after the chemical treatment and also after the adsorption of atrazine whereas Fourier transform infrared (FTIR) spectrophotometer (Shimadzu IRAffinity-1) was used to identify the functional groups present on the surface of the oil palm shell-derived adsorbent.

2.4 Batch adsorption studies

Adsorption equilibrium experiments were carried out in batch mode to investigate the effects of initial concentration of atrazine, contact time, adsorbent dosage and initial solution pH on the adsorption uptake of atrazine by oil palm shell-based adsorbent. The stock solution of atrazine was prepared by dissolving 30 mg of analytical grade atrazine in powder form in 1% of methanol. The stock solution of atrazine of 30 mg/l was diluted using distilled water to the required concentrations in the range of 5-30 mg/l. Adsorption experiments to study the effect of initial concentration were conducted using 200 mg of adsorbent with 200 ml of atrazine solution of different initial concentrations at constant temperature (30 ^{o}C). The effect of adsorbent dosage was studied using dosage range of 0.2g-2g in 200 ml of atrazine solution with initial concentration of 5 mg/l at constant temperature (30 ^{o}C). The effect of solution pH on atrazine adsorption was investigated by contacting 200 mg of adsorbent with 200 ml of atrazine solution with initial concentration of 5 mg/l at varying initial pH in the range of 2-12 at constant temperature (30 ^{o}C). Adsorption equilibrium experiments were repeated by using activated carbon under the same condition to investigate the effects of initial concentration of atrazine on the adsorption uptake of atrazine by activated carbon. This was done to compare the effectiveness of the oil palm shell-based adsorbent in removing atrazine with the commercial activated carbon. The absorbance of atrazine at maximum wavelength of 222 nm was plotted against atrazine concentration to obtain a calibration curve for determination of atrazine concentrations. The adsorption uptake at time t, qt (mg/g), was expressed using (1) [5]:

$$q_t = (C_0 - C_t)V/W \tag{1}$$

where q_t is the amount of atrazine adsorbed by adsorbent (mg/g), C_0 is the initial concentration of atrazine (mg/l), C_t is the 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

The shape of an adsorption isotherm expresses the specific relationship between the concentration of adsorbate and the adsorption capacity of the adsorbent and reflects the possible mode for the adsorption process. The Langmuir model is valid for monolayer adsorption, applicable to homogeneous adsorption on a surface. The linear form of the Langmuir adsorption isotherm equation (2) can be written as following [6]:

$$C_e/q_e = 1/Q_m K_L + (1/Q_m)C_e \tag{2}$$

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.

The Freundlich isotherm is an empirical equation based on the assumption of multilayer formation of adsorbate onto a heterogeneous surface of adsorbent. It assumes that stronger binding sites are occupied first and binding strength decreases with increasing degree of site occupation. The linear form of Freundlich isotherm equation (3) can be written as following [7]:

$$\ln q_e = \ln K_F + (1/n)\ln C_e \tag{3}$$

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 favorability 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

To examine the mechanism of the adsorption process, two kinetic models were used to fit the experimental data. A simple kinetic analysis of the adsorption was evaluated by employing the pseudo-first-order (4) and pseudo-second-order (5) equations [6]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

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.

$$t / q_t = 1/(k_2 q_e^2) + (1/q_e)t \tag{5}$$

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.

III. RESULTS AND DISCUSSION

3.1 Characterization of adsorbent.

The SEM images of the raw oil palm shell, oil palm shell-based adsorbent treated with HNO$_3$, activated carbon and oil palm shell-based adsorbent after adsorption of atrazine are presented in Figures 1(a) – (d), respectively. From Figure 1(a), the SEM micrograph shows dirt-covered and unclear pores on the surface of raw oil palm shell. There are very small pores present on the surface of the raw oil palm shell. Chemical treatment with HNO$_3$ on the oil palm shell-based adsorbent resulted in the development of pores, as shown in Figure 1(b). The results showed that the surface of the HNO$_3$ treated adsorbent was highly porous as compared to the raw oil palm shell. This proved that HNO$_3$ had the potential in changing the surface structure of the adsorbent by its chemical properties in corroding the surface of the oil palm shell and increased the porosity onto it. Besides, acid treatment might dissolve the minerals from the adsorbent surface, thus increased the pore volume and surface area of the adsorbent [4]. 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). From Figure 1(d), it could be observed that the pores developed on the surface of the adsorbent were being occupied by the atrazine molecules.

(a)

(b)

(c)

(d)
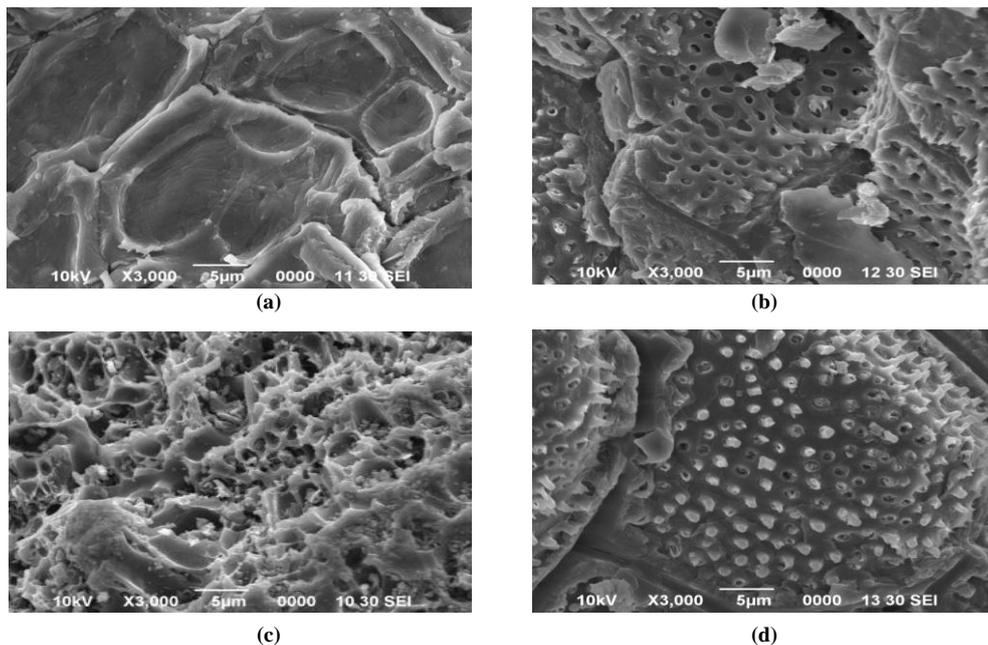
Figure 1: SEM images of (a) raw oil palm shell, (b) oil palm shell-based adsorbent treated with HNO$_3$, (c) activated carbon and (d) oil palm shell-based adsorbent after atrazine adsorption.

From the FTIR spectrum obtained, the raw oil palm shell showed six major absorbance peaks with high intensity at 3313.71 cm^{-1}, 2922.16 cm^{-1}, 2169.92 cm^{-1}, 2029.11cm^{-1}, 1753.93 cm^{-1} and 1598.99 cm^{-1} as well as two peaks at 1236.37 cm^{-1} and 1035.77 cm^{-1} with lower intensity. The peak at 3313.71 cm^{-1} might be attributed to NH stretching mode of amines or amides, while the peak at 2922.16 cm^{-1} was attributed to C-H aliphatic stretching vibration due to the existence of aliphatic groups in the oil palm shell. The peak around 1537.20 cm^{-1} could be ascribed to C=C stretching vibration in aromatic rings [5]. The peak at 1035.77 cm^{-1} was attributed to strong P-O-C interaction with the surface of the untreated oil palm shell. This indicated that the absorbance peaks were the strongest and had the highest frequencies for aliphatic compounds [5]. The FTIR spectrum for HNO$_3$ treated oil palm shell showed six absorbance peaks with high intensity at 3385.07 cm^{-1}, 3329.14 cm^{-1}, 2920.23 cm^{-1}, 1718.58 cm^{-1}, 1438.9 cm^{-1} and 1338.6 cm^{-1} as well as two peaks with lower intensity at 1238.3 cm^{-1} and 1031.91 cm^{-1}. The strong peak at 3385.07 cm^{-1} was typical of vibration originating from O–H stretching frequency of hydroxyl functional groups with hydrogen bonding [8]. The peak at 1338.6 cm^{-1} could be assigned to C=C stretching of aromatic rings polarized by oxygen atoms bound near one of the C atoms while the spectra revealed a peak at 1238.3 cm^{-1}

which indicated the presence of carboxylic group [9]. In the HNO_3 treatment of oil palm shell-based adsorbent, unstable oxygen groups (e.g. carboxyl groups) are decomposed and only hydroxyl and carbonyl groups remained whereby the successive physical and chemical treatment has helped in transforming a non-porous oil palm shell to a well developed adsorbent with favorable surface chemistry [9]. The peak occurred at 1031.91 cm^{-1} was ascribed to R–OH stretching of hydroxyl groups. The low intensities observed for the peaks could be the result of the elimination of these groups by carbonization and activation [10]. The presence of OH groups imparted negative charge to the oil palm shell surface [10]. The highest intensity peak for activated carbon was obtained at 3441.36 cm-1 and a lower intensity peak was obtained at 1525.69 cm^{-1}. The peak occurred at 1525.69 cm^{-1} was attributed to C=C stretching vibration of aromatic rings while the peak at 3441.36 cm^{-1} was ascribed to NH stretching mode of strong OH alcohols or phenols groups [6].

3.2 Effect of contact time and initial atrazine concentration

The adsorption of atrazine by oil palm shell-based adsorbent and activated carbon was studied at different initial concentrations of atrazine of 5, 10, 15, 20, 25 and 30 mg/l at 30 ^{o}C. Based on the results obtained by using UV visible spectrophotometer (Shimadzu UV mini 1240), a graph of adsorption uptake versus the adsorption time at various initial concentrations of atrazine for oil palm shell based-adsorbent and activated carbon was plotted as shown in Figure 2 and Figure 3, respectively. The adsorption uptake of the oil palm shell-based adsorbent and activated carbon was found to increase with the initial concentration of atrazine. The increase in initial concentration of atrazine has overcome the resistance to the mass transfer of atrazine between the aqueous and solid phases which also enhanced the interaction between atrazine and adsorbent as well as activated carbon [11]. As the initial concentration of atrazine increased, it increased the concentration gradient which acted as the driving force for the adsorption process [12]. Figure 2 shows that the time for the atrazine solution with initial concentration of 5 mg/l and 10 mg/l to reach equilibrium was 180 min while the atrazine solutions with initial concentration of 15 mg/l to 30 mg/l required longer time to reach equilibrium. This was due to the fact that at low concentrations, the ratio of available surface to the initial atrazine concentration was larger which had eased the adsorption process, therefore it was easier for the process to attain equilibrium. However, in the case of higher concentrations, this ratio was relatively lower, thus more time was needed to achieve equilibrium. The adsorption uptake of atrazine on activated carbon as shown in Figure 3 revealed that the adsorption process was quite rapid initially and reached equilibrium after 23 h. The initial high adsorption rate was due to the abundance of free binding sites[11]. The adsorption uptake of atrazine molecules by the activated carbon and the time required for establishment of equilibrium suggested the effectiveness of activated carbon in removing atrazine from aqueous solutions.
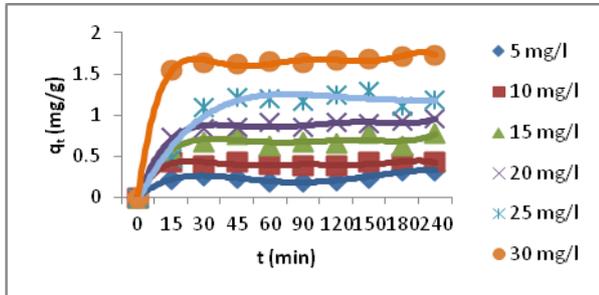
Figure 2: Adsorption uptake of atrazine at various initial concentrations on oil palm shell-derived adsorbent	Figure 3: Adsorption uptake of atrazine at various initial concentrations on activated carbon.
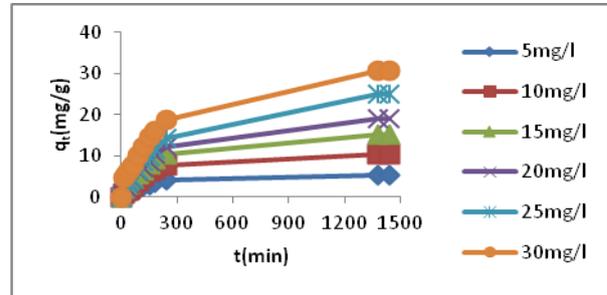
3.3 Effect of adsorbent dosage

The effect of the adsorbent dosage was studied at 30 ^{o}C by varying the adsorbent amount from 0.2 to 2 g with initial atrazine concentration of 5 mg/l. It could be seen from Figure 4 that initially the percentage removal of atrazine increased very sharply with the increase in adsorbent dosage. This trend was expected because as the adsorbent dosage increased, the number of adsorbent particles increased and thus more atrazine molecules were attached to their surfaces [12]. The percentage of removal increased rapidly up to 6 % with the increasing amount of adsorbent from 0.2 to 2 g. The initial rise in adsorption with adsorbent dosage was due to a stronger driving force and larger surface area. With a rise in adsorbent dosage, there was less corresponding increase in adsorption resulting from lower adsorptive capacity utilization of adsorbent [9].

3.4 Effect of solution pH

Batch adsorption experiments were performed at different solution pH ranging from pH 2 to 12 at 30 ºC. The initial concentration of atrazine was 5 mg/l and rotation speed of the shaker was fixed at 180 rpm. The percentage of atrazine removal decreased with an increase in the solution pH, as shown in Figure 5. This trend occurred possibly due to at low pH, the surface of the adsorbent would be surrounded by the hydronium ions, which might enhance the atrazine interaction with binding sites of the adsorbent by greater attractive forces and hence improved its uptake on polar adsorbent [13].
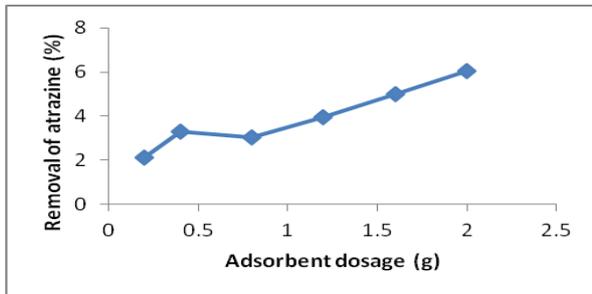
Figure 4: Effect of adsorbent dosage on atrazine removal.
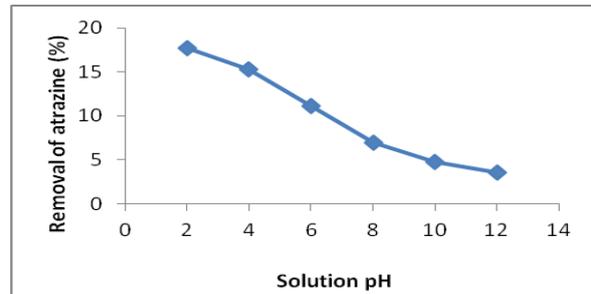
Figure 5: Effect of solution pH on atrazine removal.

3.5 Adsorption isotherms

The study of the adsorption isotherm is fundamental, and plays an important role in the determination of the adsorption capacity of an adsorbent, one of the most important criteria in selecting a suitable adsorbent [7]. In this study, two isotherm models were used in fitting the equilibrium data, namely the Langmuir and Freundlich isotherm models. The Langmuir isotherm model is valid for monolayer adsorption, applicable to homogeneous adsorption on a surface assuming that all the adsorption sites have equal solute affinity and that adsorption at one site does not affect the adsorption at an adjacent site [14]. The Freundlich isotherm is an empirical equation based on the assumption of multilayer formation of adsorbate onto a heterogeneous surface of adsorbent. It assumes that stronger binding sites are occupied first and binding strength decreases with increasing degree of site occupation [8]. The R^2 values obtained for Langmuir isotherm model was 3×10^{-5} for oil palm shell-based adsorbent and 0.0227 for activated carbon. This indicated that the adsorption of atrazine onto the adsorbent and activated carbon did not fit well to the Langmuir isotherm model. The linearized form of Freundlich isotherm model was used to evaluate the adsorption capacity of the adsorbent and activated carbon. The R^2 values obtained for Freundlich isotherm model were 0.982 and 0.997 respectively for the adsorbent and activated carbon, which indicated that Freundlich isotherm model better fitted the equilibrium data. The Langmuir and Freundlich constants were calculated from (2) and (3), respectively and are summarized in Table 1. The adsorption capacity, K_F and intensity n for adsorption of atrazine on oil palm shell-based adsorbent were 0.046 $(mg/g)(l/mg)^{1/n}$ and 0.98, respectively. The value of n which was less than one indicated that the adsorption of atrazine on oil palm shell-based adsorbent was less favorable as compared to activated carbon. However, this result is consistent with the literature where Alam et al. [15] also reported that the adsorption of atrazine using various adsorbents were well represented by Freundlich isotherm model.

Table 1: Langmuir and Freundlich constants for 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	1000	6.12E-0.5	3E-5	0.046	0.98	0.982
Activated carbon	12500	5.71E-0.3	0.022	1.140	1.045	0.997

3.6 Adsorption kinetics

Adsorption kinetics is a crucial characteristic from the point of view of analyzing the efficiency of adsorption processes which describes the solute uptake rate and evidently this rate controls the residence time of adsorbent uptake at the solid–solution interface including the diffusion process [13]. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process [16]. The Lagergren's pseudo-first-order and pseudo-second-order models [6] were used to investigate the adsorption kinetics data in order to determine the mechanism of adsorption process in this study. The pseudo-first-order and pseudo-second-order constants for oil palm shell-based adsorbent and activated carbon are listed in Table 2 and Table 3, respectively. Based on the pseudo-first-order plot, the R^2 values obtained were relatively low and the experimental q_e values did not agree with the calculated values obtained from the linear plot. This indicated that the adsorption of atrazine onto the adsorbent did not fit into the pseudo-first-order equation. However, the R^2 values obtained for the pseudo-first-order model were greater than 0.99 for activated carbon and the q_e calculated by this model were close to those obtained from the experiments. Similar trend has been reported by Gupta et al. [9] for pesticide removal from wastewater using activated carbon prepared from waste rubber tire. As the size of atrazine and methyl parathion was almost the same, their rate constants should also be similar, and the experimental rate constants were found to be nearly the same [9]. The pseudo-second-order kinetic model predicted the behavior over the whole range of adsorption and was in agreement with chemisorption being the rate controlling step [17]. The R^2 values obtained for the pseudo-second-order kinetic model were relatively high for all atrazine concentrations using the oil palm shell-based adsorbent. This further confirmed that the pseudo-second-order kinetic model was suitable in describing the adsorption of atrazine onto the adsorbent. However, an inverse relationship was observed for activated carbon which showed lower R^2 values for pseudo-second-order kinetic model, which ranged between 0.787-0.937.

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

Initial concentration (mg/l)	Experimental q_e (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
		k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g/mg.min)	q_e (mg/g)	R^2
5	0.259	0.0005	1.063	0.462	0.093	0.335	0.878
10	0.434	5E-5	1.020	0.039	0.656	0.427	0.996
15	0.769	0.0005	1.143	0.217	0.185	0.749	0.969
20	0.909	0.0007	1.111	0.627	0.172	0.958	0.998
25	1.217	0.0015	1.293	0.208	0.128	1.236	0.983
30	1.636	0.0006	1.051	0831	0.164	1.742	0.999

Table 3: Pseudo-first-order and pseudo-second-order constants for the adsorption of atrazine on activated carbon.

Initial concentration (mg/l)	Experimental q_e (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
		k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g/mg.min)	q_e (mg/g)	R^2
5	5.378	0.005	5.618	0.992	2.037E-4	11.364	0.787
10	10.378	0.005	10.740	0.992	0.837E-4	24.390	0.794
15	15.189	0.004	14.397	0.996	3,831E-4	16.667	0.917
20	19.028	0.004	19.240	0.995	0.563E-4	37.037	0.937
25	24.944	0.004	24.484	0.992	1.477E-4	27.027	0.748
30	30.734	0.003	28.078	0.996	2.987E-4	27.027	0.892

IV. CONCLUSIONS

The HNO_3 treatment facilitated in the development of a well developed porous adsorbent and integration of carbonyl and hydroxyl functional groups onto the adsorbent surface. These could be observed through the SEM micrographs and the FTIR spectrum, respectively. The optimum pH observed was at pH 2 which gave the highest atrazine removal of 17.68% whereas with adsorbent dosage of 2 g, the highest atrazine removal was found to be 6.06%. The equilibrium analysis was done using Langmuir and Freundlich isotherm equations. The Freundlich isotherm model showed a better correlation compared to Langmuir isotherm model in fitting the equilibrium data, giving the maximum adsorption capacity of 0.046 mg/g(l/mg)$^{1/n}$ at 30 ^{o}C. The adsorption process was found to follow the pseudo-second-order kinetic model for the oil palm shell-based adsorbent which suggested that the adsorption rate was dependent more on the availability of the adsorption sites than the concentration of the atrazine solutions. 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.

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