

Resistance of Mass Transfer, Kinetic and Isotherm Study of Ammonium Removal by Using a Hybrid Plug-Flow Column Reactor (HPFCR)

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ABSTRACT: Adsorption technique has been widely used for NH_4^+ removal from an effluent wastewater treatment plant (WWTP). Still, the resistances of mass transfer, kinetics and equilibrium isotherm of NH_4^+ on-to granular activated carbon (GAC) need to be verified. In this study, the hybrid plug-flow column reactor (HPFCR) with a combination of sand and GAC was used to remove NH_4^+ from a WWTP's effluent. Mass transfer model was applied to determine the global, external and internal mass transfer. The data obtained from batch study were analysed using Langmuir and Freundlich equations; Langmuir equation fitting with the NH_4^+ adsorption more appropriate. The adsorption kinetics have found match well with pseudo first-order. The dependency of resistance of mass transfer on film mass transfer was slightly higher than porous diffusion, for the bed depths of 2 to 12 cm, while the dependency of resistance of mass transfer on film mass transfer was lower than porous diffusion, for the bed depths of 15 cm. The effect of varying bed depths of column on resistance of mass transfer for the adsorption of NH_4^+ on GAC was verified to contribute to optimizing the adsorption process for the removal of NH_4^+ from wastewater of containing multi-pollutants.

KEYWORDS: Adsorption, Resistance of Mass Transfer, NH_4^+ , Activated Carbon;

1 INTRODUCTION

The high content of NH_4^+ in oxidation lagoon effluent is normally released into water bodies. An excessive of NH_4^+ in the water causes the algal blooms. It is succeeded by rapid algae growth and their subsequent death produced a greenish mucous layer on the surface water and affected to aquatic life. Filtration and adsorption methods can be applied to control NH_4^+ content in wastewater. The sand filter is widely used to trap organic and inorganic pollutants from water. Healy et al, (2010) compared the removal efficiency of sand, soil and crushed-glass filter in column study. All of the filters removed 100% of TSS, 42% to 65% of COD and over 80% of bacteria numbers. Application of coconut shell activated carbon to remove NH_4^+ has been verified in batch experiments with optimum conditions of pH 9.0, temperature 283 K, and contact time 120 min (Boopathy et al. 2013). The activated carbon produced from coconut shell has been proved in removing organic and inorganic pollutants from aqueous; however the performance of integrated filters between sand-gravel filter and activated carbon column to remove NH_4^+ in continuous runs is still not fully understood.

The experimental data of column test is often analysed using Adam-Bohart, Bed Depth Service Time (BDST), and Thomas model by many researchers

(Polowczyk et al. 2013, Sarıcı-Ozdemir 2012). The analysis results of these models commonly expressed in term of adsorption rate constant (L/mg min) and adsorption capacity (mg/g). These models cannot clarify the adsorption mechanism in aqueous solution. However, the simplest method to describe the mechanism of adsorption is using a mass transfer model developed by Fulazzaky (2011). This model is successfully used to analyse the resistance of mass transfer of adsorption in single solute, however its application in the different bed depths of column and multi pollutant solution has still not been studied. This study is aimed at carrying out tests on treatment of conventional oxidation lagoon effluent using the hybrid plug-flow column reactor. The principal objectives are: (i) to study the efficiency of the infiltration – adsorption method to treat NH_4^+ in batch and column study; and (ii) to explain the global, film and porous of mass transfer model at different bed depths in HPFCR.

2 MATERIAL AND METHOD

2.1 Material

The commercial coconut shell activated carbon (GAC) supplied by Nikom Carbon Technology Sdn. Bhd, Malaysia was used in this study. The oxidation

lagoon effluent is continuously fed into the HPFCR. The composition of WWTP effluent is as follows (mg/L): $\text{NH}_4\text{-N} = 18$; chemical oxygen demand (COD) = 136; total suspended solids (TSS) = 79; $\text{PO}_4^{-3} = 9.85$; DO = 4.29; pH = 6.63; $\text{SO}_4^{-2} = 32$.

2.2 Batch experiment

Batch experiments were conducted to determine the isotherm and kinetics of NH_4^+ adsorption with initial concentration equal to 19.75 mg/L. A UV-Spectrophotometer (HACH DR5000) was used to determine the NH_4^+ concentration using the Nesslerization Method. The adsorption capacity (mg/g) of GAC was calculated with the following equation;

$$q = \frac{(C_i - C_f)V}{W} \quad (1)$$

where C_i (mg/L) and C_f (mg/L) are the initial concentration and final concentration, respectively, V (L) is the volume of sample and W (g) is the adsorbent weight.

Synthetic solutions for NH_4^+ were prepared by dissolving an analytical grade ammonia chloride (NH_4Cl) in the distilled water. In the adsorption isotherm study, a series of 50 ml tube containing a different mass of GAC (0.2, 0.5, 0.8, 1.2, and 1.5 mg) and 40 ml solution were continually shaken at 120 rpm for 24 hours. The supernatants were taken out from the tube and filtered through 0.45 μm membrane filter before the ammonium concentration was analysed.

The adsorption kinetics experiment was performed as follows; the adsorbent (2 g) was loaded in 250 mL conical flask with added 100 mL ammonia chloride solutions. The conical flask was shaken in an orbital mode at 120 rpm. The samples were then taken from the flask at a regular time interval and filtered through a 0.45 μm membrane filter. The filtered samples were subsequently analysed for concentration ammonium.



Figure.1. Hybrid plug-flow column reactor configuration; (1) Influent tank (2) Sand Filter (3) Perforated Holes with 2mm di-

ameter (4) Silicon tube (5) Peristaltic pump (6) Columns (7) Bottles sample.

2.2 Hybrid plug-flow column reactor

The hybrid plug-flow column reactor (HPFCR) is a combination process of infiltration and adsorption in a single treatment. A lab-scale HPFCR reactor was set up in which consist of a gravel-sand filter, activated carbon columns and peristaltic pump to control flow rate.

A schematic diagram of the process configuration is shown in Fig.1. The samples were taken at the influent tank, after the sand filter tanks and at the outlet of the columns for analysis using a UV-Spectrophotometer (HACH DR 5000).

3 RESULTS AND DISCUSSION

3.1 Adsorption isotherm

The Langmuir and Freundlich equation were used for evaluating the experimental data. The linear form of the Langmuir isotherm equation can be written as

$$\frac{C_e}{q_e} = \frac{1}{kq_m} + \frac{C_e}{q_m} \quad (2)$$

where q_e (mg/g) is the equilibrium amount of adsorbate that was adsorbed by per unit mass of adsorbent, C_e is the concentration of adsorbate in the equilibrium solution (mg/L), and the values of q_m (mg/g) and k (L/mg) are the maximum adsorption capacity of the adsorbent and the adsorption energy coefficient, respectively.

The Freundlich isotherm parameters can be determined by plotting $\ln q_e$ vs $\ln C_e$ used linear regression equation as written in equation (3).

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3)$$

where K_f is Freundlich constant (mg/g), and $1/n$ is the heterogeneity factor,

Table 1. Langmuir and Freundlich parameters

Langmuir			Freundlich		
q_m	K_1	R^2	$1/n$	K_2	R^2
1.4	0.024	0.98	0.31	0.2181	0.93

The calculated data are given in Table 1 shows the Langmuir equation gives a better fit than Freundlich models. The calculated q_m in this study is lower than that reported by Halim et al. (2010) with 6.079 mg/g using coconut shell activated carbon. Vassileva et.al (2009) determined that q_m and k of NH_4^+ adsorption kinetics using coal based activated carbon were 10.25 mg/g and 0.006 L/mg, respectively.

3.2 Adsorption Kinetics

Pseudo-first order and second-order can be used to investigate the adsorption mechanisms of NH_4^+ . The first-order rate equation or so called Lagergren equation is commonly expressed as;

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

where q_e and q are the amount of adsorbate adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the Lagergren rate constant of pseudo-first-order adsorption (1/min). In order to fit an equation (4) to the experimental data, the equilibrium sorption capacity, q_e , must be known (Ho & McKay 1998). The second-order of the rate law can be expressed in linear form as follows

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

where k is the equilibrium rate constant of pseudo second order adsorption (g/mg/min). The plot of t/q_t against t of the equation (5) should give a linear relationship, from which q_e and k can be determined from the slope and intercept of the plotted graph (Ho 2006).

The kinetics parameters were listed in Table 2. In comparing these values with other coconut shell activated carbon over a range of initial NH_4^+ concentrations, Boopathy et.al (2013) reported that the k_1 and k_2 values with initial NH_4^+ concentration of 500 mg/L were 0.075/min and 0.164 g/mg.min, respectively. Halim et.al (2010) determined k_1 and k_2 at initial NH_4^+ concentrations of 1980 mg/L were 0.1488/min and 0.0174 g/mg.min, respectively.

Table 2. Pseudo first-order and Pseudo second-order parameters.

Pseudo first-order				Pseudo second-order			
q_e (exp)	q_e (cal)	k_1	R^2	q_e (exp)	q_e (cal)	k_1	R^2
0.9	0.82	0.0001	0.98	0.9	0.18	0.1812	0.97

3.3 Mass Transfer Resistance Analysis

Mass transfer resistance analysis is used to determine global mass transfer factors $[k_L a]_g$, film mass transfer factor, $[k_L a]_f$ and porous diffusion factor $[k_L a]_d$. The data from the experimental analysis were used to calculate mass transfer resistance. The Fulazzaky's mass transfer model was used for evaluation of experimental results. The plotted graph of q versus $\ln T$ of Eq.(6) is used to determine the potential mass transfer index relating to driving force for mass transfer (B) (mg/g) and adsorbate-adsorbent affinity parameter(β) (g.min/ mg)

$$q = B + \frac{1}{\beta} \times \ln T \quad (6)$$

where q is the accumulative quantity of the solute adsorbed onto adsorbent (mg/g), T is the accumulative time of feeding influent in the HPFCR (min). The parameters B and $1/\beta$ determined from the intercept and slope of plotting graphs are used in an equation (10) to calculate $[k_L a]_g$.

$$B = \frac{\ln([k_L a]_g) - \ln\{\ln\frac{C_0}{C_s}\}}{\beta} \quad (7)$$

where C_0 is the concentration of NH_4^+ at the inlet of HPFCR (mg/L) and C_s is the concentration of NH_4^+ at the outlet of HPFCR

The $[k_L a]_f$ and $[k_L a]_d$ can be calculated using equation (8) and (9) in unit 1/min, respectively.

$$[k_L a]_f = [k_L a]_g \times e^{-\beta q} \quad (8)$$

$$[k_L a]_d = [k_L a]_g - [k_L a]_f \quad (9)$$

The relatively, increasing of bed depth decreased the B value (from -0.2914 to -0.4725) Experimental data validation shows that the β value varies from 6.301 mg/g to 9.183 mg/g. The parameters β differs with changed in the bed depth because of the characteristic of the solution entering into the column. It is maybe due to the presence of pollutants from the WWTP effluent that changed driving force for mass transfer into acceptor sites (Fulazzaky et al. 2013).

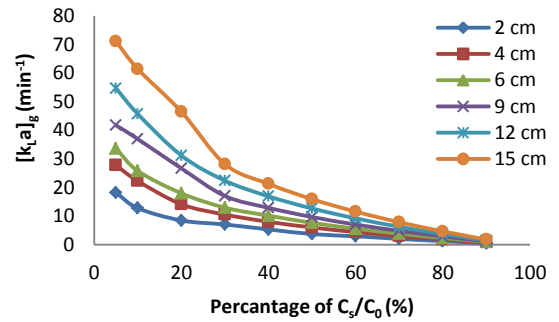


Figure 3. Global mass transfer factor to percentage of outflow.

Global mass transfer (GMT) is sum of film mass transfer (FMT) and porous diffusion (PD). Figure 3 shows that increasing of bed depth was increased the $[k_L a]_g$. The variations of $[k_L a]_g$ rapidly decrease when C_0/C_s is below 30 % of bed depth of 9, 12 and 15 cm; below 20 % of bed depth of 2, 4 and 6 cm. From this it could be deduced that an increase in bed depth makes the adsorbate to be more readily attached on the GAC because of the increased availability amount of surface area (JagadeeshBabu et al. 2010).

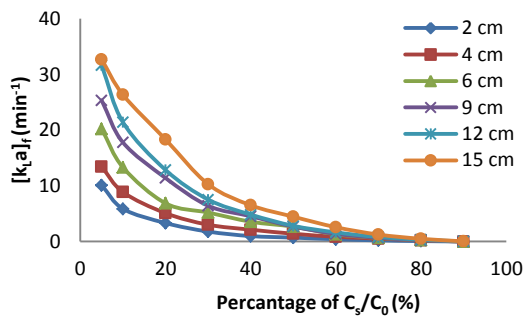


Figure 4. Film mass transfer factor to percentage of outflow.

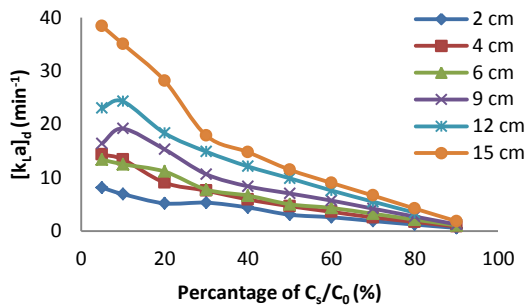


Figure 5. Porous diffusion factor to percentage of outflow.

The film mass transfer analysis showed that all the curves were rapidly decreasing when the percentage of outflow was below 20 % for bed depths of 2, 4, and 6 cm; and below 30 % for bed depths of 9, 12, and 15 cm (see Figure 4). Figure 5 shows that the three curve trends were occurring in porous diffusion analysis (1) The variations of $[k_{LA}]_d$ for a bed depth of 2, 4, and 6 cm are gradually decreasing until reaching 90 % of C_0/C_s ; this trend indicate that the adsorbate difficult to penetrate into the adsorbents pores because the adsorbate readily accumulated on the surface of GAC. (2) The curves were convex at bed depths of 9 cm and 12 cm; this gives meaning that the porous diffusion is a main mechanism of resistance of mass transfer before breakthrough occurred (Fulazzaky 2011). (3) The variation of $[k_{LA}]_d$ rapidly decreased when the percentage of outflow was below 30 % of bed depth of 15 cm. This is occasionally due to increase the porosity diffusion of mass transfer resistance and slowing mass transfer rate. It is caused by the large size particle (1.18 mm to 2.36 mm) used in this study. The long time contact occurred between adsorbent and adsorbate in the higher bed depth; thus, it easily permits the adsorbate to arrive at deeper acceptor sites of solid surface (Cussler, 2007).

4 CONCLUSION

The study used the HPFCR to remove NH_4^+ from effluent of the WWTP. The variation of $[k_{LA}]_g$, $[k_{LA}]_f$ and $[k_{LA}]_d$ were verified to understand the resistance of mass transfer for adsorption NH_4^+ onto GAC. The

rate of external mass transfer was evaluated slightly higher than an internal mass transfer for bed depths of the column of less than 12 cm. The adsorption in the effluent WWTP onto GAC of coconut shell material basis was verified to contribute to improve environmental quality of the receiving waters.

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