Remediation of Groundwater Contaminated by Heavy Metals Using Magnetic Separation Technique

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Abstract. Heavy metals pollution has become one of the most serious environmental problems nowadays. Studies on the environmental pollution indicate that water pollution by heavy metals ions has reached unprecedented levels over the past decade in many countries, with highlights to African countries. Removal of these toxic metals from contaminated water can improve human being life quality and prevent from their adverse effects. This study aims to text the ability of magnetic activated carbon (MAC) and MAC coated with wastes of colloidal silica (MACSi) for adsorption of copper, manganese and zinc ions from water and its separation from water using magnetic separation technique. The adsorption results of MAC and MACSi showed that MACSi was more effective to adsorb the ions than MAC. FT-IR spectrum and XRD pattern of MACSi indicated that silica coating onto MAC surface is in amorphous form.

1. Introduction

Heavy metals are among the wide diversity of contaminants affecting surface and groundwater. Unlike other pollutants, heavy metals are not biodegradable and cannot be decomposed. Therefore, effective methods are needed to remove and detect these toxic metals from water [1]. In recent decades, a large number of researches have been focused on the effective removal methods of heavy metals ions from water. Adsorption method is considered as an efficient and economical technique because of its simple design and facile handling process [2]. Activated carbon has been one of the widely used adsorbent for contaminants adsorption for a long time, but it suffers from a lack of structural and functional stability, low adsorption capacity and limitation to absorb heavy metals contaminants from aqueous solutions [3]. Therefore modification of activated carbon surface with functional groups to enhance its adsorption capacity for heavy metals removal attracts researchers’ attention, which is also of great practical value in the future of water treatment.

In this research we focused on colloidal silica as surface modification agent. Colloidal silica is used as a pure polishing agent but from the view point of dispersion stability unused colloidal silica is discharged when they are expired. Colloidal silica possesses an abundant number of silanol groups for surface modification and functionalization [4]. Modification of activated carbon with silane coupling agent has been reported to exhibit high adsorption capacity for heavy metals from wastewater when compared to the materials used traditionally and commercially as adsorbents [5]. In addition, adsorbents with ferromagnetic proprieties have many advantages among others, they can reduce secondary wastes because they can be recovered by the magnetic force and can be used in a high throughput and large scale-treatment.
The objective of present study, is to use non-conventional silica reagent (industrial wastes of colloidal from the expired polishing agent) along with magnetic activated carbon to prepare a low cost ferromagnetic adsorbent and test its ability for heavy metals cations adsorption and separate from solution by using a neodymium magnet.

2. Magnetic separation technique

Magnetic separation technique for a long time has stood out as an interesting and important physical driving force to separate magnetic from non-magnetic components of the mixture [6]. Magnetism is a unique physical property that independently helps in water treatment by influencing the physical properties of contaminants in water. In addition, its combination with other processes enables an improvised efficient treatment technology. The magnetic force, $F_M$ (equation 1) represents the force that attracts the target particles to the magnet, $r$ is the radius of the particles to remove, $\mu_0$ denotes permeability constant of the vacuum, $M$ is magnetization of the particles to remove and $H$ is the strength of a magnetic field. The magnetic field strength to be applied in the water treatment will be determined by the radius and magnetization of the particles to remove.

$$F_M = \frac{4}{3}\pi r^3 \mu_0 (M \cdot \nabla)H$$  \hspace{1cm} (1)

There are many types of magnetic separation for different target pollutants. In 1977 Parker categorized them in four different categories, low intensity dry magnetic separation, low intensity wet magnetic separation, high intensity dry magnetic separation, and high intensity wet magnetic separation, also known as “high gradient magnetic separation” (HGMS) [10]. For large scale treatment in this study, we suggest a low intensity wet magnetic system depending on the magnetism and particle size of the adsorbent with a superconducting magnet or a neodymium magnet shown in Figure 1.

![Figure 1: Magnetic separation principle for heavy metals removal from contaminated groundwater](image)

3. Material and Methods

Copper sulphate pentahydrate (CuSO$_4$·5H$_2$O), manganese sulphate pentahydrate (MnSO$_4$·5H$_2$O) and zinc sulphate heptahydrate (ZnSO$_4$·7H$_2$O) used in this study were of analytical grade (Fuji Film Wako Junyaku, Japan). Industrial wastes of colloidal silica were obtained from a polishing industry (Maeda Material Co. Ltd., Japan). Magnetic activated carbon (MAC) were provided from Osaka Chemical, Japan.

Contaminated water with heavy metals were artificially prepared dissolving the exact amount of salts above mentioned to make solution with 10 ppm of each ion. The concentrations of metal ions were determined by ICP-AES (ICPS-7500 Shimadzu, Japan). FT-IR was obtained as KBr pellet in the range of 4000 cm$^{-1}$ to 400 cm$^{-1}$ using Fourier-Transform Infrared spectroscopy (FT/IR-470 Plus, Jasco, Japan) and X-ray Power Diffraction measurements were performed using PANalytical Xpert$^\text{R}$ Powder with Cu Ka radiation in the range 2$\theta$ from 10 to 80 at room temperature (Malvern Panalytical, United Kingdom).
3.1. Preparation of MACSi adsorbent

The magnetic activated carbon coated with industrial wastes of colloidal silica adsorbent (MACSi) were prepared using two different methods, namely silica coating under room temperature (\( \sim 24 \) °C) and under hydrothermal reaction (\( \sim 120 \) °C) with the objective to check which method promotes effective interaction between MAC and colloidal silica. Coating of silica onto MAC surface is expected to increase the surface area and promote more active sites for heavy metals cations adsorption as represented in the Figure 2. For room temperature 0.1 g of MAC was mixed with 2 mL of colloidal silica and shook for 24 h under 160 rpm using a shaker (Incubate SHK-101B, Iwaki Glass Co. LTD, Japan) then filtrated and allowed to dry at room temperature before being used.

Under hydrothermal reaction consisted in mixing 0.1 g of MAC with 2 mL of colloidal silica, then the mixture was shook for 24 h under 160 rpm using a shaker (Incubate SHK-101B, Iwaki Glass Co. LTD, Japan). Next, the mixture was introduced into a Polytetrafluoroethylene (PTFE) lined stainless steel and introduced to reactor under 120 °C for 24 h. Then the mixture was removed from the reactor, cooled, washed three times with distilled water and dried under vacuum using vacuum oven AVO-200 NS (Misumi-vona, Japan) and it was ready to be used in batch adsorption test.

![Figure 2. Schematic diagram of MAC surface modification into MACSi.](image)

3.2. Batch Removal Experiments

Adsorption of heavy metals cations, \( \text{Cu}^{2+} \), \( \text{Mn}^{2+} \) and \( \text{Zn}^{2+} \) was carried out at pH 6 in room temperature (about 23 °C) using both MAC (as standard adsorbent) and MACSi adsorbent prepared under room temperature and hydrothermal reaction. Same quantity of MAC and MACSi, 0.05g was added in two different bottles containing each 50 mL of contaminated water with co-existence of the above mentioned heavy metals cations, each in the concentration of 10 ppm. Then shook for 3h and the adsorbents were separated from the water with a permanent magnet (Neodymium magnet; of 0.5 T).

The adsorption using MACSi adsorbent prepared under room temperature showed excess of silica in the supernatant as shown in Figure 3 (a) suggesting that silica is easily desorbed from the micropores of magnetic activated carbon due to weak interaction between both. So, after the separation the supernatant was not clean enough to be analysed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). On the other hand, Figure 3 (b) shows the supernatant descendant from adsorption using MACSi prepared under hydrothermal which is clean suggesting effective coating of silica onto magnetic activated carbon surface and the residual heavy metals cations concentration were determined by ICP-AES.
4. Results and Discussions

4.1. Adsorbent characterization

The Powder X-ray diffraction (XRD) pattern of MAC and MACSi prepared under hydrothermal condition represented in Figure 4 shows the characteristics peaks of magnetite, confirming that the cubic phase of magnetite particles are still kept after incorporating silica [13]. The broad peak in 2θ =20 °C in addition to magnetite characteristic peaks in XRD pattern of MACSi prepared under hydrothermal reaction suggest that silica coating is in amorphous form. Same results were observed in the study of Emadi et al. [8].

![Figure 4. XRD patterns of MAC and MACSi (Prepared under hydrothermal condition).](image)

![Figure 5. FT-IR results of MAC and MACSi (Prepared under hydrothermal condition).](image)

The FT-IR spectrum represented in Figure 5 correspond to MAC and MACSi. Peaks between 788 and 476 cm\(^{-1}\) correspond to both magnetite (Fe\(_3\)O\(_4\)) and Fe-O-Si vibration. The broad peak in the region of 1119 cm\(^{-1}\) in FT-IR spectrum of MACSi indicates the Si-O-Si symmetric stretching of silica phase. The pronounced shoulder in the region of 3500 cm\(^{-1}\) in FT-IR spectrum of MACSi indicate OH group present.
in silica, in form of silanol group (Si-OH). The same stretch vibration were observed in the study of Kong et al., [7]. This suggest that silica was successfully coated onto the surface of MAC.

4.2. Batch adsorption test
The adsorption efficiency ($\eta$) was calculated using equation 2, based on ICP-AES measurements, where $C_i$ (ppm) correspond to heavy metal ion initial concentration in the water, $C_f$ (ppm) heavy metal ion residual concentration.

$$\eta = \frac{C_i-C_f}{C_f} \times 100$$  \hspace{1cm} (2)

The Figure 6 shows the removal ratio of copper, manganese and zinc cations using MAC and MACSi adsorbents, and it suggest that MAC is selective in heavy metals removal as stated in many studies. The removal ratio for copper, manganese and zinc using MAC adsorbent was 83%, 9% and 11% respectively while the removal ratio using MACSi adsorbent was 98%, 87% and 98% for copper, manganese and zinc cations respectively indicating that MACSi adsorbent is effective for heavy metals removal at this pH.

![Figure 6. ICP-AES analysis of MAC and MACSi.](image)

This effective heavy metals removal of MACSi can be explained by the enlargement of MAC specific surface area during silica coating which generated more active sites for ions adsorption due to the presence of silica on its surface (Figure 2). The pH of solution is an important controlling parameter for heavy metals adsorption, depending on the pH that occur the adsorption the surface of adsorbent can be negatively or positively charged [9]. As at pH 6 (pH of solution of contaminated water) the surface of silica conjugated in MACSi is negatively charged due to the fact that is greater than its isoelectric point, pH=2 [11]. Thus the negative charges are higher than positive ions as shown in the equation 3, this make effective the electrostatic interactions between the negative charges on the MACSi surface and the tested heavy metals cations.

$$\text{SiOH} + \text{OH}^- \leftrightarrow \text{Si-O}^- + \text{H}_2\text{O}$$  \hspace{1cm} (3)

On the other hand, MAC surface is dominated by magnetite at pH 6, which is below magnetite isoelectric point (pH=8) the surface of MAC is positively charged as illustrated in equation 4 [12]. The electrostatic interactions between the MAC surface and heavy metals cations is very weak.

$$\text{Fe-OH} + \text{H}^+ \leftrightarrow \text{FeOH}_2^+$$  \hspace{1cm} (4)
The significant removal ratio difference between the heavy metals ions using MAC adsorbent it may due to solubility of ions, at pH 6 part of copper ions precipitate as Cu(OH)$_2$ and are physically adsorbed on the microporous of MAC while manganese and zinc precipitate at pH 9.52 and 7.65 respectively.

Table 1: Solubility products and precipitation pH of heavy metal ions

| Ions  | Solubility product (25°C) | Atomic weight (amu) | Conc. of solution (ppm) | Concentration (mol/l) | Precipitation pH |
|-------|---------------------------|---------------------|-------------------------|-----------------------|-----------------|
| Cu$^{2+}$ | 4.8 x 10$^{-20}$ | 63.55 | 10 | 1.57x10$^{-4}$ | 6.2 |
| Mn$^{2+}$ | 2.0 x 10$^{-13}$ | 54.94 | 10 | 1.82x10$^{-4}$ | 9.5 |
| Zn$^{2+}$ | 3.0 x 10$^{-17}$ | 65.39 | 10 | 1.53x10$^{-4}$ | 7.7 |

5. Conclusions
In this study, a new adsorbent for heavy metals cations adsorption (copper, manganese and zinc) were prepared. The method of preparation consisted on coating industrial wastes of colloidal silica onto the surface of magnetic activated carbon. Magnetic character of MAC enables to be recovered from suspension by magnetic separation. Silica coating on MAC surface allows rapid adsorption of heavy metals cations due to the generation of more active sites. The colloidal silica coating was confirmed by XRD technique and it suggests that is in amorphous form. The FT-IR spectrum confirmed the presence of silica by showing Si-O-Si symmetric stretch in the region of 1119 cm$^{-1}$. Heavy metals adsorption under MAC showed strong affinity to copper with 83% of removal ratio, 9% and 11% to manganese and zinc respectively. Adsorption under MACSi was effective to all heavy metals ions with 98%, 97% and 98% of removal ratio for copper, manganese and zinc respectively. The adsorbent was easily separated from the suspension by a Neodymium magnet of 0.5T. The pH of solution, adsorbent contact time and adsorbent amount dependence are under investigation. Future studies will feature the MACSi adsorption test with a large number of heavy metals and MACSi reusability capacity.

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