

Coffee Residue-Based Adsorbent for Ammonia Removal from Aqueous Solution

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Abstract—The preparation of low-cost adsorbent material for ammonia removal was investigated. The coffee residue was employed as a material for producing the adsorbent for the removal of total ammonia from aqueous solution. The effects of carbonization temperature, type of modifier, and contact time were studied. The adsorption studies were carried out using a batch method. Total ammonia in aqueous solution was determined by Visible spectrophotometer at the maximum wavelength of 550 nm. The coffee residues were non-carbonized, carbonized at 250, and 500°C under oxygen atmospheric condition. The adsorbents were modified with 5M of sulfuric acid (H₂SO₄) or 5M of acetic acid (CH₃COOH). The carbonization temperature and type of modifier have shown remarkable influence on surface acidity and adsorption capacity. The result indicated that the adsorbents carbonized at 500°C and modified with H₂SO₄ was found to be appropriate for efficient adsorption of ammonia in aqueous solution with the maximum adsorption removal rate as high as 90.66% and provided adsorption capacity of 361.85 mg ammonia/g adsorbent.

Keywords—Coffee residue, adsorption, ammonia, aqueous solution.

I. INTRODUCTION

AMMONIA has the potential to be one of the major problems of water pollution. It is a ubiquitous component of industrial effluents such as in petrochemical production, rubber production, refrigeration systems, and the food and beverage industry. Additionally, ammonia is also released naturally from living things, particularly from agricultural activities. These activities include animal excrement, livestock housing and fertilizer application [1], [2], [3]. Since ammonia has a deleterious effect on human and especially on aquaculture, treating ammonia is highly recommended.

Ammonia is a colorless, pungent odorous and corrosive that can cause irritation, toxic to respiratory system or can be the cause of death. It is known to be harmful for aquatic organisms at concentration above 25 µg/l [4]. Several methods have been described for the determination of the ammonia dissolved in aquatic system such as biological-nitrification-denitrification, air stripping and chemical precipitation [5]. Among these techniques, adsorption method has been recently increased attention in controlling ammonia level in water. Many adsorbents, including zeolite, [6], [7], [8], [9] limestone, and volcanic tuff have been used to

efficiently eliminate ammonia from wastewater [10], [11].

Coffee is one of the most widely consumed beverages and most internationally trade the second position next to crude oil [12]. International Coffee Organization (ICO) reported that approximately 120 million tons of coffee has been produced per year worldwide and generated the solid residues accountable for 6 million tons annually [12]. Disposal of these residues is recycled as materials for soil conditioner, or further produce useful products such as organic acids, flavors and aroma compounds [13]. Nevertheless, it has been reported that coffee residue contain a high content of carbon source, which can be used as a starting materials for producing adsorbents in many research work [12], [13], [14]. From the economic point of view, turning waste into efficient adsorbents can be another alternative way to produce low-cost adsorbent materials.

The main aim of this study was to prepare low-cost adsorbent from discarded coffee grounds derived from the local coffee shop by surface impregnation with H₂SO₄ and CH₃COOH and to study the ammonia adsorption properties in aqueous solution. The effect of carbonization temperature, type of modifier, and contact time were investigated. The adsorption studies were carried out using a batch method, ammonia adsorption removal rate and ammonia adsorption capacity of the adsorbent were observed in the adsorption study.

II. MATERIALS AND METHODS

A. Reagent and apparatus

Reagent and solution: Working NH₄Cl solutions were prepared by stepwise dilution with de-ionized water varied from 0.1 to 2.0 mg/L.

Apparatus: Absorption spectra were recorded in a Visible spectrophotometer.

B. Adsorbent preparation

The coffee residue was derived from the local coffee shop in Pathiu, Chumphon, Thailand. The material was first oven dried at 120 °C for 2 h. The dried coffee residue was then carbonized at 250, and 500°C in air atmospheric for 2 h. The obtained materials were chemically modified with 5M of H₂SO₄ or 5M of CH₃COOH at room temperature for 24 h. The resulting adsorbent materials were subsequently filtered and dried at 100 °C overnight. The prepared adsorbents were kept in desiccator until used. The obtained adsorbents material are named as NC for the non-carbonized coffee residue, NC-5S for the non-carbonized coffee residue

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modified with 5M H₂SO₄, NC-5A for the non-carbonized coffee residue modified with 5M CH₃COOH, C250 for the coffee residue carbonized at 250°C, C250-5S for the coffee residue carbonized at 250°C and modified with 5M H₂SO₄, C250-5A the coffee residue carbonized at 250°C and modified with 5M CH₃COOH, C500 for the coffee residue carbonized at 500°C, C500-5S for the coffee residue carbonized at 500°C and modified with 5M H₂SO₄, and C500-5A the coffee residue carbonized at 500°C and modified with 5M CH₃COOH respectively.

C. Chemical Characterization

The surface acidity of adsorbent materials modified with 5M H₂SO₄ or 5M of CH₃COOH was determined with back titration method. A portion of 50 mg adsorbent material was placed into a test tube and subsequently added NaOH solution. The mixture was then shaken for 24 h. The excess base was titrated with HCl solution.

D. Adsorption of ammonia

The study of total ammonia adsorption was carried out using batch method. A portion of 50 mg of adsorbent material was placed into a test tube and a 10 mL NH₄Cl solution was then added. The mixture was shaken continuously for 3 h. The NH₄Cl solution was collected and separated from the mixture every 20, 40, 60, 80, 100, 120, 140, 160 and 180 minutes. The resulting solution was then quantified the excess ammonia after adsorption study using Visible spectrophotometer.

III. RESULTS AND DISCUSSION

A. Effect of carbonization temperature

The yield of adsorbent material is considerably depended on the carbonization temperature since the adsorbent material was carried out under air atmospheric condition. The effect of carbonization temperature is shown in Table I, the yield of adsorbent carbonized at 250 °C decreased because of the loss of volatile organic compound in coffee residue and mostly diminished at 500 °C.

TABLE I
PERCENT YIELD OF NON-CARBONIZED COFFEE RESIDUE, COFFEE RESIDUE CARBONIZED AT 250 AND 500°C

Adsorbent	Yield*
NC	-
C250	72.12 ± 1.64
C500	26.27 ± 0.46

*Mean ± S.D. (n=3)

B. Effect of chemical modification on surface

Table II shows proton equivalent (H⁺ equivalent) immobilized on adsorbents modified with 5M of H₂SO₄ and 5M of CH₃COOH. The result indicates that adsorbent modified with H₂SO₄ has a higher content of proton equivalent than that modified with CH₃COOH. It is because the H₂SO₄ is a strong acid, which could generate proton equivalent on surface better than that weak acid CH₃COOH

when they are used at the same concentration.

TABLE II
PROTON EQUIVALENTS IMMOBILIZED ON ADSORBENT SURFACE

Adsorbent	H ₂ SO ₄ *	CH ₃ COOH*
	H ⁺ equivalent (mmol/g)	H ⁺ equivalent (mmol/g)
NC	3.36 ± 0.15	0.69 ± 1.34
C250	7.60 ± 0.36	1.25 ± 0.91
C500	11.91 ± 0.79	2.13 ± 0.88

*Mean ± S.D. (n=3)

C. Ammonia adsorption study

Calibration curve

The calibration curve of NH₄Cl solutions are shown in Fig.1. The NH₄Cl solutions were prepared in the range of 0.1, 0.2, 0.5, 1.0, and 2.0 mg/L. The solution was monitored by Visible spectrophotometer at the maximum wavelength of 550 nm (λ_{max}). The color of solution was found to be a light green at the lower concentration of NH₄Cl solution and turned to blue at the higher concentration of NH₄Cl solution as shown in Fig.2.

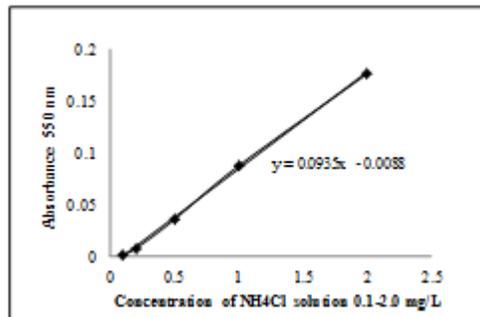


Fig.1 Calibration plots of NH₄Cl solution at the concentration of 0.1, 0.2, 0.5, 0.1, and 2.0 mg/L.



Fig.2 Color changes in NH₄Cl solution at the concentration of 0.1, 0.2, 0.5, 0.1, and 2.0 mg/L.

Effect of contact time

To investigate the effect of contact time after the ammonia adsorption study, the contact time was varied from 20 to 180 minutes and the NH₄Cl solution was collected and separated from the adsorbents every 20 minutes. The excess of total ammonia were then quantified by Visible spectrophotometer and fitting the equation obtained from the calibration plots in Fig.1. The results of ammonia removal rate of NC, C250, and C500 with both non-modified and modified with H₂SO₄ and CH₃COOH are shown in Fig.3, 4, and 5 respectively. The ammonia adsorption rate was calculated regarding to the equation (1)

$$\text{Removalrate (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

The plots of the ammonia adsorption capacities of the adsorbents with time are shown in Fig.6, 7, and 8 respectively. The adsorption capacity (mg/g) was calculated in respect to equation (2).

$$q = \frac{(C_0 - C_e)V}{M} \times 100 \quad (2)$$

Where q (mg/g) is the ammonia adsorption capacity, C_0 (mg/L) and C_e (mg/L) are respectively the initial and equilibrium ammonia concentrations in the solution, V (L) is the solution volume, and M (g) is the mass of adsorbent.

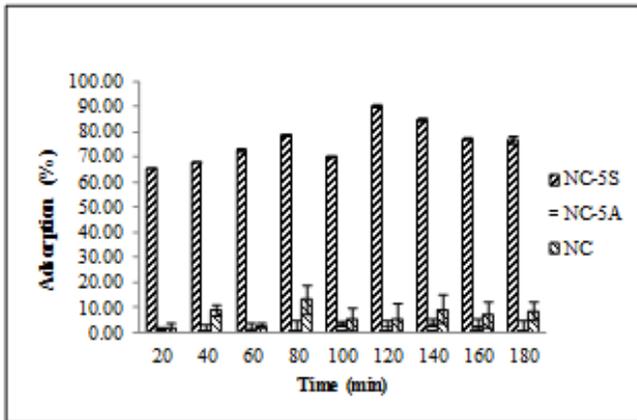


Fig.3 Ammonia removal rate of NC, NC-5A, and NC-5S.

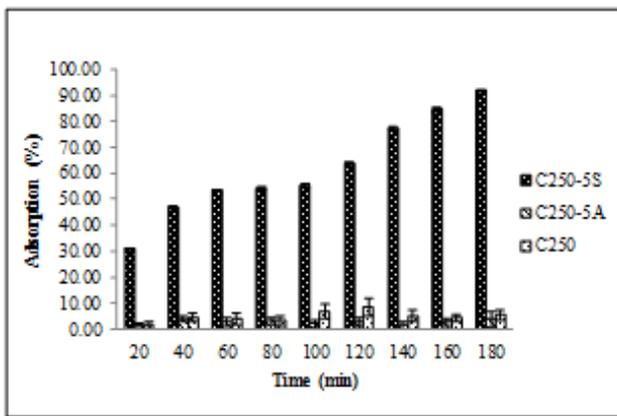


Fig.4 Ammonia removal rate of C250, C250-5A, and C250-5S.

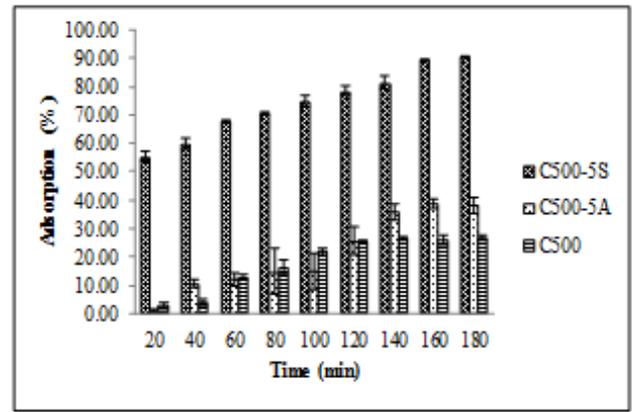


Fig.5 Ammonia removal rate of C500, C500-5A, and C500-5S.

According to the results from Fig.3-5, the ammonia removal rate of non-carbonized coffee ground, carbonized coffee ground at 250°C, which was modified and non-modified with CH₃COOH was not much different. The maximum of ammonia removal rate of NC, NC-5A, C250, and C250-5A was 12.9%, 4.03%, 8.5%, and 3.85% respectively. Whereas, the non-carbonized coffee ground and coffee ground carbonized at 500°C, which was modified and non-modified with CH₃COOH yielded a higher on ammonia removal rate, accounted for 26.5% for C500 and 38.61% for C500-5A.

On the other hand, the ammonia removal rate of non-carbonized coffee ground, carbonized coffee ground at 250°C and 500°C modified with H₂SO₄ was much larger than those modified with CH₃COOH. The ammonia removal rate of NC-5S, C250-5S, and C500-5S accounted for 89.95%, 91.73%, and 90.66% respectively.

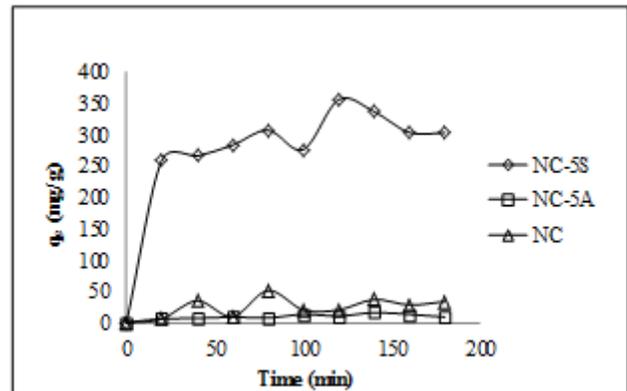


Fig.6 Ammonia adsorption capacity of NC, NC-5A, and NC-5S.

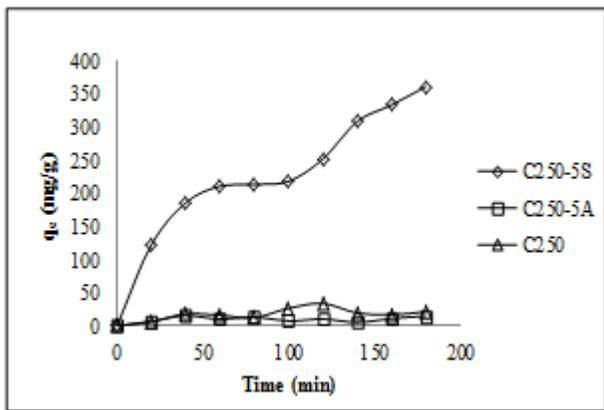


Fig.7 Ammonia adsorption capacity of C250, C250-5A, and C250-5S.

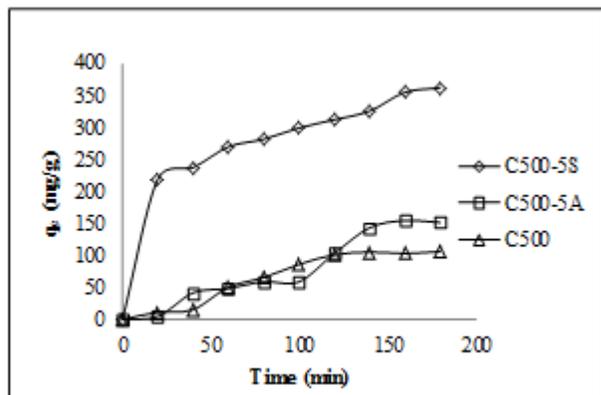


Fig.8 Ammonia adsorption capacity of C500, C500-5A, and C500-5S.

The graph in Fig.6-8 shows performance of ammonia adsorption at the equilibrium of adsorbent materials. For both of non-modified and modified with CH₃COOH of non-carbonized coffee ground and coffee ground carbonized at 250°C, the ammonia adsorption capacities were not significantly different. The ammonia adsorption capacity was in the range of 6-26 mg ammonia/g adsorbent. Meanwhile, the non-modified and modified with CH₃COOH of non-carbonized coffee ground and coffee ground carbonized at 500°C gave a higher performance in ammonia adsorption capacity, compare to non-modified and modified with CH₃COOH of non-carbonized coffee ground and coffee ground carbonized at 250°C. The adsorption capacity of C500-5A was in the range of 4-154 mg ammonia/g adsorbent.

On the contrary, the adsorbent materials modified with H₂SO₄ of non-carbonized coffee ground, coffee ground carbonized at 250°C and coffee ground carbonized at 500°C provided the better performance in adsorption capacity, compare to adsorbent materials modified with CH₃COOH. The maximum adsorption capacity of NC-5S, C250-5S, and C500-5S was found to be 356.85, 361.07, and 361.85 mg ammonia/g adsorbent respectively. Although, the adsorption capacity of NC-5S, C250-5S, and C500-5S was not significantly different but C500-5S is likely to be more effective for ammonia removal since the ammonia adsorption capacity was greater than C250-5S at the same contact time.

Moreover, the adsorption characteristic is more practical than NC-5S because the adsorption capacity of C500-5S increased as the contact time increased, whereas, the adsorption capacity of NC-5S was fluctuated regardless of time.

IV. CONCLUSION

In this study, H₂SO₄ and CH₃COOH were immobilized on coffee residue for adsorption of ammonia in solution. The adsorbent prepared by carbonization at 500°C and modified with H₂SO₄ had the best performance in adsorption in solution with the adsorption capacity of 361.85 mg ammonia/g adsorbent.

ACKNOWLEDGMENT

The authors acknowledge the support from King Mongkut's Institute of Technology Ladkrabang, Prince of Chumphon Campus.

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