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Availability of Carboxylated Magnetic Beads for Extracting Heavy Metals from Aqueous Solution

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It was examined in this study that magnetic beads, which are assumed to be environmentally functional, could be effective in processing heavy metals that are water pollutants. For the purpose, magnetic beads containing carboxyl groups, which has strong binding force with heavy metals, are mixed with each Cd, Pb, Ni, Cu and Cr(III) solution, then stirred in pH 6. As a results of the process, it was proven that heavy metals bind quickly with magnetic beads through the reaction. In order to analyze heavy metal concentration, magnetic beads bind with heavy metal were collected by external magnetic force and dissolved in acid. The graphite furnace AAS was used to get heavy metal concentration melted in the acid solution. The results showed that heavy metal extractions by magnetic beads were influenced by the type and the concentration of a heavy metal, and over 90% of a heavy metal can be extracted in ppm level save for Cr(III). It was also examined in the study whether heavy metal extraction is influenced when other ions exist in each heavy metal solution. According to experiment, adding other heavy metals to a solution did have little influence on extracting an intended heavy metal. But in case salt or heavy metal chelate was added, Ni extraction changed sensitively although extracting other heavy metals were influenced only when the concentration of an added substance is high. In conclusion, it was shown that magnetic beads could be used to treat wastewater with relatively high heavy metal concentration.

Key words : heavy metals, magnetic beads, extraction, salt, chelate

1. Introduction

The industrial revolution contributed to the prosperity of the human race through the rapidly industrial growth and unfortunately let us be in a dilemma of heavy metals, which were important in the development, for instance, they are still essential for plating, alloying, catalyzer, battery, pigment, plastic stabilizer and pesticide. However, they are, now, threatening our life and environment because of harmful side effects. Not like other harmful substances, heavy metals cannot be decomposed by microorganisms, therefore accumulated in the human body directly or indirectly. The accumulation of heavy metals disturb enzyme activities. Especially, a little amount of Cd, Pb or Hg can cause acute or chronic diseases [1].

It is also difficult to remove heavy metals from wastewater mechanically or biologically. Wastewater with heavy metals mostly goes through flocculation/precipitation methods [2, 3]. In case any additional treatment is needed, they are to be treated by the following post-treatment methods; ion exchange by ion exchange resin, filtering by active carbon or membrane, or reverse osmosis. The ferrite method was developed to treat plating wastewater in 1970 [4]. In this method, bivalent iron is added to alkaline wastewater, then oxidized with air [5]. Through this method, irons react with metal ions to produce ferrites. However, this method disadvantageously and impractically requires high cost for high temperature and oxidation. There is another interesting method, HGMS (High Gradient Magnetic Separation) applying magnetite to treat suspended solids in urban sewage [6-9]. Therefore, HGMS needs to add magnetite and flocculating agent to sewage. Then, HGMS removes precipitated suspended solids with external magnetic force. HGMS takes a shorter retention time, is effective in high separation rate and little blocks during filtering. Unfortunately, HGMS is not effective in removing heavy metals [11, 12].

As mentioned above, the importance of magnetic materials are increasing in various fields. Functional magnetic beads are made up of magnetite and polymer with functionality. Magnetic substances composed of

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magnetite and networked polymers were originally synthesized to accelerate ion exchange with large specific surface. Therefore, early magnetic beads have been mostly developed for ion exchange [12, 13]. Recently, high functionality of magnetic beads, however, makes them used for environmental or medical purpose [14-17].

2. Materials and Methods

2.1. Materials and reagents

In this experiment, PVA magnetic beads (O12) produced by a German company, Chemagen and magnetic beads combined with the carboxyl group based on PVA magnetic beads (C12) were used. Beads have diameter of 1-3 μm with 50~60% magnetite. C12 contains 900 μmol carboxyl groups pro gram. Fig. 1 shows an image of PVA magnetic beads viewed by an electron microscope.

Neodymium-magnet (diameter: 30 mm, height: 4 mm, magnetic force: 12000 gauss) of an German company, Fehrenkaemper was used in this experiment. In order to extract heavy metals, the product of an company Merck was used for EDTA (Titriplex III, Na), and the product of an company Fluka was used for the standards to measure AAS (Model Zeeman/3030, Perkin-Elmer).

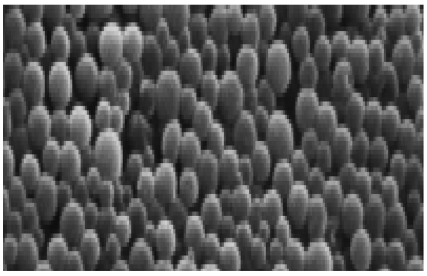

Fig. 1. SEM picture of magnetic beads (PVA basis) [18].

2.2. Extracting heavy metals from aqueous solution by using magnetic beads

In order to optimize extracting conditions based on information about interaction between magnetic beads and various ions, magnetic beads were applied to each aqueous solution of Cd, Pb, Ni, Cu and Cr(III). Fig. 2 shows this process.

First of all, 3 ml 10 ppb - 10 ppm Cd solution was put in 5.0 ml PE-tube, and set to pH 6.0. The magnetic beads (C12) were added as suspended. The amount of it is set that ligand of magnetic beads, the carboxyl group is 20 times (1.78 μmol) for 10 ppm Cd. The amount of magnetic beads could be controlled by measuring weight after drying the same volume of magnetic beads extracted by pipette. Magnetic beads and heavy metal solution were stirred for one minute in a horizontal stirrer. Then magnetic beads combined with heavy metal ions were gathered on the side of tube by a magnet. The solution without heavy metals were removed by a pipette. Finally, magnetic beads were dissolved by 3 ml 5 M HCl, and the amount of heavy metals in the solution was measured by AAS.

2.3. Extracting from heavy metal solution

Cd, Pb, Cu and Ni solutions of which concentrations were 10 ppm/100 ppb were mixed in the same volume to be solution (pH = 6) containing each 2.5 ppm/25 ppb heavy metals. One 10 ppm metal solution and three 10

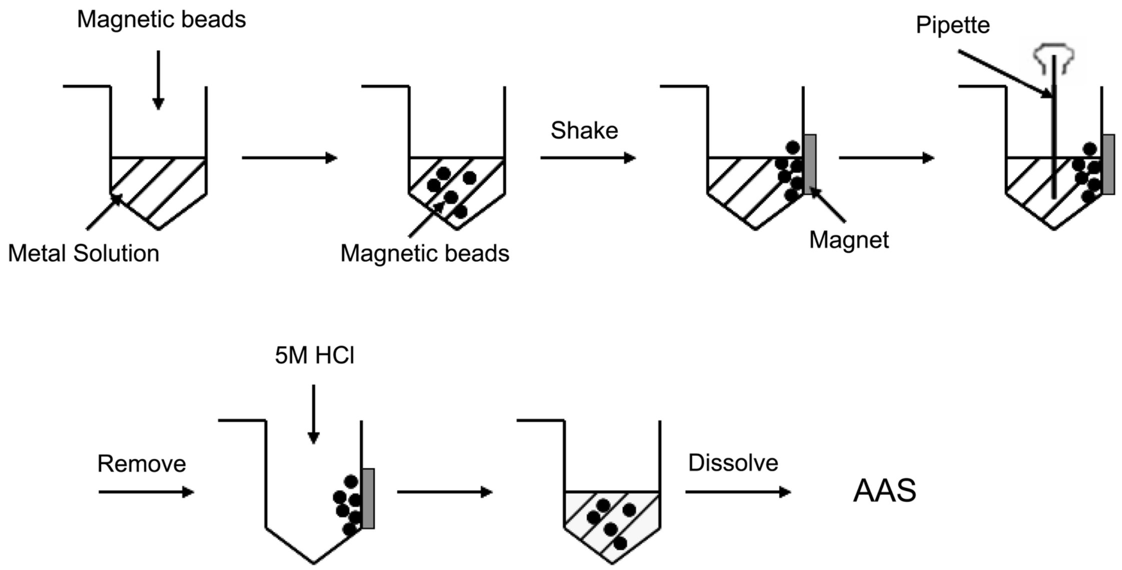

Fig. 2. Extracting heavy metals from the aqueous solution with magnetic beads.

ppb metal solutions were mixed in the same volume so that one 2.5 ppm metal solution had 100 times higher concentration than other three metal solutions (25 ppb). The process save for increasing stirring time to 10 minutes was as same as that of unit 2.2.

2.4. Influence of ion strength on extraction

100 μl 10 ppm Cd, Pb, Cu and Ni solutions were put into a 2.2 ml tube, and set to pH 6. In the same way, a 100 ppb solution was formed at the same time. Then, NaCl was added to 0.05 M concentration. Heavy metals from these solutions were extracted the same in 2.2 after 10-minute reaction. In the following experiment, heavy metals were extracted with 0.1, 0.5, 1.0 and 5.0 M NaCl. Then, according to the same way as did for NaCl, the influence of dihydrogenphosphate (KH_2PO_4) on heavy metal extraction was experimented.

2.5. Influence of the attached compound (chelate) on extraction

The influence of chelate on extraction was experimented the same way as the influence of ion strength (2.4). But instead of NaCl, EDTA is used with 25 ppb and 2.5 ppm heavy metal solutions. EDTA was set to be 1 : 0.1, 1 : 1 and 1 : 10 for entire heavy metals. Experiment was carried on only for Cd.

3. Results and Discussions

3.1. Heavy metal extraction from each heavy metal solution

Using functionalized magnetic beads with the carboxyl group, heavy metals were extracted from various concentration Cd, Pb, Ni, Cu and Cr solutions the same way described in 2.2. Then the extraction effects are compared. Fig. 3 shows the extraction results for each heavy metal.

According to the experiment results of Schubha et al. [19] which extracted heavy metal with the adsorbent with carboxyl group, it is known that provided the amount of adsorbent is the same, the larger the amount of heavy metal, the more effective accordingly. This experiment showed the similar results (Fig. 3) either. In case of Cd, more than 90% Cd could be extracted from all range of concentration. In case of Pb, since its atomic weight is 207.2 g/mol as twice as that of Cd, Pb ions decrease relatively in 10 ppm Pb solution, and the amount of magnetic beads based on Cd increase 37 times for Pb. Regarding heavy metals, although the amount of magnetic beads increases, heavy metal solution has at least more than 1 ppm concentration to extract over 90% heavy

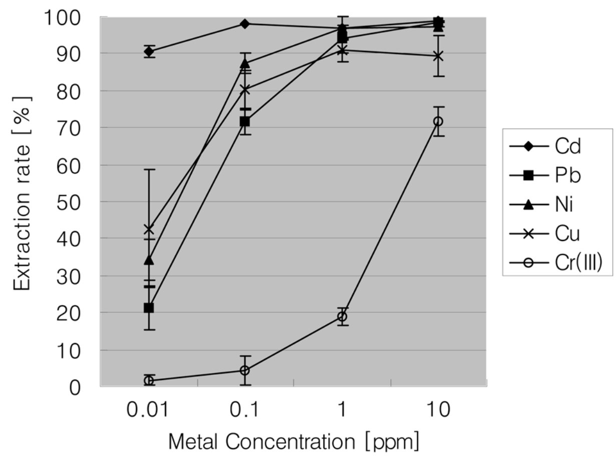

Fig. 3. Extraction rate for various concentration solutions with magnetic beads (pH=6).

metals. For the low concentration, the standard deviation of Pb solution is relatively big. This is because the accuracy of AAS drops for low concentration. On the contrary to Pb, since Ni has the half atomic weight 58.7 g/mol than Cd, ten times magnetic beads are applied to Ni solution. In case of more than 100 ppb, over 90% Ni is extracted. In addition to that, as 90% Ni can be extracted from 10 ppm Ni solution, ten times carboxyl group is sufficient for extracting heavy metals. Here again, because of limit of AAS in low concentration, there is a big standard deviation in the low concentration. As Cu has atomic weight 63.6 g/mol similar to Ni, 11 times magnetic beads are added for extraction. AAS showed that when Cu solution has over 100 ppb concentration, over 80% Cu ions are extracted by magnetic beads. Among five metals, Cr(III) is the lightest one. Cr was 52.0 g/mol. Nine times magnetic beads are applied on the basis of 10 ppm Cr solution. Compared to other metals, Cr showed the lowest efficiency. In ppb, very low extraction (under 10%) could be achieved, and only 70% Cr was extracted from even 10 ppm solution.

3.2. Heavy metal extraction from compounded solution with magnetic beads

3.2.1. Influence of heterogeneous ions composition on heavy metal extraction

Extraction rates acquired by 2.3 are shown in Table 1.

As a result, metals added had little effect on extraction. First, extraction rates were more than 95% from 2.5 ppm heavy metal solutions. Especially, Cd had 98~99% extraction rate from all kinds of mixed solution. In case of Pb, extraction rate from mixed solution had no change compared with extraction from a pure Pb solution (Fig. 3). The influence of heterogeneous ions appeared in Cu.

Table 1. Extraction rate of heavy metals (pH=6).

Metal	Extraction rate					
	4×0.025 ppm	Cd2.5 ppm+ 3×0.025 ppm	Pb2.5 ppm+ 3×0.025 ppm	Cu2.5 ppm+ 3×0.025 ppm	Ni2.5 ppm+ 3×0.025 ppm	4×2.5 ppm
Cd	98.5%	98.2%	98.7%	98.6%	98.5%	98.2%
Pb	38.9%	38.1%	97.4%	31.5%	36.0%	96.3%
Cu	91.3%	81.1%	78.7%	97.3%	79.4%	94.5%
Ni	78.1%	69.0%	62.7%	58.7%	99.4%	98.6%

Table 2. Heavy metal extraction rate from sodium chloride solutions (pH=6).

Metal	Conc.	Extraction rate				
		0.05 M NaCl	0.1 M NaCl	0.5 M NaCl	1.0 M NaCl	5.0 M NaCl
Cd	25 ppb	97.6%	97.2%	77.3%	24.6%	9.6%
	2.5 ppm	97.2%	97.1%	63.9%	27.8%	9.3%
Pb	25 ppb	43.8%	42.5%	38.6%	32.7%	19.9%
	2.5 ppm	98.1%	98.%	98.1%	97.4%	61.5%
Cu	25 ppb	93.1%	93.6%	55.9%	44.6%	42.1%
	2.5 ppm	92.8%	90.9%	89.4%	87.6%	80.0%
Ni	25 ppb	62.1%	40.0%	13.0%	–	–
	2.5 ppm	72.1%	54.2%	27.5%	8.1%	–

When the concentration of another ions were low, it had high extraction rate. Additionally, it had higher extraction rates compared to when magnetic beads were applied to the pure Cu solution. This is expected due to longer reaction time. In case of Ni, it shows a high extraction rate in 2.5 ppm solution like a pure solution, and in 25 ppb, it showed 60~70% extraction rate as its pure solution. Except Cu had higher rates, heterogeneous ions have no influence on heavy metal extraction.

3.2.2. Influence of NaCl on extraction

After experimenting the influence of ion strength, the influence of salt was examined. The solution with large amount of salt could be produced during sewage and waste water treatment. Therefore, 0.05-5.0 NaCl were added to two mixture of Cd, Pb, Cu and Ni solutions with 100 times different concentration. The tested extraction results are shown in Table 2.

It was shown that in case of Cd, when NaCl concentration is higher than 0.5 M, the extraction rate drops drastically. On the contrary, Pb is little influenced. Even in 1.0 M NaCl 25 ppb, 2.5 ppm Pb solutions had respectively 32.7% and 97.4% extraction rates like when there was no NaCl. However, when 0.5 M NaCl existed in solution, the rate dropped just like Cd. With regard to Cu, when Cu concentrations were 25 ppb and 2.5 ppm, extraction rates varied according to NaCl concentration. In the 25 ppb solution, when NaCl concentration was over 0.5 M, the extraction rate dropped significantly. And, in the 2.5 ppm solution, although NaCl concentration is 5.0 M, over 80% Cu could be extracted. In case of Ni, Even small amount of NaCl 0.05 M could influence for extraction. Therefore, under the existence of NaCl, Cd, Pb and Cu could be extracted with lower than 0.5 M NaCl.

3.2.3. The influence of KH_2PO_4 on extraction

Like Sodium chloride, phosphate used as a buffer, phosphate is added to different concentration solutions. Then the extraction rate is examined. The results are shown in Table 3.

As the results shown in Table 2, except Cd, small amount of phosphate could have a big influence on heavy metal extraction compared to NaCl. Therefore, in case of Cd, 100 mM phosphate had no impact. But in case of Pb,

Table 3. Extraction rate from phosphate solutions with magnetic beads (pH=6).

Metal	Conc.	Extraction rate		
		1 mM KH_2PO_4	10 mM KH_2PO_4	100 mM KH_2PO_4
Cd	25 ppb	92.6%	98.1%	96.7%
	2.5 ppm	99.6%	99.6%	99.6%
Pb	25 ppb	47.3%	42.9%	25.7%
	2.5 ppm	94.9%	93.2%	85.8%
Cu	25 ppb	97.6%	97.9%	79.4%
	2.5 ppm	90.6%	87.8%	74.5%
Ni	25 ppb	76.1%	76.2%	71.6%
	2.5 ppm	89.8%	71.0%	41.8%

Table 4. Extraction rate of EDTA solutions with magnetic beads.

Extr.	Conc.	Extraction rate		
		HM*:EDTA =1:0.1	HM*:EDTA =1:1	HM*:EDTA =1:10
Standard	25 ppb	100%	95.2%	88.4%
	2.5 ppm	100%	98.0%	90.0%
Beads	25 ppb	33.9%	18.6%	35.5%
	2.5 ppm	99.9%	99.9%	97.3%

*HM=Heavy metals

100 mM phosphate dropped extraction rate of 25 ppb solution by half and 10% for a 2.5 ppm solution. In case of Cu, 25 ppb and 2.5 ppm solutions dropped their extraction rate when 100 mM phosphate was added. 25 ppb Ni solution had no influence from phosphate but 2.5 ppm solution was significantly influenced.

3.2.4. The influence of EDTA on extraction

For the third parameter, the influence of EDTA was compared with the carboxyl group of magnetic bead like in 2.5. Since the influence of chelate is expected to be enormous, only Cd, which showed the best extraction results from previous experiments, was used for experiment, and the results is shown in Table 4. In the table, “Standard” is AAS value for Cd concentration in the solutions with heavy metals and EDTA. As the results, the higher EDTA concentration was, the less Cd ions were found. Therefore, the extraction rate is described in percent Cd among EDTA, not Cd among total Cd.

As the results show, extraction rates differed in 25 ppb and 2.5 ppm solutions. In case of a 25 ppb solution, only one third of free Cd was extracted when 0.1 and 10 times EDTA was added. On the contrary, almost all free Cd could be extracted from a 2.5 ppm solution. As a result, competition reaction between magnetic bead carboxyl group and EDTA could take place only with low heavy metal concentration.

4. Conclusions

In this study, the extraction rates were compared by using magnetic beads with carboxyl group, and the influence of various substance on extraction was examined. In order for this, AAS analysis checked that magnetic beads and heavy metals combined in a short time. According to the subsequent extraction experiments, the extraction rate by magnetic beads was influenced by the type and the concentration of heavy metal. In ppm level, except Cr(III), 90% of heavy metals were extracted. Also, when another heavy metal was added in solution, extraction was not influenced. However, NaCl dropped only when Ni extraction rate sensitively, and KH_2PO_4 dropped all of extraction rates except Cd. When chelate was added, 2.5 ppm Cd solution showed no change but 0.025 ppm solution had a lower extraction rate. Considering all of the results, it is expected that functionalized magnetic beads would be used to treat wastewater with high heavy metal concentration and lower heterogeneous ion concentration.

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