

Chromium (VI) removal from effluents using zeolite

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Abstract This study focused on evaluating the removal of Cr (VI) from effluents using natural zeolite. The results indicated that zeolite can adsorb Cr (III) cations, but not Cr (VI) anions (HCrO_4^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$). To increase the adsorption of Cr (VI), different surface modification methods were evaluated. The best results were obtained using zeolite modified with 100 mmol Fe (III) for 24 hours. Treatment of solutions containing 20 mg/L Cr (VI) in columns packed with modified zeolite resulted in solutions containing <0.02 mg/L Cr (VI), which meets the WHO and South African effluent discharge limits of 0.05 ppm.

Keywords zeolite, adsorption, Cr(VI)

Introduction

The impact of chromium pollution originating from the ferrochrome industry in South Africa is very poorly understood with limited information available. It has been reported that beneficiated South African chromite ores contain between 0.38 to 0.76 mg/L of Cr (VI), which is known to be toxic, carcinogenic and extremely soluble in water (Glastonbury *et al.* 2010). Over the past decades, various different Cr (VI) treatment options such as ion exchange on polymeric resin (Mohan *et al.* 2005), reduction of Cr (VI) to Cr (III), reverse osmosis and adsorption on activated carbon (Leyva-Ramos *et al.* 1994) have been investigated.

Natural zeolites have shown high sorption capacities for inorganic cations including metals (Barros *et al.* 2006). Natural zeolites are crystalline micro-porous alumina-silicates with a very well defined structure that consists of a framework formed by tetrahedral of SiO_4 and AlO_4 (Diale *et al.* 2011). The isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral results in a negative charge on the zeolitic framework, which can be balanced by exchangeable cations (Leyva-Ramos *et al.* 2008). Therefore natural zeolites can exchange cations but not anions, necessitating the sur-

face modification of natural zeolite in order to remove anions from solution. In this study the ability of modified South African zeolite to remove Cr (VI) from effluents was evaluated. The objective was to meet the South African Department of Water Affairs effluent discharge limit and the WHO limit for drinking water of 0.05 mg/L.

Methods

Materials

Natural zeolite, derived from Clinoptilolite mined in South Africa, was obtained from Prately Perlite Mining Co. (PTY) Ltd. A particle size of 2–4 mm was used for all tests.

Surface modification of zeolite

Three surface modification methods, using NaOH, NaCl and Fe (III), were investigated in this study.

Surface modification using NaOH

The zeolite was treated with 4 M NaOH at 60 °C for 24 hours, using a 1:5 zeolite to NaOH ratio. Following the 24 hour modification period, the sample was rinsed six times with dH_2O to remove any excess NaOH and the modified zeolite was dried at 25 °C for 24 hour (Foldesova *et al.* 2000).

Surface modification using NaCl

The zeolite was contacted four times, 6 hours each, with 1 M NaCl at 60 °C using a 1:10 zeolite to NaCl solution ratio. Following the 24 hour modification period, the zeolite was washed with 2 L dH₂O at 40 °C and dried at 60 °C for 24 hours (Barros *et al.* 2006).

Surface modification using Fe (III)

Zeolite (60 g) was added to 180 mL of 20 mmol Fe (III) solution. The mixture was shaken at 150 rpm at 25 °C for 24 hours. After 24 hours, the pH level of the mixture was adjusted to 9 using 2 M NaOH. The mixture was allowed to settle and the supernatant removed. The modified zeolite was washed six times with dH₂O to remove excess Fe (III) and dried at 25 °C for 24 hours (Du *et al.* 2012).

Cr (VI) and Cr (III) adsorption tests

Tests were conducted using 2.5 g each of the unmodified and modified zeolite, added to 20 mL of 20 mg/L Cr solution to determine the Cr (VI) and Cr (III) adsorption capability of the zeolite. All tests were conducted in shake flasks at 25 °C, 100 rpm for 24 hours. The filtrate from each test was analysed using Inductively Coupled Plasma (ICP) analysis.

Optimisation of the Fe (III) modification process

The tests were performed in shake flasks at 25 °C, 100 rpm for 24 hours, with a ratio of zeolite to Cr solution (20 mg/L) of 1:5. The filtrate from each test was analysed for Cr using ICP analysis.

Effect of Fe (III) concentration on zeolite surface modification

The method described by Du *et al.* (2012) was adapted to determine the effect of Fe (III) concentration on the zeolite surface modification. During the preparation of the Fe (III)-modified zeolite, 20 g of zeolite was added to 60 mL of the Fe (III) solution at concentrations ranging between 0–1 M.

Effect of contact time during surface modification on Cr (VI) adsorption

Zeolite was modified with 100 mmol Fe (III) at contact times varying from 4–96 hours using the method described previously.

Effect of Cr (VI) concentration on the Cr (VI) adsorption efficacy of zeolite modified with Fe (III)

The effect of Cr (VI) concentration on the adsorption efficacy of the zeolite modified with 100 mmol Fe (III) for 24 hours was investigated by varying the initial C (VI) concentration between 10–1000 mg/L.

Column studies

The test work was performed in 500 and 1000 mm glass columns. A 1 L synthetic solution containing 20 mg/L Cr (VI), at a pH level of 5, was passed through the columns containing zeolite coated with 100 mmol Fe (III) at a flow rate of 1.5 mL/min. The eluted solution was analysed for Cr using ICP analysis. Two approaches as indicated in Fig. 1 were used:

- In the first approach, the Cr (VI) solution was passed through the same column twice and the eluent from each cycle was analysed.
- In the second approach, a two stage column set-up was used with the eluent from column one producing the feed for column two.

Results and Discussion

Zeolite surface modification

The results obtained from the Cr (VI) and Cr (III) adsorption tests using the modified and unmodified zeolite are summarised in Table 1.

The results obtained indicated that unmodified zeolite and zeolite modified with NaCl and Fe (III) were capable of removing >98 % Cr (III) from solution, whereas the NaOH modified zeolite could only remove 59 % of the Cr (III). These results demonstrated that surface modification of zeolite is not required for the adsorption of Cr (III).

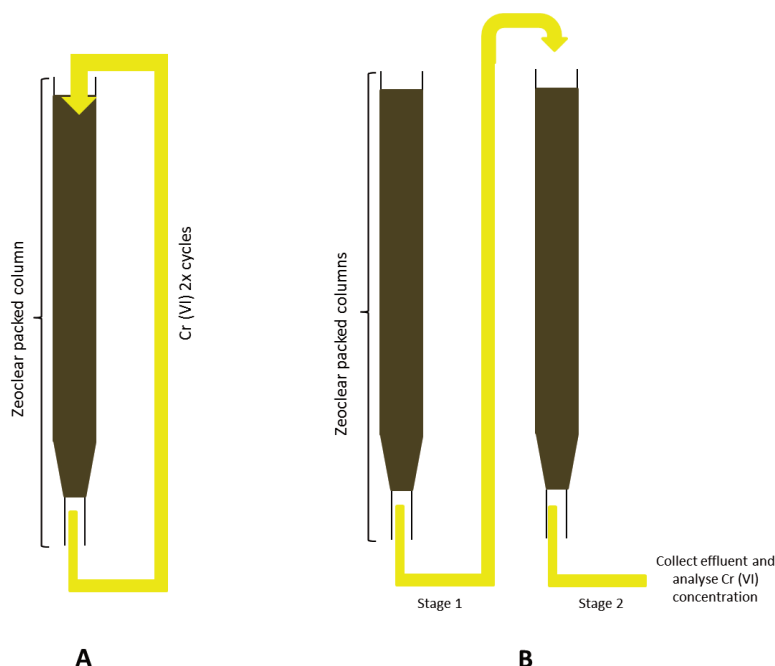


Fig. 1 The experimental design of the tests performed in glass columns (A) approach 1 (B) approach 2.

Zeolite in its unmodified state could only remove 16 % of the Cr (VI). However modification of zeolite with NaOH and NaCl resulted in an increase in Cr (VI) removal of 39 % and 20 % respectively. The highest Cr (VI) removal of 52 % was obtained when using the zeolite modified with Fe (III). These results are similar to the results obtained by Du *et al.* (2012) who showed that enhanced adsorption of Cr (VI) occurs in soils derived from volcanic ash and tuff which contained significant amounts of Fe(III) coated zeolite. In order to improve the 52 % Cr (VI) removal by Fe (III) modified zeolite, further optimisation of various process parameters such as the Fe (III) concentration, contact time and Cr (VI) concentration during the chemical surface modification process were optimised.

Optimisation of the zeolite modification process

Effect of Fe (III) concentration on zeolite surface modification

Six shake flask tests were conducted to determine the optimum Fe (III) concentration required for surface modification of the zeolite

Test	Adsorbent	Initial [Cr], 20 mg/L	Final [Cr], mg/L	Cr Adsorbed, %
1	NaOH zeolite	Cr(VI)	12.20	39
2	NaOH zeolite	Cr(III)	8.20	59
3	NaCl zeolite	Cr(VI)	16.10	20
4	NaCl zeolite	Cr(III)	0.50	98
5	Fe(III) zeolite	Cr(VI)	9.54	52
6	Fe(III) zeolite	Cr(III)	0.06	99
7	Unmodified	Cr(VI)	16.80	16
8	Unmodified	Cr(III)	0.48	98

Table 1 Summary of the results obtained during surface modification

to ensure maximum Cr (VI) removal. The results of this test are summarised in Table 2.

The results indicated that unmodified zeolite could only remove 20.5 % of the Cr (VI). The method described by Du *et al.* (2012) specified that 20 mmol of Fe (III) should be loaded onto natural zeolite for efficient Cr (VI) removal. However results from this study indicated that zeolite modified with 20 mmol Fe (III), resulted in only 47.5 % Cr (VI) removal. However when the Fe (III) concentration was further increased, there was a subsequent increase in the amount of Cr (VI) removed, with

Test	[Fe (III)] mmol	Final [Cr(VI)] mg/L	Cr(VI) removed, %	Fe in solution, mg/L
1	0	15.9	20.5	<0.02
2	20	10.5	47.5	<0.02
3	50	0.7	96.5	<0.02
4	100	<0.02	99.9	<0.02
5	500	<0.02	99.9	1.53
6	1000	<0.02	99.9	36.46

Table 2 Results obtained during determination of the effect of [Fe (III)] on zeolite surface modification and Cr (VI) removal. An initial [Cr (VI)] of 20 mg/L was used for all tests.

99.9 % removal obtained at Fe (III) concentrations of 100, 500 and 1000 mmol. However at Fe (III) concentrations of 500 mmol and 1000 mmol, Fe concentrations of 1.5 and 36.8 mg/L respectively were detected in the test solutions, which could indicate leaching of the zeolite Fe (III) coating.

Effect of contact time during surface modification on Cr (VI) adsorption

In this test, zeolite was modified with 100 mmol Fe (III) at contact times varying between 4- 96h. The results indicated that zeolite modified with Fe (III) for 4 and 8 hours, could only adsorb 93 % and 95 % of the 20 mg/L Cr (VI) present in solution (Fig. 2A). However as the modification period was increased from 8 to 24 hours, the adsorption capacity of the zeolite increased, resulting in a 99 % adsorption of Cr

(VI). Thus for all future studies, zeolite coated for 24 hours with 100 mmol Fe (III) was used.

Effect of Cr (VI) concentration on the Cr (VI) adsorption efficacy of zeolite modified with Fe (III)

The effect of Cr (VI) concentration on the adsorption efficacy of the modified zeolite was investigated by varying the initial Cr (VI) concentrations between 10 and 1000 mg/L. The results obtained (Fig. 2B) indicated that:

- At initial Cr (VI) concentrations between 10–20 mg/L, 99.9 % of the Cr (VI) could be adsorbed by the zeolite.
- At Cr (VI) concentrations between 30–100 mg/L, only 52–72 % of the Cr (VI) could be adsorbed.
- It was also noted that at Cr (VI) concentrations > 100 mg/L, the absorbance efficiency of the zeolite was significantly decreased to between 1 and 30 %.

Column tests

Approach 1: Effect of contact time on Cr (VI) adsorption

The results obtained are summarised in Table 3. After passing the Cr (VI) solution once through the 500 mm column, only 37 % (7.4 mg/L) of the Cr (VI) was adsorbed by the zeolite. When the solution was passed through the column a second time (Cycle 2), the Cr (VI) in

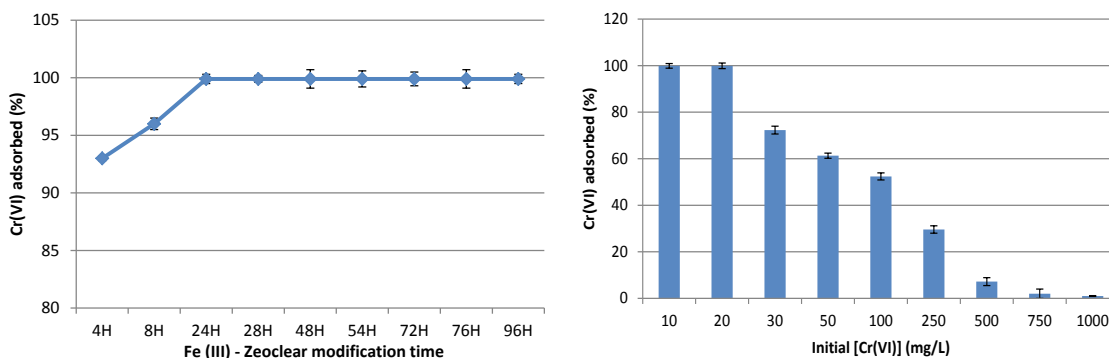


Fig. 2 (A) Effect of the surface modification time on the removal of Cr (VI) using Fe (III) modified zeolite. (B) Effect of initial Cr (VI) concentration on adsorption efficiency of Fe (III) modified zeolite

Column length, mm		Feed [Cr], mg/L	Product [Cr], mg/L	Cr adsorbed, %
500*	Cycle 1	20.0	12.6	37.0
	Cycle 2	12.6	10.3	18.2
	Total adsorption	20.0	10.3	48.5
1000**	Cycle 1	20.0	3.5	82.6
	Cycle 2	3.5	1.8	52.1
	Total adsorption	20.0	1.8	90.8

*0.9 kg zeolite used per column ** 1.8 kg zeolite used per column

Table 3 Adsorption results using glass columns packed with modified zeolite

Column length, mm		Feed [Cr], mg/L	Product [Cr], mg/L	Cr adsorbed, %
500	Cycle 1	20.0	11.8	41.0
	Cycle 2	11.8	8.5	27.9
	Total adsorption	20.0	8.5	57.5
1000	Cycle 1	20.0	3.6	81.9
	Cycle 2	3.6	<0.02	99.9
	Total adsorption	20.0	<0.02	99.9

Table 4 Adsorption results using a 2-stage glass column system packed with modified zeolite

solution decreased from 12.6 to 10.3 mg/L, which was still significantly higher than the permitted discharge limit of 0.05 mg/L.

The results obtained using the 1000 mm column indicated that after Cycle 1, 82.6 % of the Cr (VI) was adsorbed. However a significant Cr (VI) concentration of 3.5 mg/L remained in solution. During Cycle 2 only an additional 1.6 mg/L of Cr (VI) was removed, resulting in a final product containing 1.8 mg/L of Cr (VI), which is above the discharge limit of 0.05 mg/L. It should be noted that <0.02 mg/L Fe was detected in the feed and product solutions in any of the tests, indicating that the washing step during the Fe (III)-zeolite surface modification procedure was adequate.

Approach 2: Effect of adsorbent concentration on Cr (VI) removal

In order to improve Cr (VI) removal, the use of two stage column systems was evaluated. The results obtained from the 2-stage tests are summarised in Table 4. The results indicated that (using the 500 mm column) only 41 % of Cr (VI) was removed during Stage 1. However, a final eluent containing 8.5 mg/L Cr (VI) was obtained after the second stage. When using the 1000 mm columns, 81.9 % of Cr (VI) was re-

moved during Stage 1. However when a second column was added, the Cr (VI) removal increased to 99.9 %, with the eluent containing <0.02 mg/L Cr (VI), indicating that this solution can be discharged as it falls below the discharge guideline value of 0.05 mg/L. These results showed that the extent of Cr removal was affected more by the ratio of zeolite-to-solution rather than longer contact time, suggesting that the extent of metal removal is more restrained by the approach towards equilibrium than by kinetics.

Conclusions

During the process optimisation test work in shake flasks, it was found that optimum Cr (VI) adsorption of 99.9 % could be achieved when using zeolite modified with 100 mmol Fe (III). Two approaches were evaluated using 500 and 1000 mm glass columns. In the first approach the Cr (VI) solution was passed through the same column twice, providing longer contact-time. In the second approach a two stage column set-up was used with the eluent from column one producing the feed for column two (using double the amount of adsorbent, *i.e.* providing equilibrium conditions favouring greater adsorption). The results obtained indi-

cated that the second approach was a better option compared to the first approach, suggesting that during these experiments the extent of metal removal is more restrained by the approach towards equilibrium than by kinetics. The preliminary results obtained during this study indicated that the use of natural South African zeolite is a potential treatment option for Cr (VI) removal from solutions. However further test work will focus on the adsorption capacity, kinetics and scale up of the process.

Acknowledgements

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References

- Barros MASD, Zola AS, Arroyo PA, Tavares CRG, Sousa-Aguiar EF (2006) Chromium uptake from tri-component solution in zeolite fixed bed. *Adsorption* 12: 239–248.
- Du G, Li Z, Liao L, Hanson R, Leick S, Hoepfner N (2012) Cr(VI) retention and transport through Fe(III)-coated natural zeolite. *J Hazardous Materials* 221-222:118-123
- Foldesova M, Dillinger P, Lukae P (2000) Adsorption and desorption of Cr(III) on natural and chemically modified Slovak zeolites. *J Radioanalytical and Nuclear Chemistry* 245: 435–439
- Glastonbury RI, van der Merwe W, Beukes JP, van Zyl PG, Lachmann G, Steenkamp CJH, Dawson NE, Stewart HM (2010) Cr(VI) generation during sample preparation of solid samples- A chromite ore case study. *Water SA* 36: 105–110
- Leyva-Ramos R, Juarez-Martinez A, Guerrero-Coronado RM, (2012) Adsorption of chromium (VI) from aqueous solutions on activated carbon. *Water Science Technology* 30: 191–197.
- Leyva-Ramos R, Jacobo-Azuara A, Diaz-Flores PE, Guerrero-Coronado RM, Mendoza-Barron J, Berber-Mendoza MS (2012) Adsorption of chromium (VI) from an aqueous solution on a surfactant-modified zeolite. *Colloids and Surfaces A: Physicochemical Engineering Aspects* 330: 35–41.
- Mohan D, Singh KP, Singh VK (2005) Removal of hexavalent chromium from aqueous solution using low cost activated carbon fabric cloth. *Indian J Engineering and Chemical Research* 44: 1027-1042.