

Removal of arsenic from aqueous phase using magnetized activated carbon and magnetic separation

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Abstract

Arsenic (As) is one of the elements having most harmful impact on the human health. Arsenic is a known carcinogen and arsenic contamination of drinking water is affecting on humans in many regions of the world. Adsorption has been proved most preferable technique for the removal of arsenic. Many researchers have studied various types of solid materials as arsenic adsorbent, and iron oxide and its modified forms are considered as the most effective adsorbent in terms of adsorption capacity, recovery, and economics. However, most of all iron oxides have small surface area in comparing with common adsorbents in environmental application such as activated carbon but the activated carbon has weak sorption affinity for arsenic. We have used an activated carbon as base adsorbent and iron oxide coating on the activated carbon as high affinity sorption sites and giving magnetic attraction ability. In this study, adsorption properties of arsenic and magnetic separation efficiency of the magnetized activated carbon (MAC) were evaluated with variable iron oxide content. As the iron oxide content of the MAC increased, adsorption capacity has also gradually increased up to a point where clogging by iron oxide in the pore of activated carbon compensate the increased sorption capacity. The increase of iron oxide content of the MAC also affected magnetic properties, which resulted in greater magnetic separation efficiency. Current results show that magnetically modified common adsorbent can be an efficiency improved adsorbent and a feasible environmental process if it is combined with the magnetic separation.

Keywords : arsenic, adsorbent, magnetized activated carbon, environmental application, magnetic separation

1. INTRODUCTION

One of the problems frequently encountered in the environmental process is the separation of contaminants from environmental media such as water, air, and soil. Physical separation with current common technologies works for most of the decontamination process but sometimes the processes are not enough and needs modification. Magnetic separation has several advantages to be applied in environmental processes. Magnetic separation could be a cost effective process, especially it combined with current environmental technologies like sorption or precipitation.

Arsenic is a known toxic heavy metal which is found in groundwater and river water. It is a big concern due to its known high toxicity. Arsenic can cause skin-thickening, hyperpigmentation, neurological diseases, and cancer. Inorganic arsenicals have been classified as Group I carcinogens. Arsenic in soil is found mainly in the two form of oxidation states of As(III) and As(V). Groundwater contacting with soil including arsenic minerals dissolve the arsenic species and have the inorganic arsenic with oxidation states of As(III) and As(V). In comparing of the two oxidation states in the aspect of toxicity, As(III) is 60 times more toxic than As(V). Therefore the groundwater contaminated with arsenic has become a threat for people who use the

groundwater as drinking water. The threat is worldwide including Bangladesh, India, China, Chile, Mexico, and United States. More than several million people in Asia including India and Bangladesh have been at serious risk as a result of drinking arsenic contaminated groundwater [1]. The risk from drinking the contaminated groundwater is higher than the acceptable risk. World Health Organization (WHO) has lowered the As standard from 50 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$. Many countries have lowered the As standard to 10 $\mu\text{g/L}$. Engineers and scientists have tried to find an efficient way to remove arsenic from water.

There are water treatment technologies for As contaminated water. Ion exchange, membrane filtration coagulation/precipitation, and adsorption are technologies which have received attention in recent years. Coagulation/precipitation is one of the most practically used technologies for waste water treatment and it can be used for As contaminated water. However, coagulation/precipitation produce sludge and trace of coagulant can cause secondary problems. Adsorption is one candidate to be used for the As contaminated water. Among several adsorbents, iron-oxide has a high sorption capacity for As and many studies have been published dealing adsorption of As [2-3]. Iron oxide has relatively small specific surface area. Higher specific surface area and reusable adsorbents are preferred in the aspect of cost and environmental protection.

Activated carbon is one of the most widely used

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adsorbents for the removal of organic and inorganic contaminants from water and wastewater. Granular activated carbon (GAC) has been used for the environmental application due to several advantages of it. It is easy to handle GAC and reuse after recover and regeneration. Powdered activated carbon (PAC) supplies relatively fast reaction time due to the small particle and a big exposed surface area. However, it is very difficult to recover PAC from aqueous phase and regeneration. If physical treatment method can overcome the weak points of PAC, water treatment could be more cost effective and eco-friendly. Magnetic separation could be a solution for the easy recovery of PAC. At the same time it is necessary to increase the sorption capacity of PAC for As considering the relatively low sorption ability of PAC for As, even though activated carbon is very attractive adsorbent for organic contaminants. Since activated carbon has a great adsorption capacity for organic substances, related magnetization research generally focuses on the organic contaminants such as dyes [4-5].

There are some previous studies which focused on the heavy metal removal from aqueous phase using adsorbents and magnetic separation combination [6-9]. We tried to combine PAC, which has a high specific surface area, with iron oxide, which has sorption abilities for As from aqueous phase. The combination also gives advantages of magnetic separation of PAC. This has activated carbon regenerate for repeated use.

2. EXPERIMENTAL METHODS

2.1. Chemicals

Arsenic standard solution (1,000 mg/L) was purchased from Kanto Chemical. Powdered activated carbon, sodium hydroxide, sodium chloride, and ferrous sulfate were obtained from Daejung Chemical. All chemicals and materials were used without further purification.

2.2. Analytical Methods

The morphological features of the MAC were studied using a SEM/EDS (Vega II LMU, Tescan). X-ray diffraction patterns were measured with powder XRD (Ultima IV, Rigaku), and ICP-MS (7800, Agilent) was used for measurement of arsenic. Magnetic property of the MAC was analyzed by a VSM (Model 7404, Lake Shore Cryotronics, Inc.). The accuracy and precision of the analytical methods were verified against reference samples. The characteristics of the MAC separated by the magnetic force were compared with the portion passed through the separation system.

2.3. Preparation of MAC

5.0 g of powdered activated carbon and 500 mL of 5 - 80 mM ferrous sulfate was mixed in a beaker. 10 % (W/W) sodium hydroxide solution was added for precipitation of ferrous hydroxide. The mixture was heated at 90 °C using hotplate stirrer for oxidation of ferrous hydroxide. After cooling to room temperature, the product was rinsed with distilled water and dried at 50 °C for 24 hour.

2.4. Magnetic Separation

A HGMS system was used in current experiments and it was equipped with a 0.5 T electromagnet. The bore size of the magnet was 20 mm in diameter and sample channel, which is made of acrylic pipe, was fitted into the bore. The filter was wound steel mesh and it is made from stainless steel with a diameter of 0.3 mm. The filter was placed into the acrylic pipe which to be fitted into the pore of the magnet. The steel sieve size and interval were 10 mesh (0.254 mm) and 10 mm.

The magnetic separation experiments were conducted in a manner of batch process. The prepared MAC was suspended into distilled water and the liquid to solid ratio was 500:1. The MAC slurry was introduced into the acrylic pipe, in which the steel mesh was placed. The separated particle captured on the steel mesh by magnetic force was collected by removing the pipe and steel mesh from the bore after a set of experiment. The ratio of separated MAC to the part passed through magnetic filter was calculated by following equation:

$$\text{Separated ratio (\%)} = \frac{W_{in} - W_{out}}{W_{in}} \times 100 \quad (1)$$

where W_{in} and W_{out} are dry weight of injected and passed MAC. The experiments were performed by 0.5 Tesla magnetic field and 0.12 m/s of flow velocity.

2.5. Adsorption Experiment

The relationship between the equilibrium concentration of adsorbate and the amount adsorbed at the adsorbent surface is determined by a variety of available fundamental isotherm equations. The adsorption isotherm results of the activated carbon and MAC at a room temperature of 25 °C were analyzed by Langmuir and Freundlich models.

Langmuir isotherm describes the equilibrium model between the amount of solute adsorbed per unit mass of adsorbent and the solute remaining in the solution at low surface coverage. The assumptions of the Langmuir model are monolayer homogeneous adsorption, identical energy of sorption for all sites, independent of coverage binding energy and no interaction between adjacent adsorbate molecules. Langmuir model is expressed as Eq. (2).

$$q_e = \frac{q_0 \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (2)$$

where b is Langmuir equilibrium constant (L/g) and q_0 is maximum monolayer adsorption (mg/g).

Freundlich isotherm, an empirical model, describes multilayer heterogeneous adsorbent surface with different adsorption sites. Freundlich model is expressed as Eq. (3).

$$q_e = k_f \cdot C_e^{1/n} \quad (3)$$

where k_f is Freundlich adsorption capacity (mg/g) and $1/n$ represents the surface heterogeneity parameter.

In this study, isotherm test was performed through batch experiments using 0.1 g of MAC and 50 mL of arsenic solution from 1 to 200 mg/L. The reaction performed at

200 rpm for 2 hour using an orbital shaker, and the solution pH was fixed to 5.5 using 0.1 N nitric acid. After the reaction, the centrifuge was used to collect the absorbent from the solution, and each solution was quantified after filtering (0.45 μm).

Regeneration of the MAC was evaluated by comparing the adsorption capacity before and after arsenic desorption. Adsorption test was performed with a 0.1 g of MAC and 100 mg/L of arsenic solution for 2 hour. For desorption of arsenic, NaCl solution was used as desorption agent. The test was performed with 0.1 g of used MAC and 50 mL of 1.0 M NaCl solution for 2 hour. Regeneration was assessed by repeating the adsorption and desorption test.

3. RESULTS AND DISCUSSION

3.1. Characteristics of the MAC

The concentration of ferrous iron added on magnetization is the most important factor determining of magnetic property and sorption capacity of the MAC. As the iron concentration increases in magnetization, magnetism increases, but the sorption capacity can be reduced due to the clogging of pore of the activated carbon and decreased purity. In this study, moderate concentration of the ferrous iron was investigated. The activated carbon is magnetized at ferrous sulfide concentration of 5 – 80 mM. Fig. 1 and 2 shows the results of the SEM/EDS

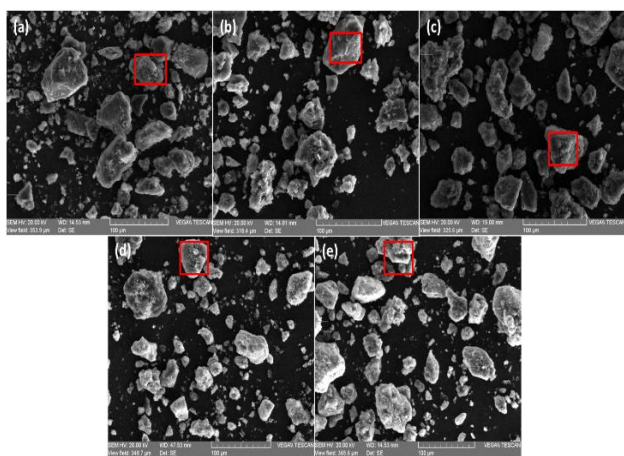


Fig. 1. SEM images of activated carbon and each condition of MACs, (a) activated carbon, (b) 5 mM FeSO_4 , (c) 10 mM FeSO_4 , (d) 40 mM FeSO_4 , (e) 80 mM FeSO_4 . [Red squares are the EDS analysis areas in Fig. 2]

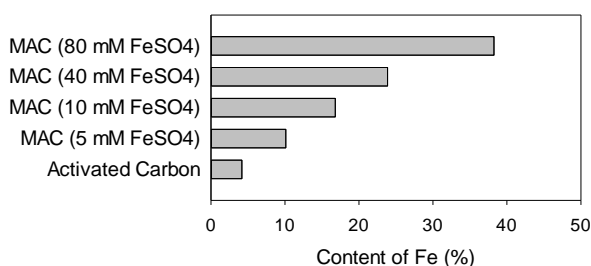


Fig. 2. Comparison of iron content. (EDS results)

analysis of the MAC. Changes in particle size were not observed depending on the magnetization condition and particle diameter of MAC were mostly measured below 70 μm . However, the iron content was gradually increased according to the magnetization condition and showed a maximum content of 38.3 %.

Fig. 3 shows the magnetic hysteresis curves of the MAC of each magnetization condition. The values of saturation magnetization (M_s) and residual magnetization (M_r) are shown in Table I. The result indicates an increase in magnetism according to the magnetization condition. There is a threshold point to make enough magnetite on the activated carbon. As a result of observing residual magnetization (0.23 – 6.41 emu/g), the MAC is identified as a ferromagnetic substance and it is a common characteristic of ferrite ($\text{MO}\cdot\text{Fe}_2\text{O}_3$) such as a magnetite.

Magnetic separation was conducted with a HGMS using the electromagnet with a relatively low magnetic field of 0.5 T. The recovered MAC was tested four times in series, repeating of recovery of MAC and resuspension of the recovered MAC for the next recovery, and the results are shown in Fig. 4. All of the tested MAC had an improved recovery ratio with an increased number of magnetic separation, which may be due to the exclusion of low-magnetism MAC by the magnetic separation. The MAC magnetized with a 5 mM of ferrous sulfate shows the lowest recovery ratio (21.8 – 43.6 %) and the MAC magnetized with 80 mM of ferrous sulfate was recovered 52.1 – 87.2 %. The recovery ratio increased as the iron oxide content increase but it is not dramatic with electromagnet of 0.5T of magnetic field. The MAC magnetized

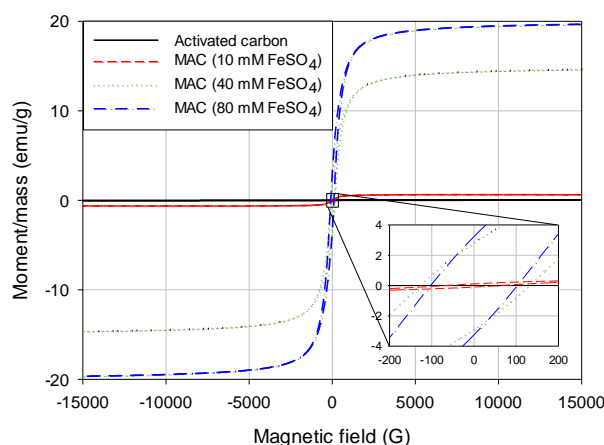


Fig. 3. Magnetic hysteresis curves of the MAC in each magnetization condition.

TABLE I
MAGNETIC PROPERTIES OF THE MAC IN EACH CONDITION.

Compounds	M_s (emu/g)	M_r (emu/g)
Activated carbon	0.02	0.00
MAC (10 mM FeSO_4)	0.63	0.23
MAC (40 mM FeSO_4)	14.62	5.72
MAC (80 mM FeSO_4)	19.65	6.41

with 10 mM of ferrous iron also demonstrated good recovery ratio (43.9 – 74.9 %). However, the magnetization trend in Figure 3 is not well matched with the magnetic separation in Figure 4. The low magnetization of 10mM showed relatively high recovery in Figure 4 indicating even low magnetization could be helpful in separation. Current experiment is carried out under the 0.5 T condition, it is possible to expect a better recovery ratio and high speed operation when applied to higher magnetic fields with superconducting magnet.

However, Excessive increase in iron content of a MAC can cause decrease of sorption capacity of the activation carbon. Table II shows the specific surface area analysis results of the MAC for each magnetization condition. As a result, it was observed that the surface area and total pore volume in the 40 mM or higher magnetization conditions were significantly reduced. This is mainly due to the activated carbon pore blockage caused by magnetization. Therefore, in this study, considering magnetic property and sorption capacity, the appropriate condition of magnetization is estimated to be 10 mM of ferrous sulfate condition.

The isotherm plots are shown in Fig. 5 and Langmuir and Freundlich isotherms parameters are summarized in Table III. The model parameters showed that the MAC has

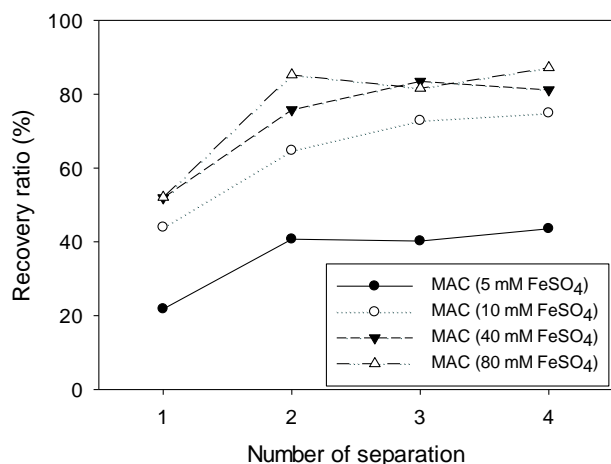


Fig. 4. Recovery ratio of MAC according to the number of magnetic separation ($V=0.12$ m/s, $T=20\pm 2^\circ\text{C}$), no activated carbon is recovered.

TABLE II
COMPARISON OF SPECIFIC SURFACE AREA MEASUREMENTS RESULTS
ACCORDING TO THE FERROUS SULFATE CONCENTRATION.

Condition	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	Pore size (\AA)
Without FeSO_4	1058.9	0.53	19.94
5 mM FeSO_4	1012.6	0.54	21.16
10 mM FeSO_4	1014.8	0.53	21.21
40 mM FeSO_4	818.4	0.42	20.98
80 mM FeSO_4	682.5	0.38	22.38

3.2. Adsorption isotherms

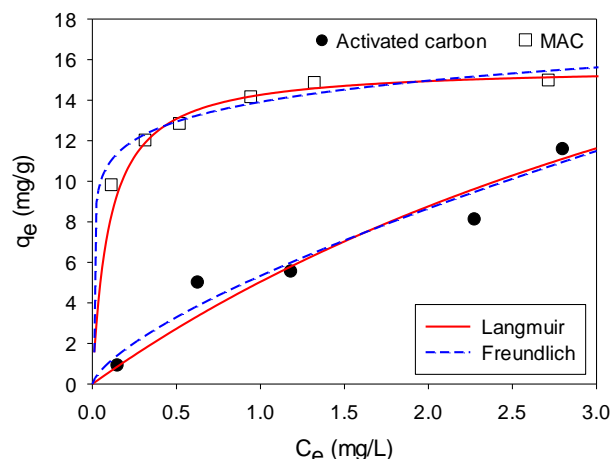


Fig. 5. Arsenic adsorption isotherm ($T=25^\circ\text{C}$, equilibrium $\text{pH} = 5.5$) for distilled water.

TABLE III
ADSORPTION CONSTANTS OF ARSENIC.

Model	Parameter	Activated carbon	MAC
Langmuir	q_0 (mg/g)	33.53	15.54
	b (L/g)	0.177	9.048
	R^2	0.907	0.969
Freundlich	k_f (mg/g)	5.342	13.62
	$1/n$	0.698	0.116
	R^2	0.933	0.892

greater sorption capacity (q_0 , k_f) for arsenic in both models. In Fig. 5, MAC showed very different sorption characteristics from the plain activated carbon. The activated carbon was better fitted to the Freundlich model, but MAC has made it fit into Langmuir model. These results were attributed to the effects of iron oxide such as magnetite on the activated carbon surface.

Comparing the shape of the isotherm curve, sorption affinity of arsenic to the MAC was stronger than that of activated carbon. So sorption capacity does not decrease significantly even when the equilibrium concentration is very low. In general, Arsenic contaminated water (e.g., naturally contaminated groundwater) is very low in concentrations ranging from 100 to 200 $\mu\text{g}/\text{L}$ and requires less than 10 $\mu\text{g}/\text{L}$ for drinking water. Therefore, the MAC with high sorption affinity is very effective for clear removal of arsenic.

3.3. Regeneration of the used MAC

Regenerable adsorbents have higher economic and environmental value. The regeneration characteristics of the MAC are shown in Fig. 6. The regeneration efficiency was calculated as a ratio of the adsorption capacity by the number of regeneration. The desorption efficiency is the ratio of adsorption to desorption. The desorption efficiency was calculated as mass balance of adsorption capacity and desorption. As a result of using the 1.0 M NaCl, the regeneration efficiency were all over 90%, and the efficiency showed a slight decline. At this time, the desorption efficiency were calculated between 72.9% and 82.5%.

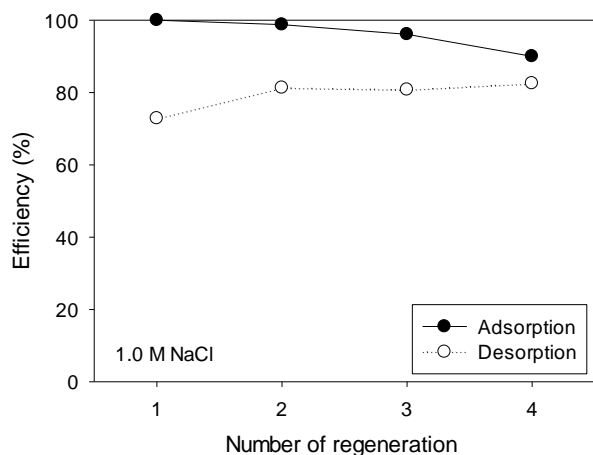


Fig. 6. Adsorption and desorption efficiency of the MAC in 1.0 M NaCl solution according to the number of regeneration process. (T=20 °C, S/L ratio = 1/500)

4. CONCLUSION

In a magnetization of activation carbon for magnetic separation of arsenic from water, a minimum magnetism is preferable as long as the adsorbent separated with magnetic force, because the content of iron oxide on the surface of activated carbon reduces the sorption capacity. In current study, activated carbon was successfully magnetized at 10 mM of ferrous sulfate condition, enhancing the two advantages: sorption capacity and magnetism. Furthermore, it was observed that the magnetization improved the sorption affinity of the activated carbon for arsenic. The MAC showed a very good performance for arsenic contaminated water treatments requiring very low concentration of As. The MAC can be recovered and regenerated via magnetic separation, so it is more economical and eco-friendly to use on-site than traditional adsorption methods.

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REFERENCES

- [1] K. Ahmad, "Report highlights widespread arsenic contamination in Bangladesh," *The Lancet*, vol. 358, pp. 133, 2001.
- [2] V.P. Simeonova, "Pilot study for arsenic removal," *Water Supply*, vol. 18, pp. 636-640, 2000.
- [3] W. Zhang, P. Singh, E. Paling, and S. Delides, "Arsenic removal from contaminated water by natural iron ores," *Miner. Eng.*, vol. 17, pp. 517-524, 2004.
- [4] L. C. A. Oliveira, R. V. R. A. Rios, J. D. Fabris, V. Garg, K. Sapag, and R. M. Lago, "Activated carbon/iron oxide magnetic composites for the adsorption of contaminants in water," *Carbon*, vol. 40(12), pp. 2177-2183, 2002.
- [5] N. Yang, S. Zhu, D. Zhang, and S. Xu, "Synthesis and properties of magnetic Fe₃O₄-activated carbon nanocomposite particles for dye removal," *Mater. Lett.*, vol. 62, pp. 645-647, 2007.
- [6] H. W. Kwon, J. J. Kim, D. W. Ha, and Y. H. Kim, "Formation of iron oxides from acid mine drainage and magnetic separation of the heavy metals adsorbed iron oxides," *Prog. Supercond. Cryog.*, vol. 18, pp. 28-32, 2016.
- [7] Y. Li, J. Wang, Y. Zhao, and Z. Luan, "Research on magnetic seeding flocculation for arsenic removal by superconducting magnetic separation," *Sep. Purif. Technol.*, vol. 73, pp. 264-270, 2010.
- [8] D. Feng, C. Aldrich, and H. Tan, "Removal of heavy metal ions by carrier magnetic separation of adsorptive particulates," *Hydrometallurgy*, vol. 56, pp. 359-368, 2000.
- [9] H. W. Kwon, J. E. Kim, D. W. Ha, and Y. H. Kim, "Decontamination of Cesium from contaminated water using a selective adsorbent and magnetic separation," *IEEE trans. Appl. Supercond.*, vol. 26, pp. 1-4, 2016.