

Expert Opinion on Environmental Biology

Review Article

A SCITECHNOL JOURNAL

Evaluation of Activated Carbon as a Substratum to Phytoremediate Eutrophic Wastewater

Linh NTT¹, Vu DB¹, Duy HK¹, Chien TM¹, Hong S² and No K^{2*}

Abstract

In this paper, we study on the use of Vietnam activated carbon made from coconut shell as the role of a substratum to phytoremediate eutrophic wastewater. To determine the ability of the activated carbon as a substratum, the characteristics of the surface of activated carbon and the adsorption kinetics models were studied. SEM images showed that the activated carbon did not have the definite shape, while FTIR result revealed the presence of SiO₂ and PO43- in the component of the activated carbon. pH PZC of activated carbon was determined in the range of 8.4-8.7 by the pH drift method. The pseudo second-order kinetics model had the highest value of R² and the equilibrium amount calculated from the pseudo second-order kinetics equation was 0.343 mg.g⁻¹ with the rate constant of adsorption was 0.096 g.mg⁻¹.min⁻¹. The Freundlich adsorption isotherm cannot be used to describe the adsorption because the value of R² was 0.114, while Langmuir isotherm had the value of R² was 0.997, and the maximum adsorption capacity for forming single layer was equal to 0.338 mg.g-1, Langmuir constant was equal to 0.292 L.mg⁻¹.

Keywords

Phytoremediation; Activated carbon; Adsorption; pH PZC

Introduction

Eutrophication, a pollution problem in lakes or reservoirs, has been increased, either directly or indirectly, by both natural reasons and human activities. The processes of sedimentation and accumulation of an excess of organic matter are a consequence of the process of eutrophication. The organic sediments are the high abundance of phosphorus, nitrogen; and the rapid decomposition of organic material by bacteria and fungi causes a depletion of oxygen and dissolution of solids [1]. Eutrophication not only typically causes dramatic changes in the aquatic food web structure but also results in significant alterations in biogeochemical cycling. Effects of the eutrophication can be recognized by a shift in the composition of algal species and an increase in the frequency and intensity of harmful algal blooms which are typically dominated by harmful cyanobacteria [2,3].

To adequately protect our lakes, rivers, and coasts, it is necessary to prevent excessive amounts of nitrogen and phosphorus from

laws. Copyright © 2018, SciTechnol, All Rights Reserved.



All articles published in Expert Opinion on Environmental Biology are the property of SciTechnol, and is protected by copyright

entering our waterways, as well as decrease these excessive amounts presenting in water. There are numerous publications in the literature available about remediation of the excessive amounts of nitrogen and phosphorus from eutrophic water in recent years [4]. Huang et al. [5] concluded the feasibility of using harmful Cyanobacterium Microcystis to help remove nitrate from eutrophic water. From living Microcystis cells, the amount of dissolved organic carbon (DOC) was secreted around 2.48 mg C mg⁻¹Chl a, as a consequent, a 2.85-fold increase in the specific NO_x^- -N removal rate. Xu et al. [6] investigated the removal of nutrients and chlorpyrifos, as well as shifts of planktonic bacterial communities in constructed microcosms to restore of eutrophic water. The results indicated that plant-treated groups showed a higher pollutant removal rate than did no-remediation controls. Yin Q et al. [7] proved that Mg-Al-modified soybean straw biochar can be used as an excellent adsorbent to remove NH_4^+ , NO_3^- , and PO_4^{3-} from the eutrophic water. The maximum adsorption capacities for NH₄⁺(0.70 mg.g⁻¹), NO₃⁻ (40.63 mg.g⁻¹), and PO₄³⁻ (74.47 mg.g⁻¹) were achieved on these materials. Hu et al. [8] indicated that aluminum chloride (AlCl₂) was more effective than polyaluminum chloride (PACl) in removing turbidity and dissolved organic matter in eutrophic water because AlCl₃ could not only generate Al¹³ species but also function as a pH control agent in the coagulation process. The survey showed that scientists have studied many physical, chemical, biological methods to remediate the eutrophic water [9,10]. Each method has its advantages and disadvantages and the choice of method depends on particular conditions of the experiment and the features of the wastewater.

In this paper, we study the use of activated carbon made from coconut shell under the technique of vertical furnaces as the role of a substratum to phytoremediate eutrophic wastewater. The role of activated carbon is to absorb the excessive amounts of nitrogen and phosphorus when the eutrophic water flows through. To obtain the purpose, the characteristics of a surface of activated carbon and the adsorption kinetics models were studied.

Methods

The commercial activated carbon in cylinder granule (2 cm of length and 0.5 cm of diameter) was made from coconut shell under the technique of vertical furnace, which is popular in Vietnam. The sample was washed with distilled water and dried at 373 K before using. Analytical-grade reagents were used without further purification. Distilled water one time was used throughout the work. Duplicates were performed for each sample and the relative standard error is \leq 3%.

Characteristics of the activated carbon

The *surface morphology* of the activated carbon was determined by scanning electron microscope *technique* (*SEM*, *S-4800 and HITACHI*). Fourier-transform infrared spectroscopy was recorded on FTIR apparatus (8400S – SHIMADZU) with the sample prepared as KBr pellet (the activated carbon powder is 1% by weight), in the 4000 to 400 cm⁻¹ range, at a resolution of 4 cm⁻¹. The resolution of the spectra was retained, as no smoothing algorithms were applied prior to deconvolution analysis.

The point of zero charges (PZC) of the surface of particles was determined by pH drift method [11] as the following steps: The pH

^{*}Corresponding author: Kwangsoo NO, Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea, E-mail: kaistksno@kaist.ac.kr

Received: July 11th, 2018 Accepted: January15, 2019 Published: January 25, 2019

doi: 10.4172/2325-9655.1000158

values of 0.01 M KCl and 0.10 M KCl solutions were adjusted in the range of 2 and 10 using 0.5 M HCl or 0.5 M NaOH. An adsorbent (0.2 g) was added to 60 ml of the pH adjusted solution in a capped vial and equilibrated for 24 h. The final pH was measured and plotted against the initial pH.

The pH at which the curve crosses the pH $_{initial}$ =pH $_{final}$ line was taken as the PZC.

The initial and final pH values were measured by using Multiparameter 900P. All experiments for charge determination were carried out under ambient laboratory conditions $(303 \pm 1 \text{ K})$.

The adsorption kinetics models

To make an experiment with the blank samples, 40 g of activated carbon was put in contact with 400 mL of distilled water, put in a stirred water bath maintained at a constant temperature of 303 K. At regular intervals, 5 mL of solution was removed from the flask, filtered through a PTFE syringe filter 0.45 μ m, made a *dilution* of 1 part solution and particular parts distilled water. The concentration of NH₄⁺, PO₄³⁻, Al³⁺ions in solution was measured by using Palintest Photometer 7100.

In the operating mode, 40 g of activated carbon was put in contact with 400 mL of NH₄Cl solution, at pH 6.7 and a constant temperature of 303 K. The initial concentration of ammonium chloride was 43.0 mg.L⁻¹. At regular intervals, 4 mL of solution was removed from the flask, filtered through a PTFE syringe filter 0.45 μ m, made a *dilution* of 1 part solution and 49 parts distilled water. The total volume removed did not exceed 10% of the initial volume of ammonium chloride in solution. The concentration of the remaining ammonium chloride in solution (C₁) was also measured by using Palintest Photometer 7100.

All the batch sorption tests and the absorption measurements were duplicated. The amount of ammonium chloride adsorbed at a time t (q_t , mg.g⁻¹) is calculated by the difference between the initial (C_o) and the instantaneous ammonium chloride concentration (C_t):

$$q_t = \frac{C_o - C_t}{D}$$

Where,

C: Initial concentration of adsorbate in solution (mg.L⁻¹)

C_t: Concentration of adsorbate in solution at the moment t (mg.L⁻¹)

D: the adsorbent dose, which is the ratio of the mass of adsorbent used (g) and the volume of the solution (L). In this case, the adsorbent dose D is equal to 100 g.L^{-1} .

The Langmuir and Freundlich isotherms [12] have been widely used to characterize the adsorption of solutes from aqueous solutions. To determine the agreeable isotherm, the activated carbon adsorption data were obtained experimentally by changing the concentration of ammonium chloride in a wide range of 43 mg.L⁻¹ to 88 mg.L⁻¹. Similarly, 40 g of activated carbon was put in contact with 400 mL of NH₄Cl solution (D, the ratio of the mass of adsorbent used (g) and the volume of the solution (L), was 100 g.L⁻¹), at initial pH 6.2~6.7, 303 K. After 8 hours, 4 mL of the solution was also removed from the flask, filtered, made a *dilution and* measured by the same apparatus as below.

The equilibrium amount of ammonium chloride adsorbed by the activated carbon $(q_e, mg.g^{-1})$ was calculated by the difference between the initial (C_o) and the equilibrium concentration of solute remaining in solution (C_e) :

$$q_e = \frac{C_o - C_e}{D}$$

Where, $q_e (mg.g^{-1})$ is the equilibrium amount of ammonium chloride adsorbed by the activated carbon.

Results and Discussion

To determine the surface morphology of activated carbon powders, the SEM image was analyzed (Figure 1). However, at the various magnifications, we cannot observe the surface morphology, as well as the pores of the material. It can be concluded that the activated carbon used in this study does not have a definite shape.

The FTIR spectrum of the activated carbon was shown in Figure 2. The free ion exhibits four fundamental modes of vibrations: v_1 (A₁) (symmetric stretching), v_2 (E) (symmetric bending), v_3 (T₂) (anti-symmetric stretching), and v_4 (T₂) (anti-symmetric bending) [13]. In the fingerprint spectral region (600–1650 cm⁻¹), the doublet at 1018 cm⁻¹ and 987.59 cm⁻¹ was assigned to the v_1 (A₁) (symmetric stretching) and v_3 (T₂) (anti-symmetric stretching) normal modes of PO₄³⁻ ion. The band at ~462 was attributed to bending modes of



Figure 1: SEM images of the activated carbon.





SiO₄ tetrahedral, assigned to rocking motion of the bridging oxygen atoms perpendicularly to the Si–O–Si plane. In the high-frequency region of the spectrum, a band at ~1100 cm⁻¹ appeared which was assigned to the anti-symmetric stretching mode of Si–O–Si group involving mainly oxygen motion along the Si-Si direction. The band at ~1072 cm⁻¹ was assigned to SiO₄ asymmetric stretching vibrations [14].

The peaks which were at around 1200 cm⁻¹ assigned to the single C-C or above 3000 cm⁻¹ assigned to O-H bond did not occur in the spectrum. The C=O double bond with intense IR absorption around 1700 cm⁻¹ also cannot be observed. The presence of SiO₂ and PO₄³⁻ in the component of the activated carbon can be interpreted by the addition of inorganic adhesives used popularly were the salts of PO₄³⁻ ions, such as aluminum phosphate. SiO₂ existed in the activated carbon granules was a role of filler. The result was rechecked by doing another experiment whose data were shown in Table 1.

Table 1 showed that in the contact time with distilled water, an amount of PO_4^{3-} , Al^{3+} free ions were diffused from activated carbon to solution because of stirring. The data not only confirmed FTIR result but also support to the next research direction. *In fact, the* presence of surface groups, which were depended on the conditions of synthesis and the nature of precursor, affected to the porosity, chemistry surface and adsorption capacity of the *activated carbon*. The influence of the surface groups was exhibited by the value of pHPZC, the pH at which the net surface charge on carbon was zero. At pH < pHPZC, the surface of material had a net positive charge, oppositely, it had a net negative charge at pH > pHPZC [15]. The pH PZC of the adsorbent can be determined from the plot by the point was the curve final pH

versus initial pH intersects the line where *initial pH* is equal to *final pH* [16].

Figure 3 showed that in case of using the solution of KCl 0.10 M, the curve final pH versus initial pH was found out as the equation:

 $y=0.034x^{3}-0.798x^{2}+6.203x-7.557(R^{2}=0.995)$

While in case of using the solution of KCl 0.01 M, the curve final pH versus initial pH was found out as the equation:

y=0.026x³-0.538x²+3.991x-2.442 (R²=0.992).

The value of pH PZC should be positive solutions of the equations in the range of initial pH from 2.5 to 11.0, which can be calculated from the equations:

x=0.034x³-0.798x²+6.203x-7.557

or x=0.026x³-0.538x²+3.991x-2.442

pH PZC of activated carbon was determined in the range of 8.4-8.7. The data indicated that the activated carbon has basic property.

Table 2 showed that the equilibrium amount of ammonium chloride adsorbed by the activated carbon, q_e , was 0.325 mg.g⁻¹. The value was smaller than that was revealed in the research published [17]. Boopathy et al. [17] concluded that the adsorption of ammonium ion by activated carbon increased when increasing pH from 5.0 to 9.0, accomplished the maximum adsorption capacity at pH 9.0 (up to 2.48 mg/g for the powders with the size of 300 µm) and the minimum equilibrium adsorption capacity at pH 5.0 (down to 0.98 mg/g) (Table 3). This was explained that the lower ammonium ion adsorption at

doi: 10.4172/2325-9655.1000158

t (minutes)	0	15	45	90	150	225	315	375
C _{PO43-} (mg.L ⁻¹)	0	19	22	21	22.5	21	23	23
C _{NH4+} (mg.L ⁻¹)	0	0	0	0	0	0	0	0
C _{AI3+} (mg.L ⁻¹)	0	0.06	0.1	0.1	0.15	0.25	0.25	0.25





C _t (mg.L ⁻¹)	43.0	29.5	24.5	21.0	17.0	14.0	11.0	10.5	10.5
t (min)	0	15	45	90	150	225	315	375	475
q _t (mg.g ⁻¹)	0	0.135	0.185	0.220	0.260	0.290	0.320	0.325	0.325
pH of the solution	6.0	6.4	6.4	7.0	7.2	7.2	7.5	7.5	7.5

Table 3: The equilibrium	concentration of	ammonium	chloride	remaining i	n solution
			0		

C _o (mg/L)	43	50	59	71	77	88
C _e (mg/L)	10.5	17	25	37	44.5	54
q _e	0.325	0.330	0.340	0.340	0.325	0.340

pH 5 was due to the competition of H⁺and NH₄⁺ions for the exchange of sites on the adsorbent surfaces. In fact, the initial pH of NH₄Cl solution having the concentrations in the range of 88-43 mg/L was slightly acidic, from 5.0 to 6.5, and ammonium ions existed mainly as NH₄⁺. In this research, the initial pH of the solution was not adjusted because the purpose of the research was to phytoremediate eutrophic water naturally. During adsorption, pH of the solution was smaller than pH PZC, so the surface of activated carbon had a net positive charge. It may be the reason for the low equilibrium amount of NH₄Cl adsorbed by the activated carbon. Moreover, Boopathy et al. [17] used activated carbon powders in micro size which had a higher specific surface area, while this study used the commercial activated carbon in cylinder granule with 2 cm of length and 0.5 cm of diameter.

In order to investigate the mechanism of adsorption, the firstorder, the pseudo first-order and the pseudo second-order kinetic models were used to test the experimental data obtained. The results were presented in Figure 4a, Figure 4b and Figure 4c. The experiment was done to measure the effect of contact time in the adsorption with the initial concentration of NH₄⁺ion 43 mg/L, temperature 303 K and solution pH 6.0 as shown in Figure 4d. The removal of $\rm NH_4^{+i}on$ increased significantly in 150 minutes of the initial contact time and then this removal was slowly reached the end of the process. The concentration of $\rm NH_4^{+i}on$ in aqueous solution decreased to 10.5 mg.L⁻¹ and remained constant even after an increase in contact time up to 475 minutes. Hence, the optimum contact time for the adsorption of $\rm NH_4^{+i}on$ onto the activated carbon was fixed at 475 min. This can be explained by the nature of adsorbent and its available active site which were responsible for the time needed to reach the equilibrium.

The first-order kinetics equation was given as:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$$

Where, k_1 is the pseudo-first-order rate constant (min⁻¹) and t is the contact time (min).

From the equation: y=-0.005x - 0.540 (R²=0.948), the calculated values of k_1 and q_e were 0.012 min⁻¹ and 0.288 mg.g⁻¹, respectively.

The calculated value of q_e was different from the experimental value. So, the first-order kinetics model was not agreeable.







The pseudo first-order kinetics equation was given as:

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

From the respective equation: y=66,66x+3.249 ($R^2=0.925$), the calculated values of k_1 was 20.52 min⁻¹ and q_e was 0.308 mg.g⁻¹.

The pseudo second-order kinetics equation was given as:

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

Where, k_2 (g.mg⁻¹.min⁻¹) is the pseudo second-order rate constant of adsorption.

From the equation: y=2.911x+88.48 (R²=0.991), the calculated values of k_2 and q_e were 0.096 g.mg⁻¹.min⁻¹and 0.343 mg.g⁻¹, respectively.

As a result, the pseudo second-order kinetics model had the highest value of R^2 and the equilibrium amount calculated from the pseudo second-order kinetics equation was similar to which



doi: 10.4172/2325-9655.1000158



was determined by the experiment. So, the equilibrium amount of ammonium chloride adsorbed by the activated carbon was 0.343 mg.g⁻¹ with the rate constant of adsorption was 0.096 g.mg⁻¹.min⁻¹.

Freundlich isotherm was an equation that was used to describe heterogeneous systems. The Freundlich multilayer adsorption was expressed as:

$$\ln q_e = \ln Kf + \frac{1}{n} \ln C_e$$

Where, K_f (mg.g⁻¹) is the Freundlich constant, 1/n is an empirical constant that represents the adsorption affinity.

Langmuir model linearization was given as:
$$\frac{C_e}{q_e} = \frac{1}{K_L Q^o} + \frac{C_e}{Q^o}$$

A plot of C_e/q_e versus C_e should give a straight line with intercept:

$$\frac{1}{K_L Q^o}$$

And slope: $\frac{1}{Q^{\circ}}$, where Q° is the maximum adsorption capacity for forming single layer, K_L(L.mg⁻¹) is the Langmuir constant.

doi: 10.4172/2325-9655.1000158



The Freundlich adsorption isotherm cannot be used to describe the adsorption for the particular adsorbent/adsorbate isotherm experiments because the value of R^2 was so small and we cannot obtain a straight line, determine constants from slope and intercept (Figure 5).

In the case of Langmuir adsorption isotherm (y=2.961x+0.866), the value of R² was 0.997, and the constants from slope and intercept can be determined.

 $\rm Q^o$ (the maximum adsorption capacity for forming single layer) was equal to 0.338 mg $\rm g^{-1}$ and $\rm K_L$ (the Langmuir constant) was equal to 0.292 L.mg⁻¹.

The complete formation of a monolayer on the surface of activated carbon may be attributed to the porous, heterogeneous surface and the variable energies of active sites.

Conclusion

The characteristics of a surface of activated carbon and the adsorption kinetics models were studied. *pH PZC* of activated carbon was determined in the range of 8.4-8.7 by the pH drift method. The adsorption onto activated carbon was properly proved to the pseudo second-order kinetics model (R^2 =0.991) which the equilibrium amount was 0.343 mg.g⁻¹ and the rate constant of adsorption was 0.096 g.mg⁻¹.min⁻¹. The maximum adsorption capacity for forming a single layer which was calculated from Langmuir isotherm (R^2 =0.997) was equal to 0.338 mg.g⁻¹, Langmuir constant was equal to 0.292 L.mg⁻¹. As a result, Vietnam activated carbon made from coconut shell can be used as the role of a substratum and will be used to study on phytoremediation of eutrophic water.

References

- Monchamp ME, Spaak P, Domaizon I, Dubois N, Bouffard D, et al. (2018) Homogenization of lake cyanobacterial communities over a century of climate change and eutrophication. Nat Ecol Evol 2: 317-324.
- Smitt VH, Joye SB, Howarth RW (2006) Eutrophication of freshwater and marine ecosystems. Limnol Oceanogr 51: 351–355.
- Dodds WK, Smith V (2016) Nitrogen, phosphorus, and eutrophication in streams. Inland Waters 6: 155-164.
- Hu C, Liu H, Qu J, Wang D, Ru J (2006) Coagulation behavior of aluminum salts in eutrophic water: Significance of al13 species and ph control. Environ Sci Technol 40: 325-331.
- Huang Y, Chen X, Li P, Chen G, Peng L, et al. (2018) Pressurized Microcystis can help to remove nitrate from eutrophic water. Bioresour Techno 248: 140-145.

- Xu XJ, Lai GL, Chi CQ, Zhao JY, Yan YC, et al. (2018) Purification of eutrophic water containing chlorpyrifos by aquatic plants and its effects on planktonic bacteria. Chemosphere 193: 178-188.
- Yin Q, Wang R, Zhao Z (2018) Application of Mg-Al-modified biochar for simultaneous removal of ammonium, nitrate and phosphate from eutrophic water. J Clean Prod 176: 230-240.
- Liu C, Cao Z, He S, Sun Z, Chen W (2018) The effects and mechanism of phycocyanin removal from water by high-frequency ultrasound treatment. Ultrason Sonochem 41: 303-309.
- Gu W, Li X, Xing M, Fang W, Wu D (2018) Removal of phosphate from water by amine-functionalized copper ferrite chelated with La(III). Sci Total Environ: 42-48.
- Zhang L, Sun Z, Xie J, Wu J, Cheng S (2018) Nutrient removal, biomass accumulation and nitrogen-transformation functional gene response to different nitrogen forms in enhanced floating treatment wetlands. Ecol Eng 112: 21-25.
- Yang Y, Chun Y, Sheng G, Huang M (2004) pH-dependence of pesticide adsorption by wheat-residue-derived black carbon. Langmuir 20: 6736-6741.
- Chung HK, Kim WH, Park J, Cho J, Jeong TY, et al. (2015) Application of Langmuir and Freundlich isotherms to predict adsorbate removal efficiency or required amount of adsorbent. J Ind Eng Chem 28: 241-246.
- Nakamoto K (2009) Infrared Spectra of Inorganic and Coordination Compounds: Part b: Applications in Coordination, Organometallic and Bioinorganic Chemistry. (6th edtn) John Wiley & Sons, New Jersey, United States.
- Lucovsky G, Wong CK, Pollard WB (1983) Vibrational properties of glasses: Intermediate range order. J Non-Cryst Solids: 839-846.
- Al-Degs Y, Khraisheh M, Allen S, Ahmad M (2000) Effect of carbon surface chemistry on the removal of reactive dyes from textile effluents. Water Res 34: 927-935.
- Faria PC, Orfão JJ, Pereira MF (2004) Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. Water Res 38: 2043-2052.
- Boopathy R, Karthikeyan S, Mandal AB, Sekaran G (2013) Adsorption of ammonium ion by coconut shell-activated carbon from aqueous solution: Kinetic, isotherm and thermodynamic studies. Environ Sci Pollut Res Int 20: 533-542.

Author Affiliations

Тор

¹Department of Chemistry, Ho Chi Minh City University of Pedagogy, Vietnam ²Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea