

Simultaneous Removal of Lead and Cr(VI) Using Chemically Combined Materials, ZanF (Zeolite anchored Fe)

ZanF (Zeolite anchored Fe)를 이용한 납과 Cr(VI)의 동시제거

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개요 : 오염된 지하수 정화에 있어 반응벽체(Permeable Reactive Barriers, PRBs)를 이용한 정화기법은 최근 가장 큰 관심을 모으고 있는 기술이다. 반응벽체의 적용에 있어 가장 중요한 사항은 오염물질의 특성을 고려하여 적절한 반응성을 가지는 충전물질을 선택하는 일이다. 지금까지 연구된 반응물질 중 제올라이트는 취득이 용이하고 가격이 저렴하여, 암모늄이나 중금속과 같은 양이온성 오염물질의 정화에 그 적용성을 인정받아왔다. 하지만 표면에 음전하를 띠는 제올라이트의 특성 때문에, 지하수내에서 음이온의 형태로 존재하는 Cr(VI) 등에는 반응성이 없는 것으로 알려져 왔다. 이에 본 연구에서는 제올라이트에 영가철을 결합한 ZanF란 물질을 개발하여 양이온성 중금속의 하나인 납과 음이온성 중금속의 하나인 Cr(VI)을 동시 제거하는 실험을 수행하였다. 실험결과 ZanF는 초기농도 2-15 mmol를 가지는 납 오염용액에 대해 90% 이상의 제거율을 보였으며, 초기농도 0.1 mmol을 가지는 Cr(VI) 오염용액의 농도를 5시간 내에 검출한계 이하로 떨어뜨리는 탁월한 효과를 보였다. 실험결과를 토대로 ZanF는 납과 Cr(VI)으로 동시에 오염된 지하수 정화에 효과적으로 사용될 수 있으리라 기대된다.

주요어 : 반응벽체, 제올라이트, ZanF, 납, Cr(VI)

1. Introduction

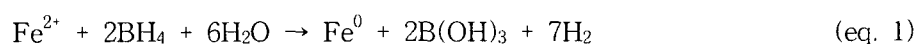
Natural zeolites have exhibited high sorption capacity for inorganic cations including heavy metals and ammonium, and were proven to be effective for environmental applications such as permeable barriers for controlling the spread of contaminated groundwater (Park et al., 2002). However zeolites have little or no affinity for anionic species, as they possess a net negative structural charge. The current research focuses on the simultaneous removal of cationic and anionic heavy metals in water by the ZanF (Zeolite anchored Fe), a product derived from zeolite modified by Fe(II) chloride followed by reduction with sodium borohydride. Lead was chosen as

the cationic heavy metals, and chromate as the anionic heavy metals due to their importance as environmental contaminants. We report here both on the cation exchange capacity of ZanF for lead, and on the reduction of chromate by the iron metal characteristics in ZanF.

2. Experimental Section

2.1 ZanF preparation

50 g of zeolite was stirred with 500 ml of 350 mmol ferrous chloride solution for 24 hrs at ambient temperature to cause Fe ions to be exchanged with exchangeable ions in the zeolite. The exchanged zeolite with Fe ions was washed several times with deionized water (18.2 MΩ, milli-Q water, milli pore, USA), and stirred in 500 ml of 0.32 mol sodium borohydride (NaBH₄, 98 %, Sigma, USA) solution for 30 min. The concentration of NaBH₄ was calculated based on the following reactions (eq. 1) to fully reduce the sorbed amount of Fe ions.



The borohydride-reduced zeolite was washed several times with deionized water, and dried in the vacuum dry oven at 90 °C for 1hr, and stored in anaerobic condition.

2.2 Lead removal

Cationic heavy metal sorptions to ZanF via cation exchange were evaluated by the batch equilibrium experiment. 1g of ZanF and 30 ml lead solution were placed in the 37 ml amber tube. Lead solution was prepared by dissolving the Pb(NO₃)₂ in deionized water, and its initial concentration was ranged from 2 mmol to 15 mmol. The tubes were shaken at 50 rpm with vertical rotary shaker for 24 hrs. Parallel experiments were also performed with no material (blank), Fe-ion exchanged zeolite without reduction and pure zeolite. After shaking, supernatant was separated for analysis from solid materials by filtering through 0.45 μm-pore membrane, and pH value of the solution was measured. To estimate the amount of Fe-ion which could be desorbed from the materials during reaction, total Fe concentration of solutions with ZanF and Fe-ion exchanged were measured after 24hr shaking. And to confirm the ion-exchange mechanism during reaction, the concentration of sodium ion, which is one of the exchangeable ions, was measured.

2.3 Cr(VI) removal

Chromate removal experiments were performed with ZanF. 3g of ZanF and 30 ml of 0.1 mmol (equivalent to 21.6 ppm) chromate solution were placed in the 37 ml amber tube. Duplicates were prepared for the test with ZanF to confirm the repeatability. Chromate solution was prepared by dissolving the potassium dichromate (K₂Cr₂O₇) in deionized water. The tubes were shaken with rotary shaker at 50 rpm for 0-50 hrs, and supernatants were separated from solid phase by filtering through 0.45 μm-pore membrane, and pH value of the solution was measured.

3. Results and Discussion

3.1 Lead Removal

To evaluate the removal capacity of ZanF against cationic heavy metal, lead sorption tests were performed by varying the initial concentration of lead solution. Figure 1 presents the variation of removal efficiency versus initial concentration of lead solution.

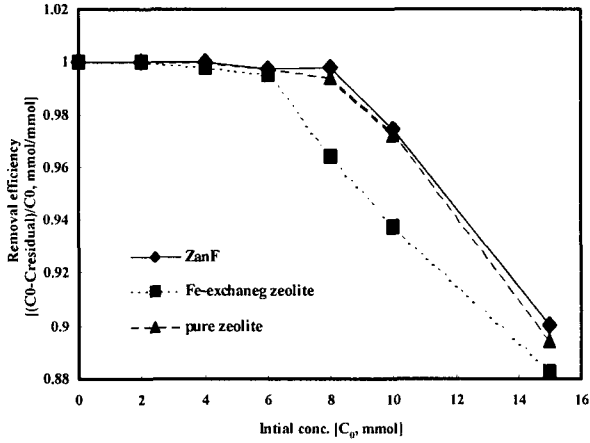


Figure 1 Variation of removal efficiency by varying initial concentration of lead solution

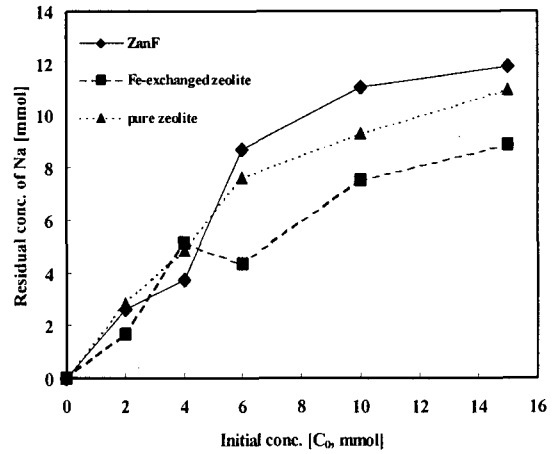


Figure 2 Variation of sodium concentration in the solution versus initial concentration of lead solution

In the range of 0-6 mmol of lead solution, all of the materials showed almost complete removal against lead as the removal efficiency of around 1 through 24 hr reaction. However above 6 mmol of lead solution, the removal efficiency began to be slightly decreased. It is because initial concentration of lead went beyond the ion exchange capacity of materials, and more severely occurred the competition of lead ion for the limited exchanging site as the initial concentration increased. In Fe-exchanged zeolite, the extent of decrease was most significant among three materials, and this indicated that Fe-exchanged zeolite possessed less ion exchange capacity than ZanF or pure zeolite. It can be explained with the loss of exchangeable ion like sodium in zeolite during ZanF making process. However, ZanF showed the similar removal efficiency with pure zeolite, and this indicated that ZanF recovered ion exchange capacity to the extent of zeolite through the reduction process. To support this discussion, the variation of sodium ion concentration was measured versus initial concentration of lead as shown in figure 2. As the amount of lead removal increases, sodium ions in solution increased. In here, the amount of sodium from ZanF was similar with that from pure zeolite while the amount of sodium from Fe-exchanged zeolite less than ZanF or pure zeolite.

3.2 Chromate removal

To evaluate the removal capacity of ZanF against the anionic heavy metals through reducing reaction, Cr(VI) removal tests were performed. Figure 3 shows the test results with the average value of duplicates.

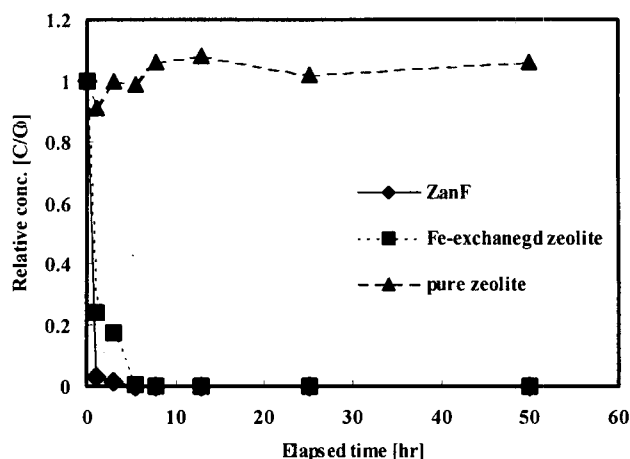
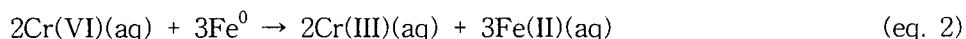
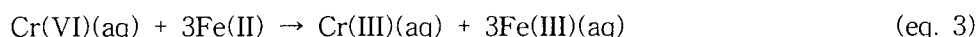


Figure 3 Variation of relative concentration of Cr(VI) for the time period of 50 hrs

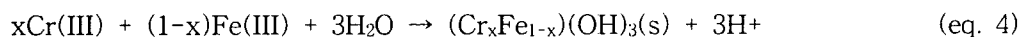
Cr(VI) concentration in the solution with ZanF or Fe-exchanged zeolite which contained additional Fe element in it, was rapidly decreased below the detection limit within 5 hrs while chromate concentration in pure zeolite maintained as constant during the reaction. These results are consistent with the previous researches in which the rates of Cr(VI) reduction appeared to be fairly rapid (many half-lives reported are <5hr)(Gould 1982). Primary removal pathway is reduction of Cr(VI) to Cr(III) and subsequent precipitation of chromium(III)/iron(III) oxyhydroxides as suggested by Blowes et al. (1997). Reducing reactions can be described as follows (eq. 2 and eq. 3) for ZanF,



and for Fe-exchanged zeolite,



And removal of Cr(III) can occur through the precipitation of chromium(III)-iron(III) hydroxide as follows (eq. 4, Blowes et al., 1997) :



References

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