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AMMONIA AND COD REMOVAL FROM SYNTHETIC LEACHATE USING RICE HUSK COMPOSITE ADSORBENT

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Abstract: Ammonia and chemical oxygen demand (COD) were the most two problematic parameters in the landfill leachate. In this study, a new composite adsorbent derived from rice husk ash waste is evaluated with respect to its ability to remove these contaminants from synthetic leachate. Results indicate that the new composite adsorbent is able to adsorb both ammonia and COD. It has a higher adsorption capacity for ammonia (Q = 2.2578 mg/g) and an almost equal adsorption capacity for COD (Q = 2.8893) when compared with commercially activated carbon. The adsorption kinetics of this new product for ammonia and COD were primarily represented by the pseudo second-order mechanism. The overall adsorption rate of the ammonia and COD adsorption processes appears to be determined by chemisorption process. The regenerated composite adsorbent indicated higher adsorption capacities of ammonia and COD, i.e. 12.9366 mg/g and 3.1162 mg/g, respectively.

Keywords: Rice husk; composite adsorbent; synthetic leachate; ammonia and COD removal

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INTRODUCTION

Adsorption is one of the effective ways to remove colour, odor, and organic and inorganic pollutants from wastewater. It is useful for the adsorbents to selectively adsorb a certain mass of component onto their surfaces. Activated carbon (AC) has been known as an alternative to biological and physico-chemical methods in wastewater treatment due to its good adsorptive ability (Ismadji & Bhatia, 2001). Despite the usefulness of activated carbon as adsorbent in wastewater treatment, its use has been restricted due to costly maintenance (El-Geundi, 1997). Activated carbon also does not have enough adsorption capacity for ammonia due to its non-polar surfaces, which causes poor interactions between some of the polar substances (Azhar *et. al*, 2010a, 2010b; Soo-Jun & Byung-Joo, 2005).

Currently, carbon–mineral materials (or CMMs) are often used for wastewater treatment. The basic distinctive features of these materials are the so-called mosaic-like structure of their surfaces, with simultaneous availability of both hydrophilic (mineral) and hydrophobic (carbon) phases on their surfaces. Such a structure allows equally effective adsorption of both polar and non-polar substances (Soo-Jun & Byung-Joo, 2005).

At present, few adsorbent materials can efficiently remove both ammonia and COD (Melgunov *et al.,* 2000). Many studies have been performed that focused on the preparation of new composite adsorbents with low-cost materials that have the additional virtue of possessing improved adsorptive properties compare to other conventional adsorbents (Azhar *et al.,* 2009; Leboda, 1993; Gao *et al.*, 2005). Rice husk yields a high ash content of 19 wt% that mainly consists of silica and carbon (Apichat & Eakachai, 2010). The typical chemical composition of rice husk ash is: 84.3% SiO_2, 12.2% loss on ignition (mainly carbon materials), 1.4% CaO, 0.6% Fe_2O_3, 0.5% MgO, 0.4% Na_2O, 0.3% Al_2O_3, and 0.2% K_2O_3 (Naiya *et al.*, 2009). Since the main components of rice husk are carbon and silica, it has the potential to be used as a raw material in composite adsorbent for both organic and inorganic pollutant removal.

Generally, landfill leachate has relatively high COD as well as ammonia nitrogen concentration (Poh-Eng *et al.*, 2010). Combinations of organic and inorganic pollutants existing in landfill leachate need adsorbents that have the ability to remove various pollutants, including organic and inorganic species. It is well known that activated carbons are the most effective adsorbents for the removal of organic pollutants from the aqueous or the gaseous phase. Therefore, this type of adsorbent finds wide application as a commercial adsorbent in the purification of water and air. Because

of the weaknesses of AC when it comes to adsorbing polar or inorganic pollutant, much research has focused on modifying the AC surfaces, or on producing composite adsorbents that have the ability to interact with both organic and inorganic adsorbates. The aim of this study is characterization of a new composite adsorbent fabricated from chemically modified rice husk ash for ammonia and COD removal from synthetic landfill leachate.

MATERIALS AND METHODS

Preparation of Composite adsorbent

The new rice husk composite adsorbent was prepared from rice husk carbon waste (75% w/w), activated carbon (8.22% w/w), and ordinary Portland cement or OPC (16.78% w/w). About 250 ml of 0.2M aluminum nitrate and 500 ml of 2.0M sodium hydroxide were added, and this mixture paste was left to harden for 24 hours and then submerged in water for a 3-day curing period. The hardened rice husk composite adsorbent was then dried in an oven at 104ºC for 24 hours. These composite media were crushed and sieved to get desired particle size (1.18 to 2.36 mm), and the adsorbent was then crushed into powder (<150 µm); the size of the adsorbent used for all the experiments is the same. Activated carbon (AC) will be used as conventional adsorbent in this study for comparison to this new adsorbent material at same particle size (<150 µm).

Preparation of Synthetic Leachate

The preparation of synthetic leachate in this study has been adapted from a previous study with modifications, as shown in **Table 1** (Nacera & Aicha, 2005; Bracklow *et al.,* 2007). The pH range was pH 5.8–6.0. Synthetic wastewater (leachate) was designed to achieve a realistic COD:TN:TP ratio and tested for long-term biodegradability. This wastewater composition is supposed to approximate the composition of municipal wastewater and has a wide range of different carbon sources; it contained polysaccharides, protein, and lipid components (Renou, 2008).

Characterization of rice husk composite adsorbent

X-ray diffraction testing with an X-ray diffraction spectrometer (D5000 model; Siemens AG) was conducted to determine the presence of minerals in the new composite material. Determination of cation exchange capacity (CEC) was performed using the ammonium replacement method (Rhoades, 1982; Thomas, 1982). This experiment was carried out by removing excess ammonium with 95% ethanol solution,

Table 1. Synthetic leachate composition

Chemical components	Amount Per liter
Acetic acid (CH_3COOH)	7 mL
Propionic acid ($C_3H_6O_2$)	5 mL
Pentanoic acid ($C_5H_{10}O_2$)	1 mL
Hexanoic acid ($C_6H_{12}O_2$)	1 mL
$MgSO_4$	156 mg
$CaCl_2$	2882 mg
Na_2CO_3	324 mg
$NaHCO_3$	3012 mg
$(COO.NH_4)_2.H_2O$	2400 mg
NaCl	1440 mg
pH (adjusted using NaOH)	5.8 – 6.0
Trans metals solution (TMS)	1 mL
Distilled water	1 liter
TMS compositions	
$CuCl_2$	40 mg
$(NH_4)_2SO_4.NiSO_4.6H_2O$	50 mg
$(NH_4)_2Fe(SO_4)_2.6H_2O$	2000 mg
$BaCl_2.2H_2O$	50 mg
$MnSO_4.4H_2O$	500 mg
Sulphuric acid (H_2SO_4) 96%	1 mL
Distilled water	1 L (Final volume)

replacing and leaching it with proton, H^+ of 0.1 N HCl. CEC testing was conducted using the new composite adsorbent. Commercial AC was used as a point of comparison.

Batch Adsorption Study

The batch adsorption study can be divided into three parts, starting with determination of optimum parameters, adsorption isotherm study, and adsorption kinetic study. The batch adsorption experiment was conducted by placing a series of nine 250-mL conical flasks, each with 5 g adsorbent media and 100 mL synthetic leachate solution. These flasks were then placed on an orbital shaker at 200 rpm for 120 minutes at 25^oC (room temperature). All the mixture solution with adsorbent was then filtered with Whatman filter paper that was 50 mm in diameter. The range of initial concentrations of ammonia and COD were 685–735 mg/L and 7330–9530 mg/L throughout the study, respectively.

The effect of pH for ammonia and COD removal was studied by adjusting the pH of solutions, in the range of 4–10 using 37% HNO_3 and 1 M NaOH. Optimum pH was obtained by the highest percentage of ammonia and COD removal from the analysis concentration of ammonia and COD in filtered solution. Optimum contact time was the time needed for adsorption process to be in equilibrium, where no changes been detected in the concentration of adsorbate after a certain time. This contact time was determined by fixing the removal of the conical flasks from the shaker to certain time intervals (at 1, 2, 5, 8, 10, 15, 20, 30, 45, 60, and 75 min). The optimum time was investigated from analysis concentrations of ammonia and COD in instances where no changes of concentration had been noted after equilibrium time.

The dosage study was conducted by preparing series of the conical flasks for two types of adsorbents; the new composite adsorbent, and conventional AC. This experiment was operated in optimum conditions that were obtained from optimum testing parameters for pH and contact time. The final concentration of ammonia and COD removal was then compared for both adsorbents. Adsorption isotherm has been carried out based on the experiment of dosage study by varying the amount of adsorbents. The most common models used in this isotherm study are Langmuir and Freundlich isotherms. The isotherm constants and least-squares correlation coefficients (R^2) of both models were compared to determine the isotherm model best-fit in this study. This isotherm study was applied to three types of adsorbent; rice husk composite adsorbent, AC, and regenerated rice husk composite adsorbent. Adsorption kinetic was studied based on four kinetic models; pseudo first-order, pseudo second-order, Elovich model, and intra-particle model. Kinetic data were obtained from the determination of contact time at equilibrium. The kinetic constants and least-squares correlation coefficients (R^2) of four models were compared to determine the best-fit kinetic model for this study.

The regeneration study was conducted by performing the desorption experiments with the regeneration solution, 0.5 M NaCl at pH > 12 (adjusted using 2M NaOH), that were used previously in the new composite rice husk composite adsorbent. After the adsorption process, the adsorbent was cleansed with distilled water to remove the balance of synthetic solution. The series of conical flasks were prepared contained 100 mL of regeneration solution and 5 g of rice husk composite adsorbent media, then shaken for 30 minutes and filtered out. This procedure was repeated for three times and all the rice husk composite adsorbent media were then dried out and weighted for dosage study after regeneration to compare with the fresh rice husk composite adsorbent composite media. The weight of ammonia was determined using the standard phenate method; COD was determined by closed colorimetric reflux standard method (APHA, 2005).

RESULTS AND DISCUSSIONS

Characterization of New Adsorbent

X-ray diffraction testing (**Fig. 1**) identified two types of aluminosilicate minerals that exist in composite adsorbent: *stilbite-calcium* (monoclinic) and *berririte* (orthorhombic); with the formula molecules $(Na)_{1.76}(Ca)_{4.00}[(Al)_{10.29}(Si)_{25.71}(O)_{72}(H_2O)_{29.4}]$ and $(Na,K,Ca)_2(Si,Al)_9(O)_{18\cdot7}(H_2O)$, respectively.

Cation Exchange Capacity

The mean CEC value for rice husk composite adsorbent is four times higher (0.39 meq/g) than that for AC (0.08 meq/g). Statistical analysis (Student's t-test) showed a significant difference between two media ($P < 0.05$). The higher CEC value of adsorbent provided the advantage of exchangeable sites for cations, and therefore may have increased the rate of adsorption. The formation of aluminosilicates contributed to the CEC improvement.

Batch adsorption study

The optimum pH for ammonia removal was at pH 6 (26.64%); for COD, it was pH 5 (49.21%), as shown in **Fig. 2**. It could be concluded that the optimum pH for this study was at pH 5–6. For ammonia, the properties of ammoniacal nitrogen in aqueous solution explain the result; the existence of two types of elements, ammonia, NH_3 (basic) and ammonium ions, NH_4^+ (acidic). Therefore, the removal of ammonia is supposed to be higher at low pH, and vice versa, due to the cation exchange mechanism in aqueous solution (Demir *et al.*, 2002). However, ammonia removal dramatically decreases at pH < 5 because of H^+ competition. COD components were contributed by organic acids in synthetic leachate, which can be in two forms: acidic (R- COOH) and basic (R- COO$^-$). The adsorption data for the uptake of ammonia and COD versus contact time is presented in **Fig. 3**. Results showed that contact time required for the adsorption of ammonia and COD was 45 minutes and 30 minutes, respectively.

The results indicated that percentage-range removal of ammonia using rice husk composite adsorbent media was higher (7.09–51.06%) than with AC (2.84–34.04%); conversely, the removal for COD was higher using conventional activated carbon (24.20–36.48%) compare to rice husk composite adsorbent media (13.64–27.61%), as shown in **Figs 4a–4b**. There are also significant differences for both percentage removals in t-test statistical analysis.
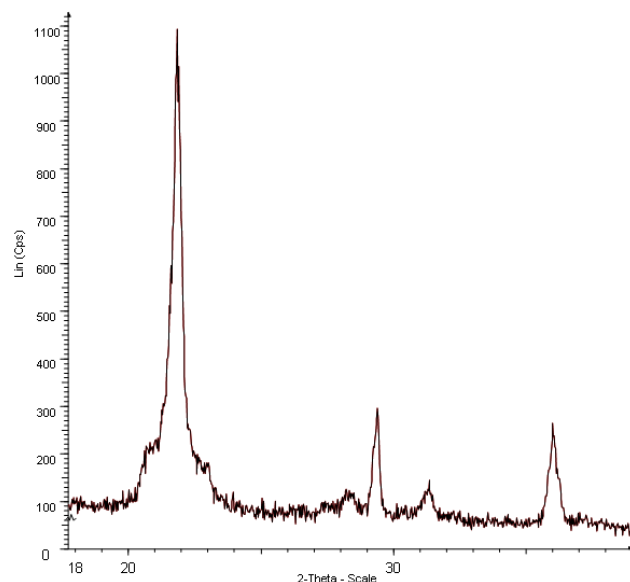
Fig. 1 X-ray diffraction spectrum of new composite adsorbent (rice husk composite adsorbent).
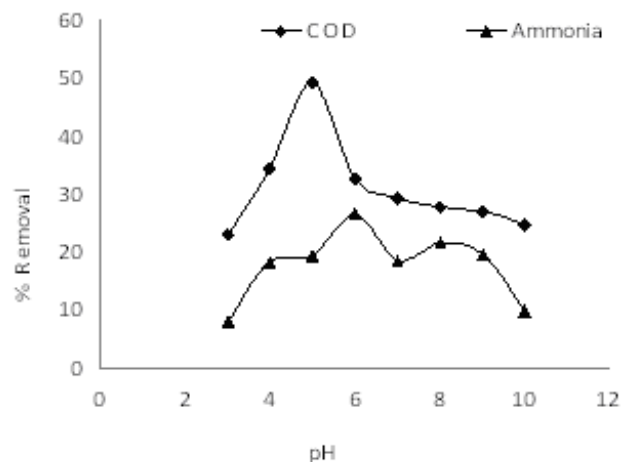
Fig. 2 Optimum pH for ammonia and COD removal.
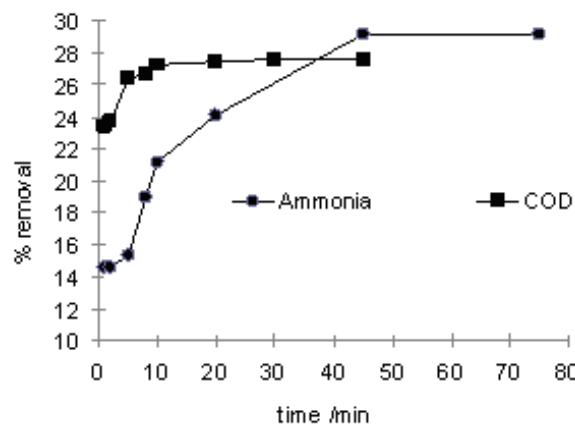
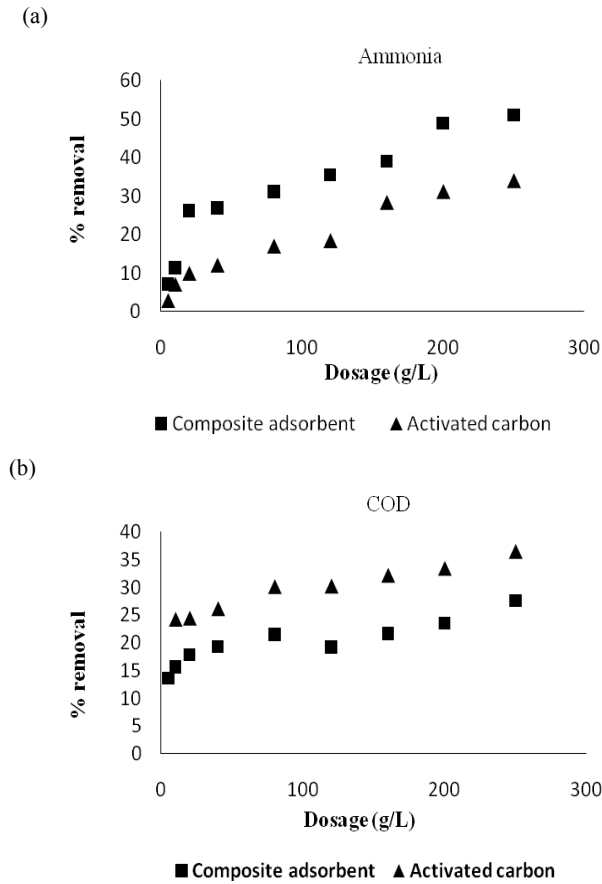**Fig. 3** Optimum contact times for ammonia and COD removal.

(a)

Ammonia

■ Composite adsorbent   ▲ Activated carbon

(b)

COD

■ Composite adsorbent   ▲ Activated carbon

Fig. 4 Dosage effect for (a) ammonia and (b) COD removal.

The higher CEC value reported for rice husk composite adsorbent media may affect the result obtained for ammonia removal. This indicated that the cation (NH_4^+) exchange mechanism towards rice husk composite adsorbent media was greater than with AC. This indicates that the removal rate for ammonia increased during the adsorption process. The lowered rate of ammonia removal reported for AC was probably due to AC's non-polar surfaces, which cause poor interaction between the polar substances (Soo-Jin & Byung-Joo, 2005). On the other hand, the higher COD removal reported for AC was due to the hydrophobic surfaces themselves; micropore structure, high adsorption capacity, and active surfaces may make AC more suitable in adsorbing organic materials.

Adsorption Isotherm

Adsorption isotherm was an equilibrium plot of solid phase (q_e) versus liquid phase concentration (C_e). Two isotherm models are Langmuir model with linear plotted $1/q_e$ versus $1/C_e$ and the following equation:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{k_L q_m C_e}$$ (1)

where q_e is the equilibrium adsorbate concentration in solution; q_m is the maximum adsorption capacity; and K_L is Langmuir constant in L/mg.

Freundlich model with linear plotted log q_e versus log C_e shown in the following equation;

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$ (2)

where K_f is, roughly, an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. A linear form of the Freundlich expression will yield the constants K_f and $1/n$.

The results indicated that the removals of ammonia and COD were conforming more to the Langmuir model due to highest R^2 value for all adsorbents used (**Table 2**). The Langmuir adsorption isotherm model describes the surface as homogeneous, assuming all the adsorption sites have an equal adsorbate affinity and that adsorption at one site does not affect adsorption at an adjacent site (Mohan & Pittman, 2006). The comparison of Langmuir constant, or maximum adsorption capacity, q_m indicated that higher value noted for rice husk composite adsorbent (2.2578 mg/g) compared to AC (0.7351 mg/g). These q_m values were derived from the intercept of the linear graphs obtained. The differences between these two adsorbent media were probably due to the higher cation exchange mechanism towards rice husk composite adsorbent media during ammonium adsorption compared to AC.

It is found that the coefficients of determination obtained (R^2) from the Freundlich model were lower than those obtained with the Langmuir model, as given in **Table 2**. The Freundlich isotherm model is widely used but does not provide information on the monolayer adsorption capacity. The obtained Freundlich constant

Table 2. Langmuir isotherm constants for adsorption of ammonia and COD onto different adsorbents

Adsorbent	Constant		
	R^2	q_m	K_L
Fresh Rice husk composite adsorbent			
Ammonia	0.9840	2.2578	0.0012
COD	0.9789	2.8893	0.0001
Activated Carbon			
Ammonia	0.9454	0.7351	0.0012
COD	0.9975	2.2962	0.0002
Regenerated Rice husk composite adsorbent			
Ammonia	0.9384	12.9366	0.0006
COD	0.9445	3.1162	0.0002

*(q_m in mg/g and K_L in L/mg).

(as shown in **Table 3**) represents adsorption intensity; n was less than 1 ($n < 1$) for all types of adsorbent media, while $n > 1$ shows good adsorption, that is, demonstrates that good adsorption is occurring throughout the concentration range (Chiou & Li, 2003). Therefore, the results indicate that the equilibrium data is not fitted well with the Freundlich isotherm model compared with the Langmuir isotherm model.

Adsorption Kinetic study

An adsorption kinetic study was conducted to determine the kinetic and adsorption mechanism of ammonia and COD removal onto rice husk composite adsorbent. In order to analyze the adsorption kinetics for these new media, the pseudo first-order, pseudo second-order, Elovich models, and intra-particle kinetic models were used to analyze the experimental data. The pseudo first-order linear equation describes the kinetics of the adsorption process as follows (Chairat *et al.*, 2008):

$$\ln = (q_e - q_t) = \ln(q_e) - k_1 t \tag{3}$$

where q_e (mg/g) and q_t (mg/g) are the amount of adsorbate adsorbed at equilibrium and at t time respectively, and k_1 is the rate constant of this first-order model. The pseudo second-order equation can be written in linear form as follows (Ho & McKay, 1999):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

where the slope and intercept of (t/q_t) versus t are used to calculate the pseudo second-order rate constant, k_2 and adsorbate adsorbed at equilibrium, q_e. This model used to explain the probability of overall adsorption properties was suited to a chemical adsorption mechanism. Chemically, the adsorption process usually involves monolayer adsorption because of specific bonding between adsorbates and the surface of adsorbent (Cooney, 1998).

Table 3. Freundlich isotherm constants for adsorption of ammonia and COD onto different adsorbents

Adsorbent	R^2	n	K_F (mg/g)(mg/l)^n
Fresh Rice husk composite adsorbent			
Ammonia	0.9699	0.4066	7.91×10^{-7}
COD	0.8255	0.0749	1.81×10^{-50}
Activated Carbon			
Ammonia	0.8935	0.2805	2.80×10^{-10}
COD	0.8837	0.0964	1.40×10^{-38}
Regenerated Rice husk composite adsorbent			
Ammonia	0.9020	0.7570	1.48×10^{-3}
COD	0.9815	0.0837	2.51×10^{-44}

The Elovich equation assumes that the real media surfaces are heterogeneous based on their energy, which explains the pseudo second-order kinetic (Azhar *et al.*, 2009). The linear equation form as follows:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{5}$$

where α and β are the Elovich coefficients representing initial adsorption rate and desorption constants, respectively.

The intra-particle diffusion model used to show the adsorptions are by intraparticle mixing. A linear equation for an intraparticle diffusion model can be defined as follows;

$$q_t = k_{i1} t^{0.5} + c \tag{6}$$

where k_i is the intraparticle diffusion constant and c is intercept.

The kinetic study results show that the adsorption of ammonia and COD were suited to pseudo second-order kinetic model by possessing the highest R^2 value for both; ammonia ($R^2 = 0.9963$) and COD removal ($R^2 = 1$). These results were also supported by the values of adsorption capacity at equilibrium time q_e from both calculations and experiment.

The results have been shown that the calculated q_e values show good agreement with the experimental values, indicating that the second-order kinetic model well describes the removal of ammonia and COD using new composite rice husk composite adsorbent media as an adsorbent as shown in **Table 4**.
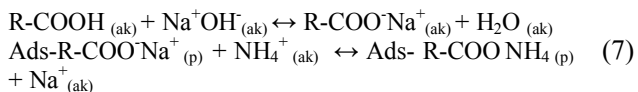
Regeneration

The ability to regenerate is one of the important characteristics of good adsorbent. One of the AC weaknesses was the difficulty to regenerate in addition to the high costs incurred via energy use or necessity of using expensive chemicals. **Figures 5a–5b** show the results of the regeneration study of rice husk composite adsorbent media. They indicate that the percentage removal of ammonia increased after regeneration (13.61–57.14%), compare to fresh rice husk composite adsorbent (10.21–41.13%), a result supported by t-tests that showed a significant difference ($P < 0.05$). Based on a previous isotherm study (**Table 2**), the increasing value of adsorption capacity q_m has been noted for regenerated rice husk composite adsorbent media (12.9366 mg/g) compared to fresh rice husk composite adsorbent (2.2578 mg/g).

Table 4. Kinetic models constants for adsorption of ammonia and COD onto new composite Rice husk composite adsorbent media

Kinetic Model		NH$_3$	COD
First order	R^2 k_1 (min^{-1})	0.9606	0.9335
	$q_{e,calc}$ (mg/g)	0.0594	0.1995
	$q_{e,exp}$ (mg/g)	2.2380	8.0518
		4.00	52.60
Second order	R^2 k_2 (g/mg.min)	0.9963	1.0
	$q_{e,calc}$ (mg/g)	0.0655	0.0744
	$q_{e,exp}$ (mg/g)	4.1982	52.9101
		4.00	52.60
Elovich	R^2 α (mg/g.min)	0.9155	0.8666
	β (g/mg)	11.2688	5633
	$q_{e,calc}$ (mg/g)	1.8359	0.4276
	$q_{e,exp}$ (mg/g)	3.0082	12.8906
		4.00	52.60
Intra-particle	R^2 K$_i$ (mg/g.min$^{1/2}$)	0.9208	0.6681
	c $q_{e,calc}$ (mg/g)	0.3014	1.3524
	$q_{e,exp}$ (mg/g)	1.7141	45.46
		3.7360	52.87
		4.00	52.60

This phenomenon indicated that there were the additions of cation exchangeable sites onto the surface of rice husk composite adsorbent media after regeneration, providing more exchangeable sites and increasing ammonia removal during adsorption. Exchangeable sites are added onto rice husk composite adsorbent composite media derived from carboxylic organic acids in synthetic leachate components. This phenomenon will be explained as follows:

R-COOH $_{(ak)}$ + Na$^+$OH$^-$$_{(ak)}$ ↔ R-COO$^-$Na$^+$$_{(ak)}$ + H$_2$O $_{(ak)}$
Ads-R-COO$^-$Na$^+$$_{(p)}$ + NH$_4$$^+$$_{(ak)}$ ↔ Ads- R-COO NH$_4$$_{(p)}$ (7)
+ Na$^+$$_{(ak)}$

Figure 5b shows the results of COD removal using rice husk composite adsorbent media before and after regeneration. Results show the difference in COD removal between two rice husk composite adsorbent media–fresh (15.00–21.59%) and regenerated (11.73–22.92%).

There were no significant differences reported in the statistical t-test ($P > 0.05$). Based on the results obtained, this shows that the rice husk composite adsorbent media were applicable to COD removal even after regeneration, and can be reused with almost the same capacity for COD removal.

CONCLUSION

New composite rice husk composite adsorbent possesses a higher CEC value compared to conventional AC. Based on the batch adsorption study, the removal of ammonia and of COD was well-fitted with the Langmuir isotherm model. This shows that the adsorption process was by monolayer adsorption due to specific bonding between adsorbate and the surface of adsorbent. This was also supported by the results of kinetic study for both ammonia and COD removal, which were obtained following the pseudo second-order model. This model, used to explain the probability of overall adsorption properties, was suited to the chemical adsorption mechanism. The ability to regenerate has been proved for new composite media. The adsorption capacity of ammonia has been increased with no appreciable difference in COD removal between fresh and regenerated composite media.

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