



Removal of Ammonia Nitrogen NH-N and Hexavalent Chromium (VI) From Wastewater Using Agricultural Waste Activated Carbon

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ABSTRACT

Highly porosity characterized activated carbon (AC) was achieved using agricultural waste as raw material used as adsorbent to treat wastewater through removal of ammonia nitrogen (NH-N) and hexavalent chromium (Cr (VI)). The preparation method of AC included using zinc chloride as activation agent. Characterizations of the porosities of AC preparations were performed using N₂ adsorption-desorption to ascertain surface area and pore volume. Existing groups on the AC surfaces were resolved using Fourier Transform Infrared Spectroscopy (FTIR) analyses. Scanning electron microscopic (SEM) was used to assess AC morphologies. Maximal surface areas of AC preparations were discovered to be 1190.41 m²/g at activation temperatures of 700 °C. Adsorption isotherm was analyzed using two models Langmuir and Freundlich. The kinetic study was represented through Pseudo first order and pseudo second order.


Keywords: Activated carbon, Agricultural waste, Adsorption, Wastewater.

INTRODUCTION

Environmental conservation protection takes a great consideration over the years in all over world, especially the protection of water from pollution. One of the most toxic pollutants in wastewater which affect human healthy is the high concentration of hexavalent chromium and

ammonia nitrogen. Previous studies showed that high concentration of ammonia nitrogen is inhibit the biological degradation by the microorganism^{1,2}. Hexavalent form of chromium is toxic and is suspected to be carcinogenic. It affects the kidney and liver and causes dermatitis, diarrhea³. For these reasons, its important to treat wastewater effluent before discharging it to environmental.



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Various technologies have been investigated for treatment of wastewater including physical and chemical methods, ion exchange, electrochemical treatment (Erabee *et al.*, 2017a). Membrane separation and AC adsorption⁴. Adsorption onto AC has several advantages over other water treatment methods, primarily as a very simple technology and more efficient in removing high molecular weight compounds from aqueous matrix (Erabee *et al.*, 2017b). Nowadays, good source for AC preparation is agricultural material because of low cost and availability⁵ (Erabee *et al.*, 2017c). The most widely used precursor for production of AC is jute and coconut fibre⁶, apricot stone⁷, coconut husk⁸, and rice husk⁹. This study aimed to treat sample of wastewater by producing low cost adsorbent with high porosity for removal of ammonia nitrogen and hexavalent chromium. Also, to study the equilibrium and kinetic mechanism of NH-N and Cr (VI) adsorption onto the prepared activated carbon, and to identify characteristics of prepared activated carbon including functional groups and surface area.

EXPERIMENTAL

Analysis of Sample Solution

The waste water that used in this study was collected from Mini STP (Sewage Treatment Plant) at faculty of engineering in University Putra Malaysia (UPM) which is located at Selangor state in Malaysia. The sample of wastewater is followed by laboratory testing in order to evaluate levels of organic and inorganic contaminants based on the Examination of Water and Wastewater methods. Table (1) shows the parameters limits of sample and effluent of Standard B which stated in the Sewage and Industrial Effluents Regulations 1979 by Department of Environmental Malaysia.

The measuring of PH, TDS, salinity and electrical conductivity were made using Tracer Pocket tester (Code:1766, LaMotte, Taiwan). TSS of the sample was determined by pouring a well-mixed sample (20 ml) through a pre weighted filter paper that was mounted on a vacuum filtration apparatus. A standard laboratory procedure was used to measure COD and BOD of sample. In testing the turbidity a multi-detector optical turbid meter was used. For measuring NH-N and heavy metals a multi-detector optical colorimeter (Hach DR/890 Colorimeter).

Table 1: Initial characteristics of raw wastewater sample

Parameters	Unit	Value	Malaysian Standards*
pH	-	7.11	5.5 – 9.0
TDS	ppm	270	-
TSS	mg/L	1050	100
Salinity	ppm	330	-
Turbidity	NTU	276	-
Electric conductivity	iS/cm	688	-
COD	mg/L	470	100
BOD	mg/L	135	50
NH-N	mg/L	65	-
Zn	mg/L	0.1	1.0
Cr (VI)	mg/L	70	0.05
Mn	mg/L	0.1	1.0

*Sewage and Industrial Effluents (Standards B), 1979, DOE Malaysia

Preparation of AC

Garden waste, which is the small branching of trees, collected from the agricultural waste of UPM gardens. These garden waste is used as a raw material for the AC preparation. Washed and cleaned raw materials were crushed and grinded to small particles (0.3-0.6 mm) and dried in at 100 °C for 24 h 10 g of the dried sample was carbonized at 300 °C for 4 h using electric tubular furnace at a rate of 10 °C/min. and under continuous 100 ml/min. N₂ flow. After carbonization, the sample was mixed with chemical activation agent of ZnCl₂ at impregnation ratio of 1.5/1 (weight of ZnCl₂/ weight of precursor, w/w) for 12 h, then dried heated at activation temperatures of 700 °C. Holding time at final temperature was 1 hours. Hot distilled water was used for washing the resulted sample after cooling until neutral PH. The sample was dried at 100 °C for 24 h and stored in desiccator.

Characterization of activated carbon

SEM analysis was used to indicate textural morphology of prepared AC. Chemical functional groups of activated carbon were identify using Fourier transform infrared spectroscopy (FTIR) in the scanning range of 400-4000 cm⁻¹. The surface properties was characterized with Micrometrics ASAP 2020, using adsorption of N at 77 k.

Batch Adsorption study

In this test, different adsorbent doses (1, 2, 3, 4 and 5 g/L) of AC prepared from garden waste (AC-GW) were mixed with 100 mL volume of electrolyzed leachate sample. Incubation of the conical flasks was at room temperature, then agitated at 200 rpm using a mechanical shaker (Orbital Shaker, 100-240 VAC, HS4010A), Different retention times at 30, 60, 90, 120, 180, 240, 300, and 360 min. respectively, were employed.

The following formula is used to evaluate the removal efficiencies¹⁰.

$$RE\% = \frac{(C_0 - C_e)}{C_0} \times 100$$

Where C_0 initial concentration, C_e concentration at time t .

Ascertainment of AC's sorption capacity was done by calculating using following equation.

$$q_e = \frac{(C_0 - C_e)V}{m}$$

Where m adsorbent mass and V volume of leachate sample.

Adsorption Equilibrium Isotherms

Equilibrium adsorption study was analysed using two models Langmuir and Freundlich as follows.

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m}$$

Where K_L (L/mg) and q_m (mg/g) are represent energy of adsorption and adsorption capacity, respectively. The constant q_m and K_L are characteristics of the Langmuir equation which can be determined from the slope and intercept of the plot C_e/q_e against C_e . The equilibrium parameter R_L can be found from the following equation:

$$R_L = \frac{1}{(1 + K_L * C_e)}$$

Unfavourable adsorption was assumed when $R_L > 1$, while linear adsorption at $R_L = 1$, favourable ($0 < R_L < 1$), and irreversible when $R_L = 0$.

Adsorption Kinetic Study

Pseudo first order and pseudo second order models were used to represent kinetic study, as follows.

Pseudo first order Model

Integral form of pseudo first order equation was indicated in the following equation¹¹.

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t$$

Where

q_e (mg/g) is the amount of adsorbate at the equilibrium, q_t (mg/g) is the amount of adsorbate at time t (min.), respectively and k_1 (L/min.) is the rate constant. The adsorption rate constant, K_1 , can be calculated by plotting $\log(q_e - q_t)$ versus t .

Pseudo-Second Order Model

Linearized integral form of pseudo second order kinetic model is represented as

$$\frac{t}{q_t} = \frac{1}{K_2 * q_e^2} + \frac{1}{q_e} t$$

where q_e and q_t (mg/g) are the amount of adsorbate at the equilibrium and at time t (min.), respectively k is the pseudo-second order rate constant of adsorption (g/mg.min). K_2 and q_e can be obtained from the intercept and slope by plotting t/q_t versus t .

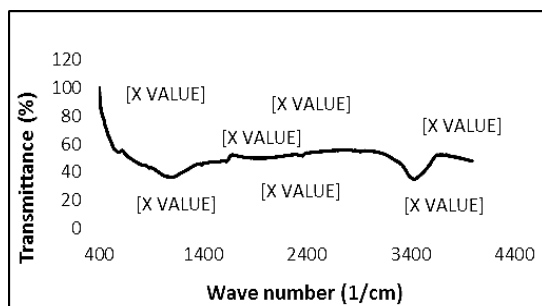
RESULTS AND DISCUSSION

AC Characterizations

The nitrogen adsorption isotherms are used to obtain the surface physical parameters which were indicated in Table 1. The surface area, pore volume, micropore surface area and micropore volume of AC-GW was 1190.41 m²/g, 0.43 cm³/g, 568.752 m²/g and 0.299 cm³/g, respectively. Fig. 1 presents the surface chemistry of the prepared AC with ZnCl₂ activation. The FTIR of AC illustrated simple surface chemistry, the band at 3361 cm⁻¹ is due to the presence of N-H stretching. The shorted peak at 2314 cm⁻¹ was attributed to presence of C-N stretching. The broad peak between 1673 cm⁻¹ to 1544 cm⁻¹ is a result of the N-H bond.

Table 2: Porosity characteristics of prepared AC

Properties	Value
Surface area	1190.41 m ² /g
Pore volume	0.430 cm ³ /g
Micropore surface area	568.752 m ² /g
Micropore volume	0.299 cm ³ /g

**Fig. 1. F.T.I.R analysis of prepared AC**

SEM test used to perform surface morphology of AC-GW as shown in Fig. 2. Its clear from the figure that well-developed porous in the surface of prepared AC which were considered as channels to microporous network.

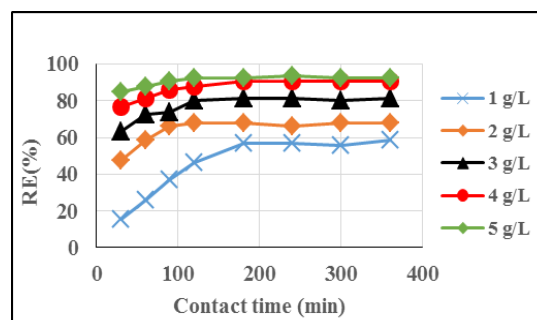
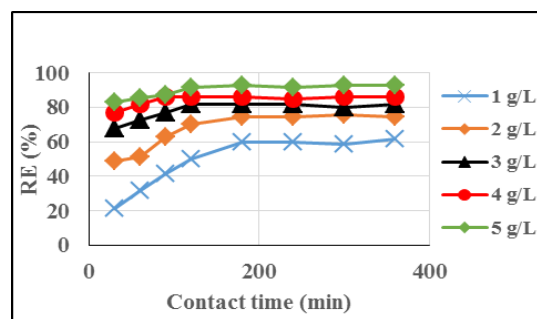
**Fig. 2. SEM image of prepared AC-GW**

Batch Adsorption Process

Effect of contact time and Adsorbent Dose on Removal Efficiencies of Parameters

The adsorption process was done using prepared activated carbon made from Sago palm bark. The final concentration of NH-N and Cr (VI) were analyzed after different intervals of contact time (30, 60, 90, 120, 180, 240 and 300 min.). Fig. 3 and 4 illustrate the effect of contact time and

adsorbent dose of AC-GW in the removal efficiencies of NH-N and Cr (VI). Different adsorbent doses 1, 2, 3, 4 and 5 g/L of AC-GW were used to adsorb contaminates from the sample at different contact time intervals from 30 to 360 minutes. It is clear from the figure that the removal efficiencies of parameters were increased with increasing of contact time and reach the maximum removal percentages after 180 min. of contact time. NH-N and Cr (VI) have their optimum removal efficiencies with 5g/L adsorbent dose and contact times from 30 to 360 minutes. Maximum RE for NH-N as shown in Fig. 3, are 85, 88, 91, 92, 90, 92 %, respectively. Maximum RE for Cr (VI), as shown in Fig. 4, are 83, 86, 87, 91, 93, 91, 93 and 93%, respectively.

**Fig. 3. Effect of adsorbent dose and contact time on removal efficiency of Zn using AC-SPB****Fig. 4. Effect of adsorbent dose and contact time on removal efficiency of Cr (VI) using AC-SPB**

As a result, the removal efficiencies of NH-N and Cr (VI) increased with increasing of contact time due to the active sites abundance on the surface of adsorbent^{12,13}. The slow removal capacity with the subsequent time may be due to the diffusion of heavy metal ions onto the surface of AC and fewer binding sites¹⁴. The same results were

conducted by Kyzas¹⁵ who concluded that the end of adsorption was at 180 minutes. Babel and Kurniawan¹⁶ observed that removal efficiency increased with an increase in contact time. The adsorbent dose is strongly effected removal percentage in adsorption process¹⁷. From Fig. 3 and 4, it can be observed that removal efficiencies of NH-N and Cr(VI) improved with increasing adsorbent doses due to availability of more adsorption sites¹⁸.

Maximum removal percentages were obtained at 5 mg/L adsorbent dose and 180 min. of contact time for all different dosages of parameters. These results were noted as optimum conditions for subsequent studies.

Equilibrium Adsorption Models

The adsorption Langmuir isotherm for NH-N is represented in Fig. 5. The Langmuir constants and their correlation coefficients R_2 for adsorption of NH-N and Cr (VI) via AC-GW, are listed in Table 2. For NH-N, the value of R_L is 0.0015 which indicates favorable adsorption of NH-N using AC-GW. Fig. 6 shows Freundlich isotherm for NH-N removal by AC-GW at 3 h of contact time. The Freundlich isotherm constant (KF and n) and their correlation coefficients R_2 are summarized in Table 2. The value of n for Freundlich isotherm for NH-N is equal to 1.883, represent moderately good adsorption between 1-2¹⁹. The results showed that the Freundlich isotherm model better fits the experimental data.

The Langmuir adsorption isotherm for Cr (VI) by AC-GW was shown in Fig. 7. Value of R_L equal to 0.001 as determined in Table 2 and correlation coefficient is equal to 0.870.

While Freundlich adsorption isotherm for Cr (VI), as in Fig. 8, showed that high correlation coefficient (0.992) with value of n (1.137) between 1 and 2, and represented good adsorption. From the results, the Freundlich isotherm of Cr (VI) better fits to experimental data than Langmuir isotherm.

Table 2: Langmuir and Freundlich isotherms parameters

Parameters	NH-N	Cr (VI)
Langmuir		
KL(L/g)	10.453	14.232
RL	0.0015	0.001
qm (mg/g)	3.61	3.268
R2	0.893	0.870
Freundlich		
KF	5.211	2.163
1/n	0.531	0.879
R2	0.821	0.992

Kinetic Adsorption Models

Figures 9 and 10 show the plots of the first order model of NH-N and Cr (VI) adsorption, respectively.

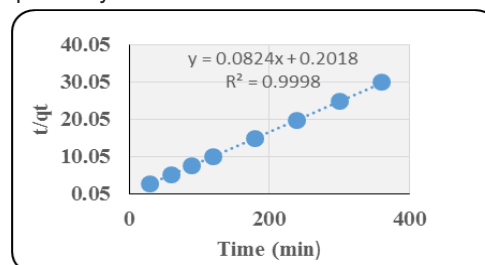


Fig. 9. Pseudo first order of NH-N adsorption

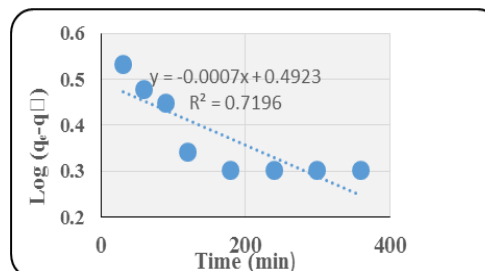


Fig. 10. Pseudo first order of Cr(VI) adsorption

Figures 11 and 12 show the plots of the second order models for adsorption of NH-N and Cr (VI), respectively.

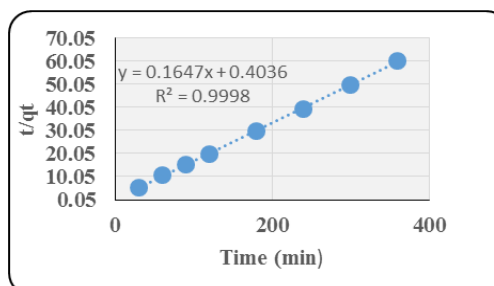


Fig. 11. Pseudo second order for adsorption of NH-N on AC-GW

Tables 3 and 4 show Pseudo first order and pseudo second order parameters of NH-N and Cr (VI), respectively, on AC-GW. The correlation coefficients (R²) values of pseudo first order were found to be 0.858 and 0.719, respectively, for NH-N and Cr (VI), respectively. While pseudo second order model demonstrated much linearity

agreement recording R² are equal to 0.999 and 0.999, for NH-N and Cr (VI), respectively. The higher correlation coefficient and predicated values of q_e which were in agreement with the corresponding experimental values, it was suitable to describe the kinetic adsorption process of NH-N and Cr(VI), respectively.

Table 3: Pseudo first order parameters

Parameter	K1	q _e (mg/g)	R ²
NH-N	0.0039	1.949	0.858
Cr (VI)	0.00161	3.111	0.719

Table 4. Pseudo second order parameters

Parameter	K2	q _e (mg/g)	R ²	Q _e (exp.) (mg/g)
NH -N	0.0333	12.195	0.999	12
Cr (VI)	0.0149	13.227	0.999	13

Comparison of Adsorption Capacity of Prepared AC with Different Precursors

Table 5 and 6 show the comparison of

removal efficiencies of different types of precursors which were used as adsorbents for NH-N and Cr (VI) from wastewater.

Table 5: Comparison of removal efficiencies of NH-N using different adsorbents

AC-Precursor	pH	initial concentration (mg/L)	Adsorbent dose (g/L)	Removal (%)	Source
Nigerian waste bamboo	6.67	58.7	123.5	80.4	20
Coconut shell	7	1890.95	5	35	21
Sugarcane bagasse	8.30	1113.2	50	41	22
Garden waste	7.11	65	5	92	Present study

Table 6: Comparison of removal efficiencies of Cr (VI) using different adsorbents

AC-Precursor	pH	initial Concentration (mg/L)	Adsorbent dose (g/L)	Removal (%)	Source
Jatropha husk	2	10	60	61	23
Coconut shell charcal	4	20	12	85	16
Commercial coconut shell	4	20	6	90	16
Tamarind wood	5.68	10	2	99	24
Trapa natans husk	6	10	1.5	94.6	14
<i>Eichornia crassipes</i> root	4.5	100	10	92.24	25
Peanut shell	4	30	0.1	46.63	26
Modified activated carbon	2	30	1	50.60	27
Rice husk	2	100	0.2	94	28
Powder activated carbon	2	10	2	95.84	29
Mango kernel	2	20	10	100	30
Garden waste	7.11	70	5	93	Present study

CONCLUSION

The treatment of wastewater was examined using agricultural waste collected from

garden waste activated carbon assisted adsorption process. The porosity characterizations of prepared activated carbon indicated that garden waste is good adsorbent due to its highly surface porosity

and effective precursor for adsorption of pollutants from wastewater such as NH-N and Cr(VI). The results illustrated that the Freundlich isotherm of NH-N and Cr(VI) better fits to experimental data. Kinetic adsorption study shows pseudo second order model was suitable to describe the kinetic adsorption process of NH-N and Cr(VI) onto AC-GW. The removal efficiencies of NH-N and

Cr (VI) using AC-GW were found to be equal 92 and 93%, respectively.

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