

# Adsorption of chromium species from industrial effluent using magnesium-bentonite clay composite: kinetics, equilibrium and risk assessment study

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## Introduction

To counter for pollution hazards imposed by anthropogenic activities on the environment, government, national and international scientific communities are in a quest to find pragmatic chromium depollution techniques. More prevalently, chromium enriched effluents emanate from mining, electroplating, leather tanning, chromite beneficiation, fertilizer and several other industries, thus, posing serious environmental problem when introduced to aqueous environments (Yu and Zhang, 2014, Zewail and Yousef, 2014, Zhang and Huang, 2014, Zhang et al., 2014). Both natural and human activities contribute to the introduction of chromium into the environment (Baral and Engelken, 2002, Ghorbel-Abid et al., 2009, Fabbricino et al., 2013, Zuo and Balasubramanian, 2013). It mainly exists as an oxyanion at circumneutral to basic pH conditions (Sultana et al., 2014). The species of concern are although inorganic chromium can exist in a range of valence states from 2+ to 6+, Cr (III) and Cr (VI) are the most common oxidation states. Chromium (III) and chromium (VI) are species of main environmental concern. They are interchangeable in the natural environment, depending on the pH and redox potential of the medium and the presence or absence of a strong oxidant or reductant (Rengaraj et al., 2001, Peng et al., 2014, Rangasamy et al., 2014, Saha and Saha, 2014).

Cr toxicity is highly dependent on its oxidation form and Cr (VI) is more toxic than Cr (III) for plants, animals and microorganisms (Alloway, 1990, Selinus et al., 2013). High Cr (VI) concentrations have significant harmful effects on human health including lung cancer, kidney, liver and gastric damage (Chen et al., 2011). Department of Water Affairs and Sanitation (DWS) in South Africa recommended < 0.1 mg/L in drinking water bodies. It has very narrow range of significance in living organisms (Sajidu et al., 2008, Africa et al., 2010). This element needs to be regulated in drinking water bodies.

Several water depollution technologies have been developed and implemented for removal of chromium from wastewaters. These include: adsorption, precipitation, ion exchange, reverse osmosis,

electroplating, phytoremediation and wetlands (Vlasov and D'Yakonov, 1965, Tan et al., 1993, Qu et al., 2014, Sultana et al., 2014, Yu et al., 2014, Zhang et al., 2014, Zinicovscaia et al., 2014). Traditionally, precipitation methods were the best, however, generation of sludges which are rich in contaminants were a challenge since it incur disposal problem especially when there is stringent waste management and disposal regulations (Kidd, 2011). Adsorption has been regarded the best desalination technique which is environmentally friendly (Dimos et al., 2012). Dolomite (Albadarin et al., 2012), magnesium (Lee et al., 2013) and calcium (Pakzadeh and Batista, 2011) based materials have been evaluated for water depollution. Cryptocrystalline magnesite has never been evaluated for removal of chromium ions in contaminated water bodies. The present study therefore evaluates the feasibility of using cryptocrystalline magnesite/bentonite clay composite for removal of chromium from aqueous solutions.

## **Materials and methods**

### **Feedstock**

Raw magnesite rocks were collected prior any processing at the mine from the Folovhodwe Magnesite Mine in Limpopo Province, South Africa (22°35'47.0"S and 30°25'33"E). Magnesite samples were milled to a fine powder for 15 mins at 800 rpm using a Retsch RS 200 miller and passed through a 32 µm particle size sieve. After sieving, the samples were tightly kept in zip lock plastic bags until application for wastewater amelioration.

### **Preparation of standard working solutions**

1000 mg/L standard solution of chromium from Lab Consumables Supply, South Africa was used to prepare the working solutions. 60 mg/L working solution was prepared by extracting 60 mL of 1000 mg/L standard solution and transferring into a 1000 mL volumetric flask. The volumetric flask was topped to the mark by adding ultra-pure water.

### **Characterisation**

Elemental analysis of raw and processed water samples was done by Inductively Coupled Mass Spectrometry (ICP-MS) (ELAN 6000). The accuracy of the analysis was monitored by analysis of National Institute of Standards and Technology (NIST) water standards. pH was monitored using CRISON MM40 portable pH/EC/TDS/Temperature multimeter

### **Optimization**

Optimization experiments were done in batch experimental procedures. Parameters optimized include time, dosage, chromium concentration and pH. To evaluate effect of equilibration time on reaction kinetics, time was varied from 0 - 360 minutes (10 mg/L chromium, 1 g magnesite, 250 rpm and 26 °C). To evaluate effect of dosage on reaction kinetics, the dosage was varied from 0.1 - 8 grams (10 mg/L chromium, 250 rpm, 30 minutes of reaction time and 26 °C). Chromium removal with

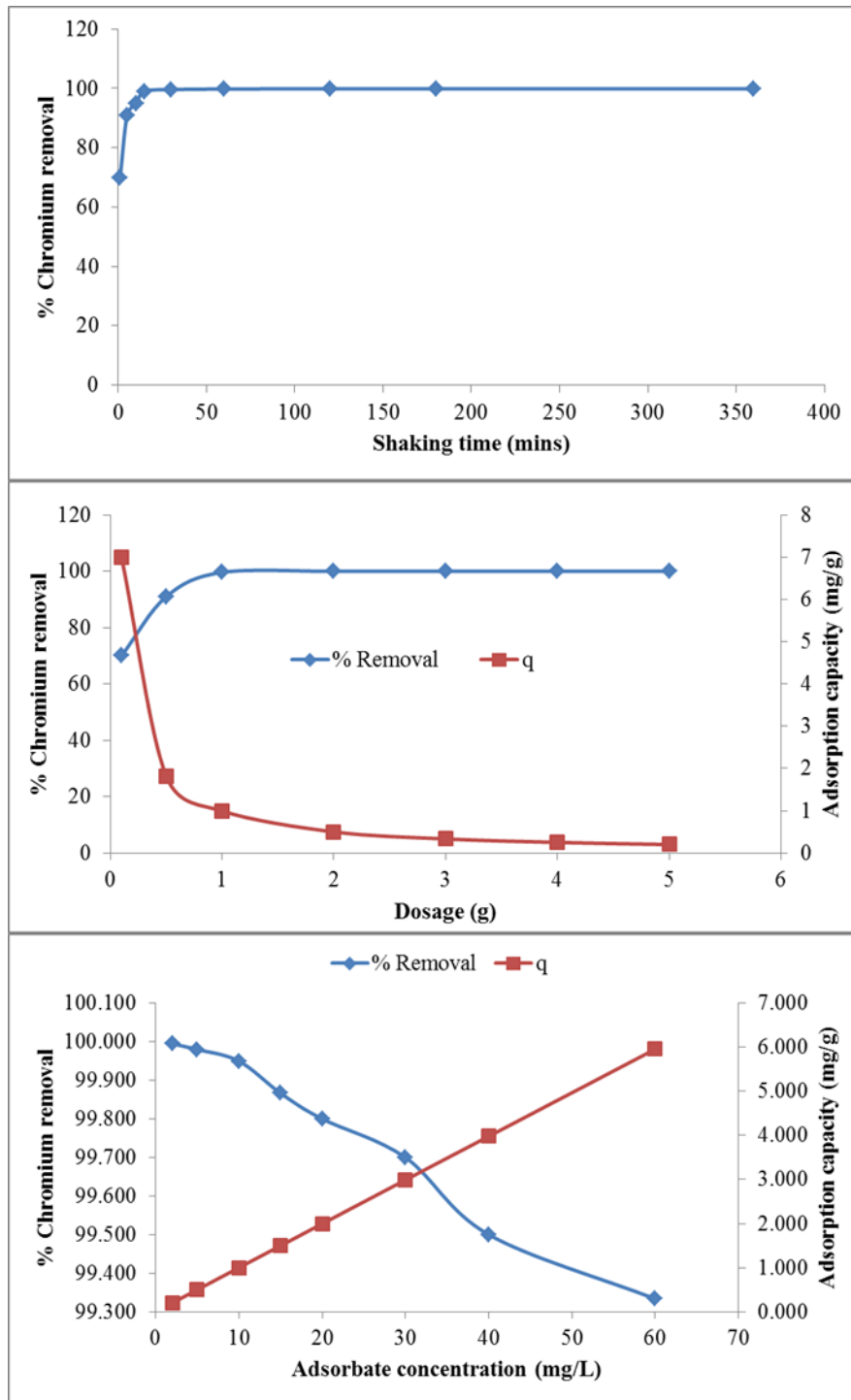
respect to ions concentration was conducted over a range of 0.1 – 60 mg/L. A table shaker was used for all the experiments (1300E, Labcon, Petaluma, CA, USA). Optimized condition for testing the feedstock capacity to remove chromium was evaluated using raw mine effluents.

## **Results and discussion**

The influence of shaking time on the adsorption of Cr (VI) from aqueous solution by cryptocrystalline magnesite was investigated. It can be seen from Figure 1 that the rate of Cr (VI) removal from aqueous solution increased with an increase in contact time. From the first minute of equilibration, the removal was very rapid and attains equilibrium at 30 mins of shaking. The removal efficiency increased from 70% at 1 min to 99% at 30 mins. Thereafter no significant increase in removal efficiency was observed. As such 30 min was observed to be the optimum condition for removal of Cr (VI) from aqueous solution using cryptocrystalline magnesite. This study showed quicker equilibrium as compared to other studies. The use of polyaniline/silica gel composite for Cr (VI) removal attained equilibrium after 60 mins [29].

The dependence of Cr (VI) adsorption onto cryptocrystalline magnesite dosage was evaluated by varying the adsorbent dosages. As shown in Figure 1, the removal of Cr (VI) from aqueous solution was observed to increase with an increase in dosage. The inverse proportion was observed for adsorption capacity, when the dosage of the adsorbent increases the amount of Cr (VI) mg/g of cryptocrystalline magnesite was going down hence depicting that more surfaces are becoming available for adsorption of Cr (VI) species from an aqueous system. The decrease in adsorption capacity is attributed to the splitting effect of the concentration gradient between sorbate and sorbent with increased magnesite dosage leading to a decrease in the amount of Cr (VI) onto unit weight of cryptocrystalline magnesite. This phenomena was recorded by using dolomite for Cr ions removal [26]. The removal efficiency was noted to increase from 70% at 0.1 g to > 99% at 1 g of magnesite dosage. This is attributed to more surfaces being available for adsorption hence depleting all the Cr (VI) that are in aqueous solution. Thus, 1 g was chosen as the optimum dosage for further batch experiments.

Figure 1 shows the influence of Cr (VI) ion initial concentration on the removal percentage with cryptocrystalline magnesite. The results revealed that the removal percentage decreased with an increase in Cr (VI) concentration. This may be attributed to surfaces becoming finite and saturated as more species are becoming available for adsorption. From 2 – 60 mg/L the adsorption efficiency was > 99 % hence depicting higher efficiency. The adsorption capacity was also shown to increase with an increase in Cr (VI) species concentration. Hence 60 mg/L was chosen as the concentration that will be used for further experiments. The results are in agreement with the results of other researchers [29].



## Conclusion

Referring to the above bench laboratory tests the following conclusions may be drawn:

- I. Cryptocrystalline magnesite has been successfully utilised for attenuation of Cr (VI) ions from aqueous solution

- II. Effect of various parameters on removal of chromium were evaluated and optimised. Optimum conditions were observed to be 30 mins of shaking time, 1 g of adsorbent dosage, and 60 mg/L of species concentration.
- III. Removal of Cr (VI) from aqueous solution was observed to be independent of pH.
- IV. The adsorption isotherms fitted well to Freundlich isotherm than the Langmuir adsorption isotherm hence proving multilayer adsorption on heterogeneous surfaces.
- V. Comparison studies elucidated that cryptocrystalline magnesite has high adsorption capacity as compared to other studies that has been used for chromium removal and it can be used for removal of chromium from aqueous systems.

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