Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.994109

57 (2016) 4597–4605
February

Taylor & Francis
Taylor & Francis Group

Pre-oxidation effect on ammoxidation of activated carbon and its influence on Cu(II) adsorption

Mohammad Hassan Mahaninia[a,*], Tahereh Kaghazchi[b], Mansooreh Soleimani[b], Paria Rahimian[c], Ali Esfandiari[b]

[a]*Department of Chemistry, University of Saskatchewan, Saskatoon, SK, Canada, Tel. +1 306 2215705; email: m.h.mahaninia@usask.ca*
[b]*Department of Chemical Engineering, Amirkabir University of Technology, Tehran, Iran, Tel. +98 2164543152; email: kaghazch@aut.ac.ir (T. Kaghazchi), Tel. +98 2164543182; email: soleimanim@aut.ac.ir (M. Soleimani), Tel. +98 9123212140; email: alie.esfandiary@gmail.com (A. Esfandiari)*
[c]*Department of Textile Engineering, Amirkabir University of Technology, Tehran, Iran, Tel. +98 9195336142; email: Paria.rahimian1990@gmail.com*

Received 12 June 2014; Accepted 26 November 2014

ABSTRACT

Modification of activated carbon in order to enhance heavy metal removal is one of the most efficient methods. Here, the effect of pre-oxidation on ammoxidation of commercial activated carbon was introduced. Then, influence of these modifications on the characteristics and adsorption properties of activated carbon toward Cu(II) was investigated. Characterization of samples was performed by several analyses. The ammoxidation with two methods results in the introduction of new nitrogen functional groups in the structure of the activated carbon, but also changes the acid–base character of their surface and deteriorates their textural parameters slightly. Introduction of nitrogen into the structure of activated carbons improves their adsorption capacity toward Cu(II). The best adsorption capacity is obtained for the ammoxidized activated carbon with pre-oxidation.

Keywords: Activated carbon; Ammoxidation; Cu(II) adsorption; Nitric acid pretreatment

1. Introduction

Activated carbon is a traditional porous adsorbent with specific physical properties such as developed surface area, high porosity, suitable pore size distribution, and also the surface functional groups. Functional groups have significant influences on the adsorption properties of this material [1,2]. One of the most important advantages of using activated carbon in wastewater treatment is removal ability for both inorganic and organic pollutants.

Unfortunately, Cu has an accumulative and unbreakable nature which can cause many problems in human health and the environment. Drinking water with a high amount of Cu may cause illnesses such as vomiting, diarrhea, stomach cramp, and nausea [3]. According to the Water Sanitation and Hygiene guideline attached to the World Health Organization (WHO), the permissible concentration of Cu is 1.5 mg L^{-1}. Therefore, developing new methods to remove heavy metals from aqueous solution is critical

---

*Corresponding author.

[4–7]. One of the traditional methods used for the removal of heavy metals has been the adsorption with activated carbon [8–16]. However, activated carbons are more effective for adsorption of organic compounds rather than metal ions and inorganic pollutants. Therefore, activated carbon modification is seems to be necessary [13]. For this reason, recently, several modification techniques have been proposed to boost the surface adsorption affinity and selectivity toward metal ions [17–21].

Several studies have been carried out on the preparation of modified activated carbon by incorporation of nitrogen with the aim of developing new adsorbents [22–25]. Recently, some works have been conducted to modify activated carbon with nitrogen in order to enhance the adsorption of heavy metal ions [26,27], but few of them have been conducted for modification toward removing copper ions from water [27]. In our previous work, we discussed the amination of activated carbon and investigated its effect on copper ion removal [2]. Ammoxidation is another route to obtain nitrogen enriched adsorbents [28–31]. During ammoxidation, ammonia reacts with the oxygen groups present on the carbon surface, and forms ammonium salts and amine groups, which convert to amides, nitriles, and pyridine- and pyrrol-like functional groups, through the dehydration and dehydrogenation reactions [32,22].

In this work, two different ammoxidation methods were studied for the preparation of ammoxidized activated carbon to survey the effects of pre-oxidation on the ammoxidation. The first method was ammoxidation without any pretreatment and the other method was pre-oxidation of activated carbon before ammoxidation. The purpose for oxidation of activated carbon prior to ammoxidation was firstly, for producing a substrate with the potential to be converted to the desired functional groups and secondly, for introducing higher amounts of both oxygen and nitrogen functional groups to the surface of the activated carbon. Characterizations of functional groups, surface area, and also the adsorption affinity of samples toward copper ions have been investigated.

2. Experimental

2.1. Materials

The starting activated carbon, which was donated as SAE, and is commercially available, was purchased from Norit Company (SAE SUPER) with a 425 kg m^{-3} apparent density and 15 μm particle size (D_{50}). Other reagents were purchased from Merck.

2.2. Modification procedure

The ammoxidation procedure was carried out through two different approaches in this study: (i) ammoxidation of non-oxidized activated carbon and (ii) ammoxidation of oxidized activated carbon with nitric acid.

2.2.1. Pretreatment with nitric acid

In order to carry out oxidation of activated carbon before the ammoxidation, 10 g of washed and dried activated carbon [19] was mixed with 100 mL solution of nitric acid (5 M) and distilled water at a ratio of 1:10 (v/v). Then, it was heated at 358 K for 5 h by a heater and oxidation was continued with stirring at 250 rpm. Afterward, the oxidized carbons were washed with distilled water in a Soxhlet apparatus, until the pH of the residue was fixed at 6. Finally, the oxidized sample was dried in an oven at 383 K for 12 h, and was denoted as ACO.

2.2.2. Ammoxidation procedure

The ammoxidation of activated carbons was accomplished in a quartz tube reactor where a flow of ammonia and air circulates at a ratio of 3:1 (v/v). In each test, about 3–5 g of ACO or SAE was weighed and placed in ceramic boats at the center of an electric furnace quartz tube. The temperature was raised with the heating rate of 10 K min^{-1} from ambient temperature to 573 K. For the rising step, nitrogen gas (%99.99 purity) with a flow rate of 100 cm^3 min^{-1} was employed. Then, when the samples reached the target temperature (573 K), the flowing gas was changed to NH_3 (%99.99) with a flow rate of 150 cm^3 min^{-1} and air with a flow rate of 50 cm^3 min^{-1}. These two gases were blown from the beginning of the tube. The samples were kept at the target temperature for 5 h and cooled to ambient temperature under this atmosphere. Afterward, the samples were placed in a desiccator and ready for further characterization and adsorption tests. The ammoxidized sample with pre-oxidation was denoted as ACOOX and without pre-oxidation was denoted as ACOX.

2.3. Characterization

2.3.1. Elemental analysis

All samples were analyzed by an elemental analyzer (model Carlo Ebra 1106). The samples were weighed accurately on an aluminum foil and then put into the instrument. Prior to the flash combustion process, the system was purged with helium carrier gas. Flash combustion was performed at 2,073 K, and the gaseous combustion products were quantified using a thermal conductivity detector. Results were obtained as percentages of carbon, hydrogen, and nitrogen. The oxygen content was determined by the differentiation method.

2.3.2. Fourier transform infrared spectroscopy

The PerkinElmer spectrophotometer instrument (model Paragon 1000PC) was applied for Fourier transform infrared spectroscopy (FTIR) analysis of samples. At first, the samples were dried under vacuum at 423 K, and then were grounded with KBr salt followed by compression between two stainless steel cylinders in order to form a thin transparent solid film. The samples were kept purging with nitrogen during the entire experiment. The spectrometer collected 64 spectra in the range of 400–4,000 cm^{-1} with a resolution of 4 cm^{-1} and 100 scans.

2.3.3. Porosity properties

Nitrogen adsorption was carried out with a Quantachrom NOVA 1000 instrument equipped with commercial software of analysis and calculation. Initially, all samples were out gassed at 423 K for 2 h under vacuum prior to the N_2 adsorption/desorption tests. By the Brunauer–Emmett–Teller (BET) equation, specific surface area was calculated based on assumption that a nitrogen molecule surface area is 0.162 nm [33]. The total pore volume and the volume and surface area of micro- and mesopores were also determined.

2.3.4. Determination of pH_{zpc}

The point of zero charge measurement for samples was carried out according to the method suggested by Noh and Schwarz [34]. This method was conducted by recording the obtained equilibrium pH, before and after shaking the suspensions of carbon samples in distilled water for 24 h. The initial pHs of the suspensions were selected in the range of 2–11. After measuring the equilibrium pHs, the limiting values were taken as the pH_{zpc}.

2.3.5. Temperature programmed desorption

In order to study the properties of surface chemistry of the carbons, Temperature programmed desorption (TPD) tests were carried out with heating rate of 15 K min^{-1} up to 1,273 K, with a Ar flow rate of 50 cm^3 min^{-1}. Approximately, 200 mg of samples were placed in a quartz reactor connected to a quadruple mass spectrometer (Dycor, Model M200) for measuring the evolved gases.

2.4. Cu(II) adsorption experiments

The removal capacity of copper (Cu(II)) from aqueous solutions of commercial activated carbon (SAE), oxidized activated carbon (ACO), and the ammoxidized carbons (ACOOX and ACOX) was determined during a batch mode adsorption experiment. Stock solution of 1,000 mg L^{-1} Cu(II) ions was prepared by dissolving of 2.12 g $CuCl_2$ in deionized water, acidified by 5 mL of concentrated HCl, and then diluting to 1 L volume.

In order to compare the rate and capacity of Cu(II) adsorption by the produced activated carbons, the kinetic and equilibrium experiments were carried out. In the kinetic tests, 0.01 g of adsorbent was added to a number of 50 mL glass flasks consist of 30 mL of Cu(II) solution with the initial concentration of 40 mg L^{-1}. Then, they were shaken at 150 rpm at 298 K, and after certain amount of time, 4 mL of the solutions were sampled by a 10 mL plastic syringe and were filtered by a Whatman No. 42. Samples were analyzed for copper concentration using an atomic absorption spectrophotometer (PerkinElmer, A Analys-300).

After that, adsorbents were added into a series of 100 mL glass bottles with the initial pH of (~6.0) with respect to this fact that the precipitation of Cu(II) ions with hydroxide ions would be occurred at $pH > 6$ [35]. The equilibrium isotherm of Cu(II) adsorption was established and shacked at 150 rpm at 298 K for 24 h, and after that the solutions were filtered and analyzed using an atomic absorption spectrophotometer. All the above procedures were repeated three times and the average values were reported.

3. Results and discussion

3.1. Porosity properties of adsorbents

Table 1 shows porous texture properties of different studied activated carbon samples. The results indicated that after ammoxidation procedure, the surface BET areas of oxidized and ACOOX and ACOX have little reduction. Also, SAE carbon has higher surface area compared to ACO, ACOOX, and ACOX. The smaller BET surface area can be related to ammonia, and air treatment at high temperatures that simultaneously cause an increase in the mesoporosity of carbons that is called the etching effect. This

Table 1
Comparison of the porous texture of virgin and modified activated carbons

Samples	SAE	ACO	ACOX	ACOOX
S_{BET} (m^2 g^{-1})	1,180	1,050	956	789
Microporous volume (cm^3 g^{-1})	0.38	0.23	0.34	0.28
Mesoporous volume (cm^3 g^{-1})	0.17	0.06	0.09	0.05
Total volume (cm^3 g^{-1})	0.55	0.29	0.48	0.33
pH_{zpc}	6.52	5.94	7.15	6.92

phenomenon causes a decrease in the contribution of micropores in the structure of activated carbons, so after this ammoxidation, the surface area was decreased [36]. As a result of acid treatment, it can be seen that the surface area and porous texture of the ACOOX sample were decreased more compared with ACOX, so it can be concluded that acid treatment can partly damage some micropores of the activated carbon [37].

Nitrogen adsorption isotherm (Fig. 1) clearly shows that all ammoxidized samples have less developed porous texture and BET surface area. This limitation is particularly visible in the range of mesoporosity. Since the thermal conditions of ammoxidation were identical for all samples, we may suppose that the limitation of porous texture's development is due to heteroatoms added during ammoxidation. Probably, the presence of nitrogen and oxygen functional groups in structure has a blocking effect on activated carbon. Based on this assumption, the highest blocking effect occurred for ammoxidation with highest efficiency where heteroatoms were introduced to the precursor highly.

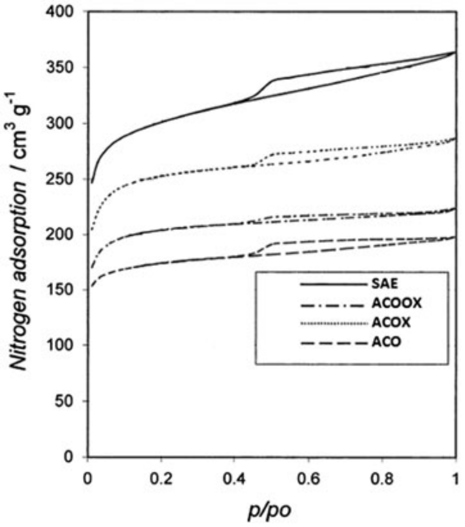

Fig. 1. Nitrogen adsorption isotherms obtained for carbon materials.

3.2. Elemental analysis of adsorbent

The results of elemental analysis of all samples were shown in Table 2. The elemental analysis indicated that there is a considerable increase in the nitrogen content of adsorbent (in the form of basic nitrogenated functions). As expected in this work, both procedures have a relatively high ability for introducing nitrogen into the structure of activated carbons. Thus, it can be considered as the efficient method for ammoxidation of materials. On the other hand, as seen in Table 2, the ACO could be an appropriate precursor for modifying activated carbon according to low ash and volatile matter content but high carbon content. The ammoxidized samples present lower volatile matter than the SAE (original carbon) due to the heat treatment and surface reactions. Thus, it can be revealed that pre-oxidation of the sample was effective. As indicated in Table 2, the ACOOX sample that underwent pre-oxidation and then exposure to ammonia and oxygen gas, leads to produce an adsorbent with a nitrogen content of about 2.4 times higher than ACOX that was prepared with ordinary methods. This increase in the nitrogen content in adsorbent reveals the extensive effect of the pre-oxidation on ammoxidation. The reason for the higher efficiency of ammoxidation is oxygen functional groups that bonded to the graphite sheet in the pre-oxidation stage. In the ammoxidation stage, oxygen functional groups probably play reactive sites that

Table 2
Elemental analysis of virgin and modified activated carbons

	Proximate analysis (wt.%, db)		Ultimate analysis (wt.%, daf)			
Samples	VM	Ash	C%	H%	N%	O%
SAE	13.6	4.7	82.5	0.3	0.1	17.1
ACO	13.1	3.2	81.6	0.2	0.1	18.1
ACOX	8.2	5.3	80.2	0.2	1.3	18.3
ACOOX	10.7	4.3	77.1	0.2	3.1	19.6

stabilize nitrogen functional groups. Therefore, more nitrogen containing functional groups on the surface of ACOOX are consequences of the oxygen content of the pre-oxidized sample (more than SAE activated carbon) were replaced with NH3 molecules in the ammoxidation stage.

3.3. pH of zero point charge (pH_{zpc})

The results for determination of pH_{zpc} were given in Table 1. Clearly, ammoxidation causes a shift in pH_{zpc} because of the presence of basic nitrogen functionalities. Moreover, during ammoxidation, acidic oxygen groups are consumed in the reaction, so ACOOX has a higher pH_{zpc} compared with ACO. However, this increase is not very significant to drive this conclusion that ammoxidation is in favor of amide formation which has very weak basic properties.

3.4. Temperature programmed desorption

Fig. 2 illustrates evolved NH_3, HCN, CO, and CO_2 gases. Two distinct maxima for NH_3 emissions can approximately be seen at 500 and 980 K. The pick at 500 K comes from the decomposition of labile amines, while pick at 980 K comes from the decomposition of amides and lactams [25,26]. The maximum pick of HCN emissions is at around 1,220 K. This emission probably comes from the decomposition of nitriles, but also it may have come from the decomposition of amides, lactams, and imides [25,26]. The ammoxidized samples showed a maximum pick in the spectra of CO emission at 950 K that is outside the temperature range of the starting carbons (SAE, ACO). Since the CO and NH_3 emission are approximately similar at this range of temperature, it can be inferred that decomposition of amide-like functionalities is probable [26]. From CO_2 profiles, replacement of CO_2-evolving

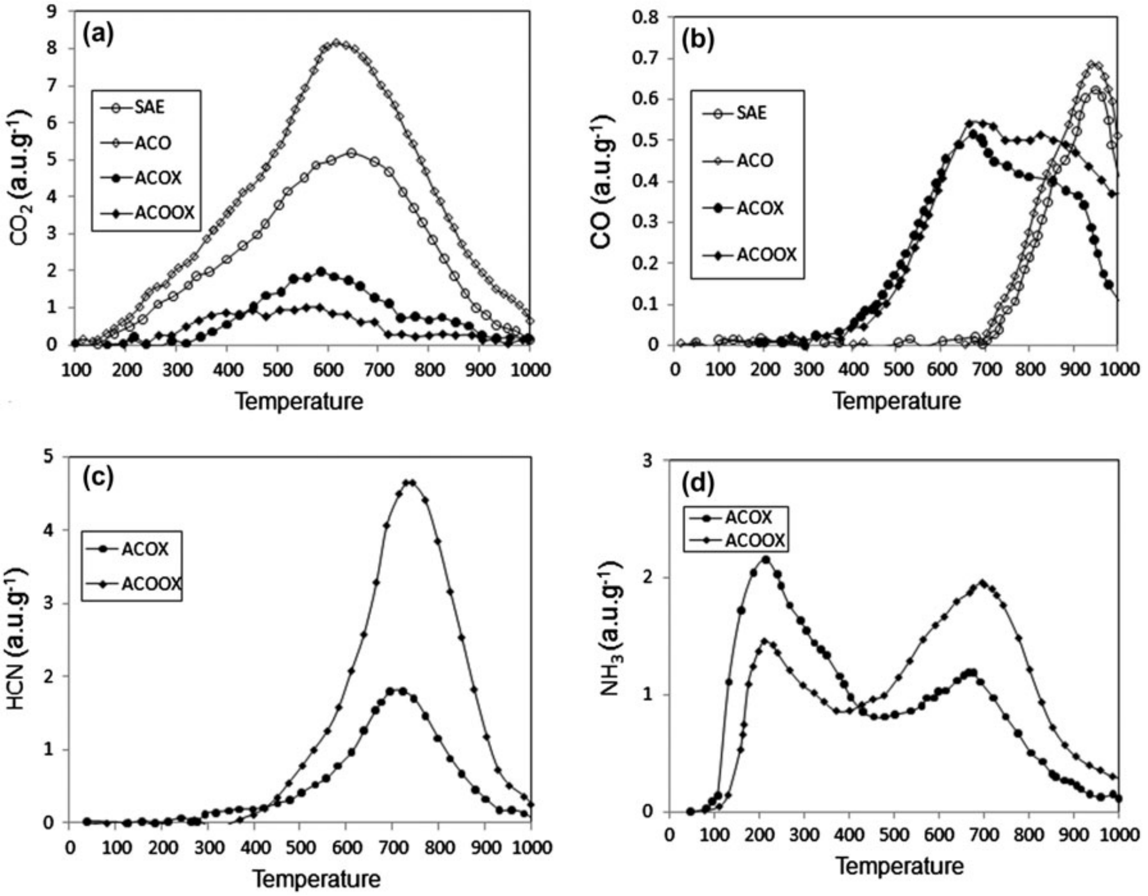

Fig. 2. CO_2 (a), CO (b), HCN (c), and NH_3 (d) evolution profiles of samples during heating at 15 K min^{-1} up to 1,300 K min^{-1} in 50 cm^3 min^{-1} of Ar.

groups (carboxyls, anhydrides, and lactones) with other functional groups during ammoxidation is obvious.

3.5. Fourier transform infrared spectroscopy

Using FTIR analysis, the functional groups of the activated carbons were studied. The resultant spectra are shown in Fig. 3. Peaks seen in near 1,600 cm^{-1}, corresponding to the aromatic ring stretching of both C=C and C=N groups. The bands at 1,512, 1,540, and 1,570 cm^{-1} are possibly due to pyridinic, pyridonic, and pyrrolic (or indolic) structures [38]. Another peak is a relatively small peak for C=O stretch vibrations around 1,700 cm^{-1}. From the obtained data in Fig. 3, it can be concluded that the ammoxidation of SAE and ACO has led to the elimination of carboxylic acid groups from the surface of these samples. This conclusion can be implied by the disappearance of the 1,717 cm^{-1} band in the spectra of ACOX and ACOOX samples that existed in the spectrum of the SAE and ACO samples.

Small peaks around 1,650 cm^{-1} show that amides may be present on the surface of the activated carbon, while the slightly more intense peaks around 1,710 cm^{-1}, predominantly for ACOOX and ACOX, likely indicate the presence of lactams. Imides show absorbance at a somewhat lower wavenumber (near 1,600 cm^{-1}). Detection of imides due to the other strong absorbances is quite difficult.

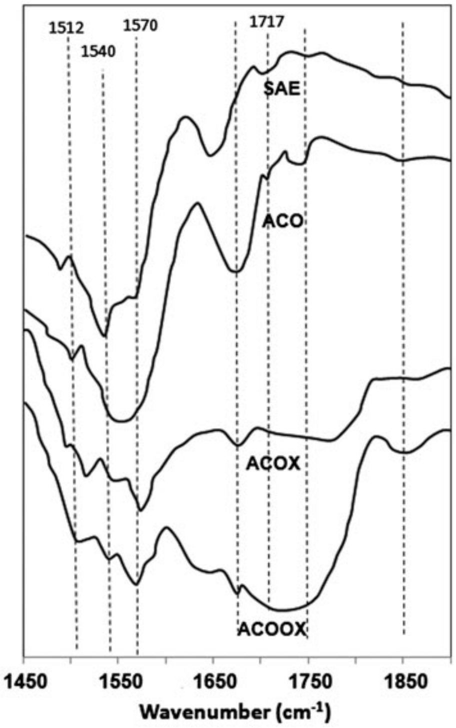

Fig. 3. The FTIR spectra of virgin (SAE) and modified activated carbons.

3.6. Cu(II) adsorption tests

In Fig. 4, the adsorption of Cu(II) from aqueous phase versus time was shown. As expected, the initial adsorption rate of ACOOX and ACOX is larger than the virgin (SAE) and oxidized (ACO) samples; and adsorption rate of ACOOX is above all. This higher adsorption rate can be connected to the effect of pre-oxidation on ammoxidation that causes higher amount of nitrogen-containing functional groups to be introduced on the surface of ACOOX. On the other hand, this high amount of nitrogen containing functional groups and less surface area of ACOOX compared with other samples indicated that adsorption was occurred mostly chemically, so chemisorptions were more effective than physisorption in this case.

It can be seen that in less than 1 h, the process was achieved at a 35–45% removal capacity, and the adsorption was then gradually reached at a steady state condition. The kinetically rapid adsorption by ACOOX implied the generation of strong Cu-binding to the surface sites.

Equilibrium adsorption tests were carried out to define the Cu(II) adsorption capacity of the ammoxidized activated carbons. The results were shown by plotting the equilibrium adsorption capacity of adsorbents $q_e[=V(C_0 - C_e)/M]$ vs. C_e as shown in Fig. 5. C_0 and C_e are the initial and equilibrium concentrations

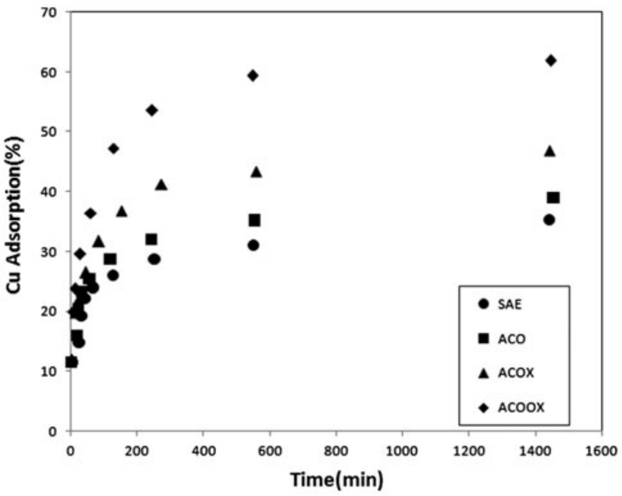

Fig. 4. Percentages of Cu(II) adsorption as a function of contact time; operating conditions: t = 24 h; pH = 6.0; and T = 298 K.

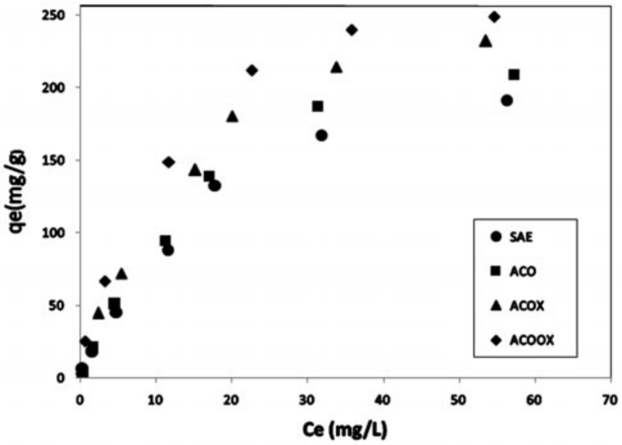

Fig. 5. Equilibrium isotherm of the Cu^{2+} adsorption; operating conditions: $t = 24$ h; pH = 6.0; and $T = 298$ K.

of Cu(II) ion in the solution, *V* is the volume of solution, and m is the weight of the adsorbent.

The adsorption isotherm of copper ions onto the different activated carbons is shown in Fig. 5. In comparison with the Giles classification system [39], it can be concluded that adsorption isotherm of copper ions onto this adsorbents corresponds to L-type sorption isotherm. The initial slope of L curve shows that the adsorbate has a high affinity for the surface. As more sites in the adsorbent are filled it becomes increasingly difficult for a solute molecule to find a vacant site.

Also, it can be observed from Fig. 5 that the amount of Cu(II) ions adsorbed by ammoxidized activated carbons (ACOOX and ACOX) at equilibrium conditions is higher than the SAE and ACO samples.

The presence of functionalities, such as imines (pyridine), lactams, and amides (pyrrole), in the structure of modified activated carbons is an account for the high adsorptive capacity of ACCOX & ACOX due to the formation of strong Cu-bands with –NH2 and –NH functional groups on the adsorbent surface as a result of ammoxidation treatment. Therefore, ammoxidation treatment has considerable enhancement on the capacity of activated carbons toward adsorption of Cu(II) ions. Meanwhile, the higher nitrogen containing functional group in the ACOOX sample has a significant effect on the equilibrium adsorption capacity toward Cu(II).

Besides, the amount of Cu(II) adsorbed by oxidized sample (ACO) at equilibrium conditions is higher than the SAE sample. It can be explained by differences at the zero point of charge (pH_{zpc}) for the adsorbents that was determined as 6.52 and 5.94 for SAE and ACO, respectively. pH_{zpc} is the point at which the net charge of the adsorbent is zero. While pH of solution was 6 and higher than pH_{zpc} for ACO sample, the carboxylic acids on surface of activated carbon adsorbent act as a negative surface and attract the positively charged Cu(II) ions. Generally, the net positive charge decreases with increasing pH value and leads to decrease in the repulsion between the adsorbent surface and metal ions, and as a result enhances the adsorption capacity [35]. Whereas, pH_{zpc} of both ACOX and ACOOX is higher than 6, thus, the carboxylic acid on the surface of these samples is charged positively, and activated carbon adsorbent acts as a positive surface and repulses the positively charged Cu(II) ions. It is obvious that another adsorption behavior is probable for ACOX and ACOOX samples. The nitrogen functional groups, like pyridinic, amine, pyrrolic, and pyridonic groups fixed on the ACOX and ACOOX, gave a basic characteristic to it. This basic nature could strengthen the reaction of activated carbon surface with Cu (II) ions according to the acid–base Lewis theory [2].

4. Conclusions

Ammoxidation of activated carbons was carried out by two different methods in order to investigate the effect of pre-oxidation on ammoxidation of activated carbons. It was indicated that pre-oxidation of activated carbon prior to ammoxidation leads to production of higher amounts of nitrogen and oxygen content at the same time, rather than ammoxidation without pre-oxidation. The variety of characterization techniques leads to the experimental observation that the pretreatment with HNO_3 prior to ammoxidation results in increasing nitrogen content, probably in the form of amines and amides, as compared with ammoxidation alone. In addition, according to the Lewis Acid and Base theory, non-bonding pair electrons on the nitrogen atoms can act like a base to bond with copper ions through its empty orbital. As a result of this affinity, the adsorption capacity for Cu(II) was enhanced in case of ammoxidized adsorbents. This higher adsorption capacity is a consequence of the basic nature of nitrogen functional groups such as pyridinic, amine, amide, pyrrolic, and pyridonic groups. In addition to the obvious existence of these functional groups on ACOOX samples, the amount of carboxylic and lactonic and phenolic groups was also noticeable. Lactones and carboxylic acids seem to react with ammonia to give amide functions.

The Cu(II) adsorption tests showed that the ammoxidized activated carbons, according to the method proposed in this work, could adsorb Cu(II) ions with a higher initial rate and greater capacity than the virgin adsorbent.

References

[1] L. Gu, D. Wang, R. Deng, H. Liu, H. Ai, Effect of surface modification of activated carbon on its adsorption capacity for bromate, Desalin. Water Treat. 51 (2013) 2592–2601.

[2] M.H. Kasnejad, A. Esfandiari, T. Kaghazchi, N. Asasian, Effect of pre-oxidation for introduction of nitrogen containing functional groups into the structure of activated carbons and its influence on Cu (II) adsorption, J. Taiwan Inst. Chem. Eng. 43 (2012) 736–740.

[3] R. Gündoğan, B. Acemioğlu, M.H. Alma, Copper (II) adsorption from aqueous solution by herbaceous peat, J. Colloid Interface Sci. 269 (2004) 303–309.

[4] M. Streat, D.J. Horner, Adsorption of highly soluble herbicides from water using activated carbon and hypercrosslinked polymers, Chem. Eng. Res. Des. Part B 78 (2000) 363–382.

[5] J. Lach, E. Okoniewska, L. Stępniak, A. Ociepa-Kubicka, The influence of modification of activated carbon on adsorption of Ni(II) and Cd(II), Desalin. Water Treat. 52 (2014) 3979–3986.

[6] B. Saha, M.H. Tai, M. Streat, Metal sorption performance of an activated carbon after oxidation and subsequent treatment, Chem. Eng. Res. Des. Part B 79 (2001) 345–351.

[7] S. Biniak, M. Pakuła, G.S. Szymański, A. Świątkowski, Effect of activated carbon surface oxygen- and/or nitrogen-containing groups on adsorption of copper(II) ions from aqueous solution, Langmuir 15 (1999) 6117–6122.

[8] T.Y. Kim, H.J. Jin, S.S. Park, S.J. Kim, S.Y. Cho, Adsorption equilibrium of copper ion and phenol by powdered activated carbon, alginate bead and alginate-activated carbon bead, J. Ind. Eng. Chem. 14 (2008) 714–719.

[9] C. Shin, J.S. Bae, Performance of an activated carbon adsorber in a water reclamation system with an electrolysis reactor, J. Ind. Eng. Chem. 15 (2009) 179–184.

[10] M. Soleimani, T. Kaghazchi, The investigation of the potential of activated hard shell of apricot stones as gold adsorbents, J. Ind. Eng. Chem. 14 (2008) 28–37.

[11] L.H. Wang, C. Lin, The removal of heavy metal ions from spiked aqueous solutions using solid wastes—Comparison of sorption capability, J. Taiwan Inst. Chem. Eng. 41 (2010) 585–590.

[12] N.H. Shaidan, U. Eldemerdash, S.h. Awad, Removal of Ni (II) ions from aqueous solutions using fixed-bed ion exchange column technique, J. Taiwan Inst. Chem. Eng. 43 (2011) 40–45.

[13] L. Monser, N. Adhoum, Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater, Sep. Purif. Technol. 26 (2002) 137–146.

[14] M. Soleimani, T. Kaghazchi, Activated hard shell of apricot stones: A promising adsorbent in gold recovery, Chin. J. Chem. Eng. 16 (2008) 112–118.

[15] H. ShamsiJazeyi, T. Kaghazchi, Investigation of nitric acid treatment of activated carbon for enhanced aqueous mercury removal, J. Ind. Eng. Chem. 16 (2010) 852–858.

[16] K. Nakagawa, S.R. Mukai, T. Suzuki, H. Tamon, Gas adsorption on activated carbons from PET mixtures with a metal salt, Carbon 41 (2003) 823–831.

[17] M.R. Mostafa, Adsorption of mercury, lead and cadmium ions on modified activated carbons, Adsorpt. Sci. Technol. 15 (1997) 551–557.

[18] F.S.h. Mohamed, W.A. Khater, M.R. Mostafa, Characterization and phenols sorptive properties of carbons activated by sulphuric acid, Chem. Eng. J. 116 (2006) 47–52.

[19] K.P. Bhabendra, N.K. Sandle, Effect of different oxidizing agent treatments on the surface properties of activated carbons, Carbon 37 (1999) 1323–1232.

[20] C.A. Toles, W.E. Marshall, M.M. Johns, Surface functional groups on acid-activated nutshell carbons, Carbon 37 (1999) 1207–1214.

[21] J.P. Chen, S. Wu, K.H. Chong, Surface modification of a granular activated carbon by citric acid for enhancement of copper adsorption, Carbon 41 (2003) 1979–1986.

[22] R.J.J. Jansen, H. van Bekkum, Amination and ammoxidation of activated carbons, Carbon 32 (1994) 1507–1516.

[23] R.J.J. Jansen, H. van Bekkum, XPS of nitrogen-containing functional groups on activated carbon, Carbon 33 (1995) 1021–1027.

[24] T. Kaghazchi, N. Kolur, M. Soleimani, Licorice residue and Pistachio-nut shell mixture: A promising precursor for activated carbon, J. Ind. Eng. Chem. 16 (2010) 368–374.

[25] P.J. Lu, H.C. Lin, W.T. Yu, J.M. Chern, Chemical regeneration of activated carbon used for dye adsorption, J. Taiwan Inst. Chem. Eng. 42 (2011) 305–311.

[26] Z. Liu, L. Li, L. Tang, R. Shi, Q. Gu, X. Liang, X. Yao, Investigation of adsorption performance on 1,2-dichloroethane by heat and acid modified activated carbon, J. Environ. Chem. Eng. 1 (2013) 131–136.

[27] A. Swiatkowski, M. Pakula, S. Biniak, M. Walczyk, Influence of the surface chemistry of modified activated carbon on its electrochemical behaviour in the presence of lead(II) ions, Carbon 42 (2004) 3057–3069.

[28] D. Cagniant, P. Magri, R. Gruber, S. Berlozecki, P.D. Salbut, J. Bimer, G. Nansé, Ammoxidation of cellulose: A structural study, J. Anal. Appl. Pyrolysis 65 (2002) 1–23.

[29] R. Pietrzak, H. Wachowska, P. Nowicki, K. Babeł, Preparation of modified active carbon from brown coal by ammoxidation, Fuel Process. Technol. 88 (2007) 409–415.

[30] M.G. Plaza, C. Pevida, B. Arias, J. Fermoso, F. Rubiera, J.J. Pis, A comparison of two methods for producing CO_2 capture adsorbents, Energy Procedia 1 (2009) 1107–1113.

[31] J. Starck, P. Burg, S. Muller, J. Bimer, G. Furdin, P. Fioux, C. Vix_Guterl, D. Begin, P. Faure, B. Azambre, The influence of demineralisation and ammoxidation on the adsorption properties of an activated carbon prepared from a Polish lignite, Carbon 44 (2006) 2549–2557.

[32] M.S. Shafeeyan, W.M.A. Wan Daud, A. Houshmand, Ah. Shamiri, A review on surface modification of activated carbon for carbon dioxide adsorption, J. Anal. Appl. Pyrolysis 89 (2010) 143–151.

[33] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, J. Am. Chem. Soc. 60 (1938) 309–319.

[34] J.S. Noh, J.A. Schwarz, Estimation of the point of zero charge of simple oxides by mass titration, J. Colloid Interface Sci. 130 (1989) 157–164.

[35] E. Demirbas, N. Dizge, M.T. Sulak, M. Kobya, Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon, Chem. Eng. J. 148 (2009) 480–487.

[36] S.A. Dastgheib, T. Karanfil, W. Cheng, Tailoring activated carbons for enhanced removal of natural organic matter from natural waters, Carbon 42 (2004) 547–557.

[37] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, Modification of the surface chemistry of activated carbons, Carbon 37 (1999) 1379–1389.

[38] Y.F. Jia, B. Xiao, K.M. Thomas, Adsorption of metal ions on nitrogen surface functional groups in activated carbons, Langmuir 18 (2002) 470–478.

[39] G.H. Giles, T.H. MacEwan, S.N. Nakhwa, D. Smith, 786. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids, J. Chem. Soc. 3 (1960) 3973–3993.