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Superparamagnetic Adsorbent for Removal of Uranium in Groundwater, South Korea

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ABSTRACT

The feasibility of magnetic adsorbent (P-Fe-CMK-3) for the removal of uranium using column based adsorption study has been performed. The synthesized material is efficient to capture natural uranium from groundwater. The Phosphonate and UO_2^{2+} interactions were responsible for uranium adsorption. This study confirmed the removal of natural uranium from groundwater (with initial uranium concentration around 107 ppb) within 10 min of contact time. However, the uptake values were not as high as compared to the values observed in batch study due to small contact time between adsorbent and the contaminant. Based on these results, the adsorbent material could be used in large scale treatment of uranium contaminated groundwater and waste streams including domestic uranium filters.

1. Introduction

Groundwater is preferred as a primary source of drinking water in many countries. Nevertheless, it naturally contains several toxic chemical components including uranium. The high concentration of natural uranium in groundwater is due to the dissolution of the rocks containing uranium rich minerals such as coffinite ($U(SiO_4)_{1-x}(OH)_{4x}$), pitchblende (U_3O_8), and uraninite (UO_2) [1, 2]. Uranium and its daughter progenies radon can cause severe health problems if exist in higher concentration in groundwater [3]. Nephrotoxicity is the chemically induced effect of uranium ingestion which is more harmful as compared to radiotoxicity [4].

In South Korea, Groundwater has been used for domestic, agricultural and industrial purposes; where ~19 % of total population uses groundwater as a drinking water [5]. In South Korea, the groundwater with high uranium concentration is widely used for drinking purposes through public and/or private wells, especially, in the rural areas. In a recent studies of groundwater in Korea, the uranium concentration ranged from 0 to 3610 μg L^{-1} with arithmetic mean of 8.0 μg L^{-1}, and median value of 0.7 μg L^{-1} [6]. More importantly, 160 out of 4140 groundwater wells contained higher uranium concentration than United States Environmental Protection Agency prescribed maximum contaminate level of 30 μg L^{-1} [7]. These wells were located mainly in the plutonic bedrock region where uranyl carbonate was the predominant phases under the Korean groundwater circumstances. Thus, these wells must be remediated to decrease the uranium levels in groundwater.

Conventional treatment methods such as Ion exchange, Precipitation, Coagulation, etc., are energy-intensive and generate enormous amounts of sludge contaminated with radionuclides [8]. However, the use of nano-sized adsorbents in the radioactive waste management is attaining global attention. Particularly, magnetic carbon containing composite played an important role to reduce solid waste generation due to its relatively high adsorption capacities accompanied by different factors, such as high surface area, high chemical stability and magnetic sensitivity. Moreover, the selectivity and affectivity of these adsorbents can be easily altered by proper surface modification to remove low levels of radionuclides in large quantity of water. In contrast to traditional methods, less energy consumption has been observed for the separation of magnetic particles via strong magnet [9].

Majority of the documented studies evaluated the adsorption of radionuclides in deionized (DI) water via batch method in detail, which is an initial stage to test the efficiency of any sorbent to capture radionuclides; however, it is not considered as a suitable strategy for industrial scale treatment of water because DI water does not reflect the actual environmental water. Moreover, industries usually prefer the column based operation for water treatment because it can be used directly at a continuous water supply unlike the batch process. However, the emerging magnetic adsorbents are in the form of fine powders, they tend to agglomerate due to magnetic attraction and cause the choking of filter pores with reduce flow rates. Fortunately, these technical problems can be well compensated by the engineered synthesis of porous magnetic composites.

Herein, we studied the application of phosphonate modified magnetic mesoporous adsorbent for treatment of uranium contaminated natural groundwater through column based adsorption process. The detailed synthesis of P-Fe-CMK-3 adsorbent has been reported previously [10].

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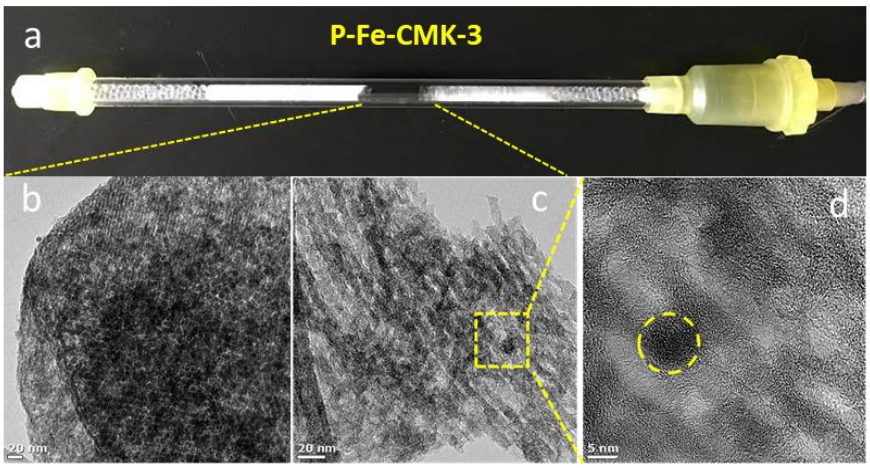

Fig. 1: (a) Packed column used in the study with (b), (c) and (d) TEM images of P-Fe-CMK-3.

Table 1. Properties of groundwater.

Sample location	U Conc. (µg/L)	pH	Eh (mV)	DO (mg/L)	EC (µS/cm)
Bugokdong	107	6.86	158.67	11.67	987.01

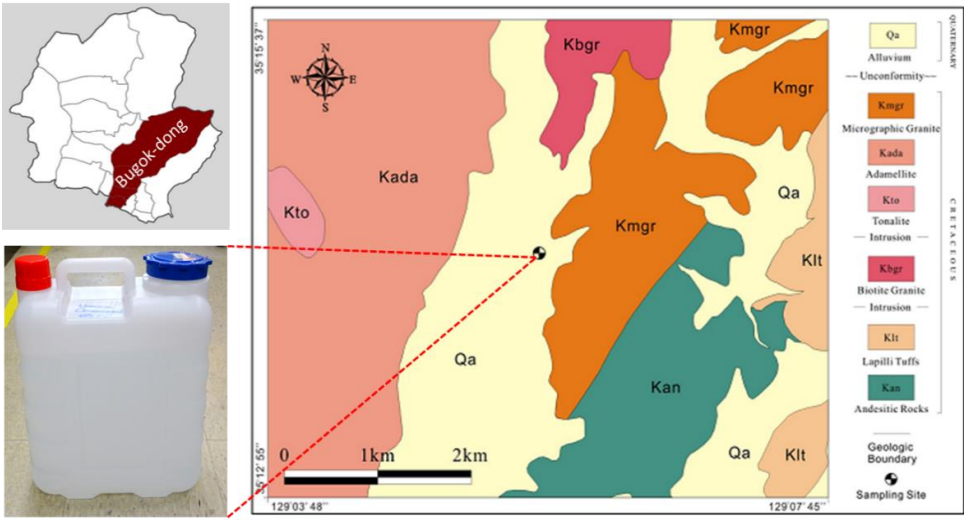

Fig. 2: Location and geological maps around the groundwater sampling sites.

2. Experimental Section

Uranium contaminated natural groundwater was collected from Bugokdong, Busan, South Korea. Glass Econo-column (Bio-Rad) (length = 20 cm, diameter = 0.5 cm) were used to pack adsorbent (Fig. 1a). The P-Fe-CMK-3 adsorbent height was 2 cm (weight = 100 mg), supported and surrounded by 5 and 4 cm alternate layers of glass wool (Sigma Aldrich) and glass beads (2 mm in diameter), respectively. The TEM images reflect average size of Fe_3O_4 nanoparticles around 10 nm which confirms the superparamagnetic nature of the used material. (Fig. 1b, 1c and 1d). A four channel, eight rollers peristaltic pump (Master Flex® L/S® 7519-20) was used to provide the constant flow at 2 RPM through the column. Influent was introduced against gravity to remove the air inside the column. The effluent concentration of U(VI) was measured at different time intervals with ICP-MS (Perkin Elmer, NexION 300). Controlled experiments indicated that the adsorption of U(VI) on glass wool was negligible.

3. Results and Discussion

The concentration of natural uranium in groundwater was more than three times of EPA maximum contaminant levels with neutral pH as given in Table 1. The higher concentration was expected due to the uranium rich geological rocks such as alluvial and micrographic granite in the surroundings of the sampling site as shown in Fig. 2.

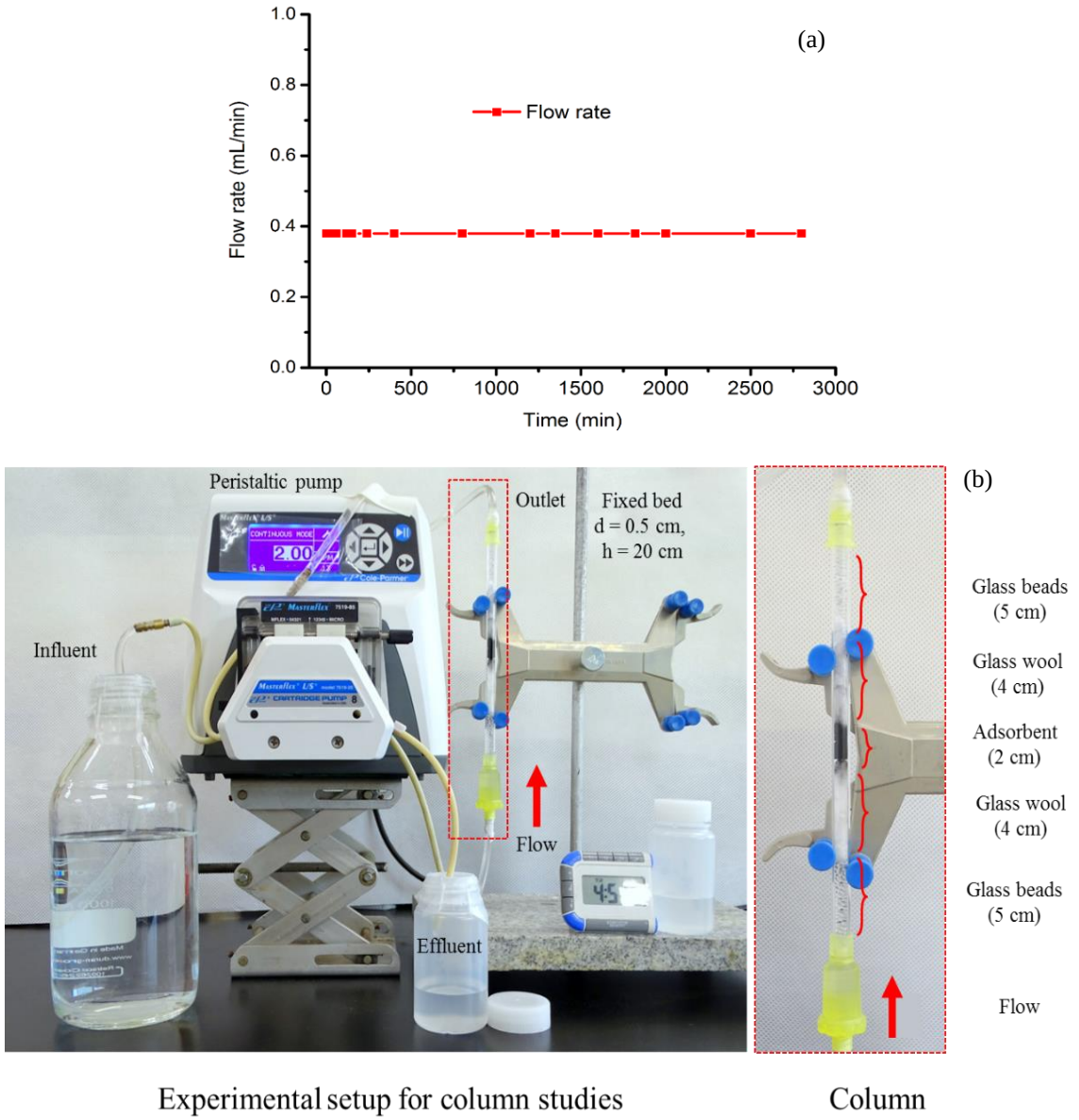

Fig. 3: (a) Column saturation and flow rate adjustment, (b) Photographs of the fixed bed column and the adsorbent bed used in this study.

Table 2. Operational parameters.

RPM	Flow rate (mL/min)	Column residence time (min)	Adsorbent residence time (min)	Weight (mg)
2	0.38	9.20	1.14	100

3.1 Flow Rate

Flow rate is an important parameter in column design because the low flow rate may cause clogging, whereas, the high flow rate is responsible for lower uptake due to reduction in contact time between the contaminant and the adsorbent. After the column packing, the flow rate of 0.38 mL/min was maintained by passing the DI water for 46 hours (Fig. 3a). We also tried to increase the flow rate by increasing the RPM but due to high back pressure, the leakage was observed at various joints. Therefore, RPM = 2 was used throughout this study. The column residence time was around 9.20 minutes (Table 2). The setup for the fixed bed study is depicted in Fig. 3b. The filtered ground water was introduced from the bottom and the effluent samples were collected at regular intervals of time for the analysis; and finally break through curve was drawn as represented in Fig. 4a. The column was exhausted within 3 hours of reaction time under present conditions (Fig. 4b). However,

it could hold the natural uranium from the groundwater and can provide the clean water. Based on these results we can consider the application potential of the magnetic mesoporous carbon adsorbent in the fixed bed removal of uranium for the natural contaminated site. After the adsoprtion, the U loaded adsorbent was characterized with XPS as shown in Fig. 4c. The presence of U 4f peaks proved the adorbent's capablilty to capture urainum from water. We checked the reactivity of this material towards other metals (As^{5+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+} and Zn^{2+}) and observed that it can remove Pb^{2+} as well but the extent of adsorption was less than Uranium [10].

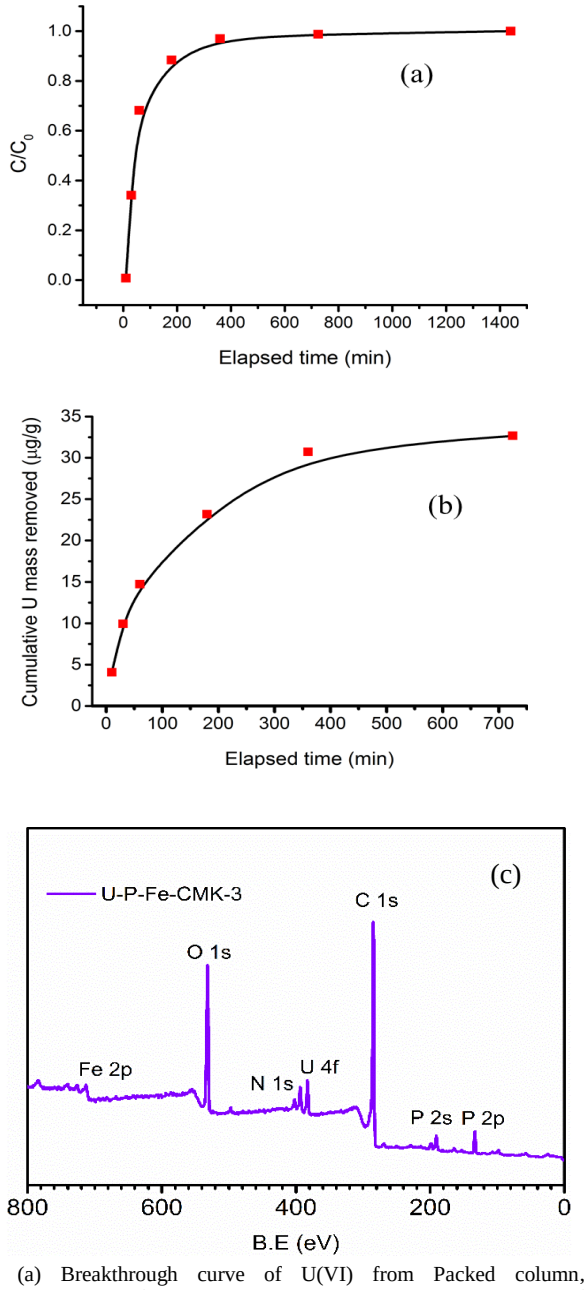

Fig. 4: (a) Breakthrough curve of U(VI) from Packed column, (b) amount of uranium adsorbed and (c) XPS survey scan of U-adsorbed P-Fe-CMK-3.

3.2 Regeneration

The disposal of the contaminant loaded adsorbent is another environmental issue due to its hazardous nature to the environment. This issue can be resolved with help of elimination methods such as elution, incineration and pyrolysis. For large scale application of adsorbents regeneration processes is necessary for the economic feasibility of the process. Therefore, regeneration of the P-Fe-CMK-3 fixed bed column was investigated to assess the possibility for the reuse of adsorbent and recovery of uranium. In order to regenerate the column 0.1 M $NaHCO_3$ was used as a desorbing agent for the continuous four adsorption-desorption runs because it did not cause damage to adsorbent (Fig. 5). The column was regenerated well but capacity of the packed column was found to decrease after second cycle due to incomplete desorption of uranium from the adsorbent or the loss of the adsorbent with flow rate.

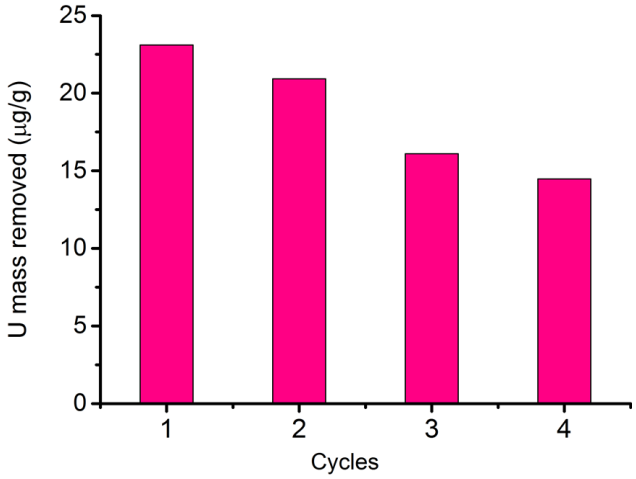

Fig. 5: Recycling performance of the P-Fe-CMK-3 packed column for four cycles.

4. Conclusions

We have presented the real application for the removal of uranium from natural contaminated groundwater. This study confirmed the removal of natural uranium from groundwater (in South Korea where initial uranium concentration was around 107 ppb) within 10 min of contact time. The column was regenerated and reused for four cycles. Consequently, the as prepared P-Fe-CMK-3 can be utilized as a promising adsorbent for the removal of uranium from contaminated environmental waters.

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