

# AMD TREATMENT USING MODIFIED SISAL/CHITOSAN NANOCOMPOSITE AS AN ADSORBENT

GS PERRY<sup>1\*</sup>, W NHETA<sup>1</sup>, ER SADIKU<sup>2</sup>, MS ONYANGO<sup>2</sup>

<sup>1</sup>UNIVERSITY OF JOHANNESBURG, DEPARTMENT: METALLURGY, PO BOX 524, AUCKLAND PARK, 2006, SOUTH AFRICA

<sup>2</sup>TSHWANE UNIVERSITY OF TECHNOLOGY, DEPARTMENT OF CHEMICAL, METALLURGICAL AND MATERIALS ENGINEERING, PRIVATE

**ABSTRACT:** This study evaluates the ability of a sisal–chitosan microcomposite (SC) to remove Cr<sup>6+</sup> and Mn<sup>2+</sup> from acid mine drainage (AMD). Experimental conditions that influence adsorption performance were systematically examined. An optimal dosage of 1.5 g of SC produced the best metal removal. The SC3 formulation achieved the highest performance, reaching a maximum adsorption capacity of approximately 200 mg/g at 25°C, with an average metal removal efficiency of 97%. Adsorption of both metals was exothermic, with peak uptake at pH 2.0. EDX analysis confirmed attachment of metal ions to the composite surface.

**Keywords:** Adsorption, Chromium(VI), Manganese(II), Sisal fibre, Chitosan

## I. INTRODUCTION

Natural fibres have long played an important role in various industries, with historical records indicating the use of fibre–clay composites in ancient Egypt over three millennia ago. Despite a decline in the use of some traditional plant fibres, materials such as sisal, jute, kenaf, and hemp remain valuable due to their abundance, biodegradability, and favourable mechanical properties. Their increasing use in composites is driven by the global shift toward environmentally responsible, renewable materials that can substitute petroleum-based products or hazardous synthetic fibres such as asbestos.

Chitosan, derived mainly from crustacean shells, is widely recognised for its biodegradability, biocompatibility, and adsorption potential. In agriculture, it is used to enhance plant growth and improve resistance against pathogens. Its chemical structure, rich in amino and hydroxyl groups, makes chitosan particularly effective for binding metal ions.

Acid mine drainage remains one of South Africa’s most pressing environmental concerns. When sulphide-bearing rocks are exposed to oxygen and water, acidic, metal-rich effluents are generated. AMD can release high concentrations of toxic metals including chromium and manganese into surface and groundwater systems. Mining activities intensify sulphide exposure, while naturally occurring bacteria can accelerate the oxidation process. Because AMD varies considerably between sites, predicting and mitigating its impact remains a major challenge. Traditional AMD treatment technologies are often expensive or insufficiently effective. Consequently, the development of affordable, bio-based adsorbents has gained attention. Chitosan-based materials have been explored for their potential to bind metals, but their adsorption characteristics can be limited by pore structure. Combining chitosan with natural fibres such as sisal can improve porosity, surface area, and structural integrity, creating composites tailored for effective AMD remediation.

## 2. EXPERIMENTAL

### 2.1 AMD Sample Characterisation

AMD samples were collected from a South African mine known for its extensive water-treatment monitoring systems. ICP analysis, performed at a SANAS-accredited CSIR laboratory, revealed manganese at 14.01 mg/L and chromium at 80 mg/L. Manganese concentrations above 0.02 mg/L can lead to pipe deposition, highlighting the high contamination level of the collected sample.

RESULTS

3.1 EDX analysis

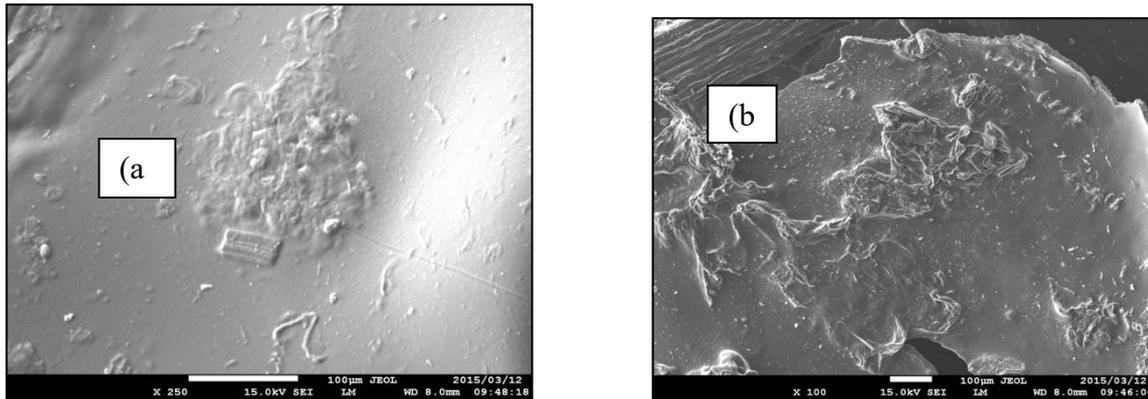


Figure 1a & b: EDX scans showing the SC3 composite surface prior to and following AMD interaction

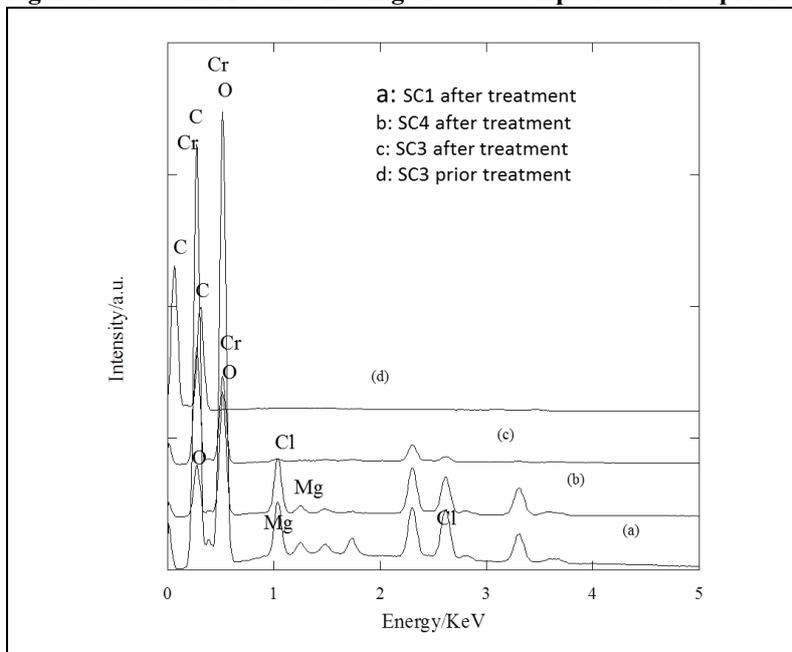


Figure 2: Energy-dispersive X-ray (EDX) profile of the SC3 sisal/chitosan composite prior to contact with AMD

Table 1: Pre-treatment elemental profiling of the SC3 sisal/chitosan microcomposite prior to AMD Exposure

| Element Line | Weight % | Weight % Error | Atom % |
|--------------|----------|----------------|--------|
| C            | 48.66    | ± 0.14         | 55.55  |
| N            | 5.79     | ± 0.44         | 5.67   |
| O            | 44.99    | ± 0.18         | 38.56  |
| Mg           | 0.04     | ± 0.01         | 0.02   |
| Si           | 0.08     | ± 0.01         | 0.04   |
| P            | 0.03     | ± 0.01         | 0.01   |
| Cl           | 0.12     | ± 0.01         | 0.05   |
| K            | 0.15     | ± 0.01         | 0.05   |
| Ca           | 0.13     | ± 0.02         | 0.04   |
| Total        | 100.00   |                | 100.00 |

Table 2: Pre-treatment elemental profiling of the sisal/chitosan microcomposite (SC1) post the AMD Exposure

| Element Line | Weight % | Weight % Error | Atom % |
|--------------|----------|----------------|--------|
| C            | 47.00    | ± 0.20         | 56.00  |
| O            | 45.06    | ± 0.14         | 40.31  |
| Na           | 2.19     | ± 0.02         | 1.37   |
| Mg           | 0.26     | ± 0.01         | 0.15   |
| Si           | 0.50     | ± 0.01         | 0.25   |
| S            | 1.34     | ± 0.02         | 0.60   |
| Cl           | 1.57     | ± 0.02         | 0.63   |
| K            | 1.27     | ± 0.02         | 0.47   |
| Cr           | 0.73     | ± 0.01         | 0.20   |
| Fe           | 0.08     | ± 0.02         | 0.02   |
| Total        | 100.00   |                | 100.00 |

Table 3: Pre-treatment elemental profiling of the sisal/chitosan microcomposite (SC3) post the AMD Exposure

| Element Line | Weight % | Weight % Error | Atom % |
|--------------|----------|----------------|--------|
| C            | 46.68    | ± 0.16         | 54.58  |
| O            | 50.16    | ± 0.14         | 44.03  |
| Na           | 0.43     | ± 0.01         | 0.26   |
| Mg           | 0.04     | ± 0.00         | 0.02   |
| Al           | 0.36     | ± 0.01         | 0.19   |
| Si           | 0.12     | ± 0.01         | 0.06   |
| P            | 0.02     | ± 0.00         | 0.01   |
| S            | 1.09     | ± 0.01         | 0.48   |
| Cl           | 0.46     | ± 0.01         | 0.18   |
| K            | 0.15     | ± 0.00         | 0.05   |
| Ca           | 0.05     | ± 0.00         | 0.02   |
| Cr           | 0.40     | ± 0.02         | 0.11   |
| Fe           | 0.06     | ± 0.01         | 0.02   |
| Total        | 100.00   |                | 100.00 |

Table 4: Pre-treatment elemental profiling of the sisal/chitosan microcomposite (SC4) post the AMD Exposure

| Element Line | Weight % | Weight % Error | Atom % |
|--------------|----------|----------------|--------|
| C            | 33.44    | ± 0.26         | 44.94  |
| O            | 41.12    | ± 0.12         | 41.48  |
| Na           | 7.70     | ± 0.04         | 5.41   |
| Mg           | 0.48     | ± 0.02         | 0.32   |
| Al           | 0.30     | ± 0.02         | 0.18   |
| Si           | 0.15     | ± 0.01         | 0.08   |
| S            | 5.67     | ± 0.03         | 2.85   |
| Cl           | 5.31     | ± 0.03         | 2.42   |
| K            | 5.00     | ± 0.03         | 2.06   |
| Cr           | 0.83     | ± 0.03         | 0.26   |
| Total        | 100.00   |                | 100.00 |

The results presented in Figure 2 and Tables 1–4 clearly demonstrate that the polymer surface successfully captured metal ions from the AMD solution. All analysed spectra show elevated carbon levels, which is expected because both sisal and chitosan are organic materials naturally rich in carbon and oxygen. Figure 1d illustrates the SC3 composite before exposure to AMD, while Figures 2a–2c depict the material after treatment. As anticipated, the post-treatment samples of SC1, SC3, and SC4 display detectable amounts of chromium and other metal species. Chromium, a highly hazardous metal commonly associated with industrial effluents, appeared at atomic percentages of 0.20%, 0.11%, and 0.26% in SC1, SC3, and SC4 respectively, whereas it was absent in the untreated sample. This confirms the strong metal-binding capability of the developed adsorbent. The EDX micrographs in Figures 1a and 1b further support this observation: before AMD exposure, the composite surface appears relatively smooth, with minimal bonding activity. After adsorption, the morphology becomes noticeably more irregular, indicating structural changes associated with heavy-metal attachment to the polymer matrix.

### 3.2: Effect of sisal/chitosan microcomposite in acid mine drainage

To assess the performance of the composite in treating AMD, the material first had to be optimized for maximum uptake of chromium and manganese. Figure 3 shows that the most effective dosage for the SC3 formulation was 1.5 g, which produced the highest removal efficiency. Following the initial ICP analysis, batch adsorption tests were conducted under controlled temperature conditions. To determine how varying chitosan content influences the uptake of Cr<sup>6+</sup> and Mn<sup>2+</sup>, different masses of the composite (ranging from 0.1 to 2.5 g) were introduced into 50 mL AMD samples. Each mixture was agitated at 200 rpm in a thermostatic shaker maintained at 298 K. After a 24-hour contact period, the adsorbent was separated by filtration, and the remaining metal concentrations in the filtrate were measured.

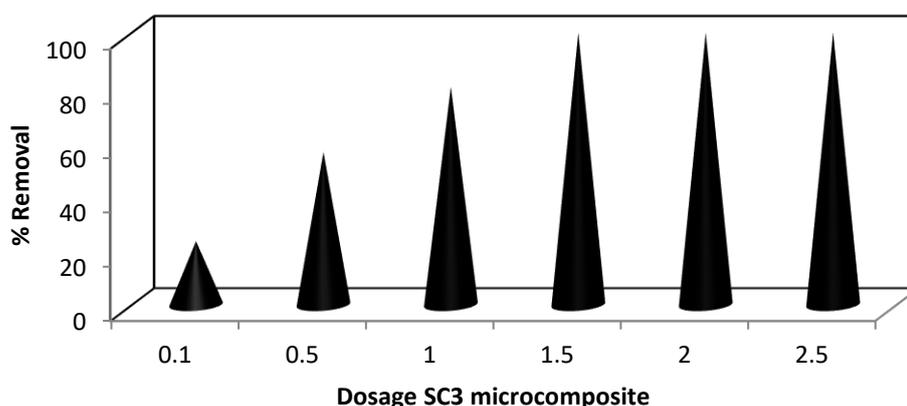


Figure 3: Optimisation of the composite for AMD on Cr (VI)

Table 5: Removal Efficiency and Peak Adsorption Capacity of Sisal–Chitosan Composite 1 (SC1)

| AMD Substance | Co (mg/L) | SC1: Ce (mg/L) | Co-Ce (mg/L) | % Removal | qm (mg/g) |
|---------------|-----------|----------------|--------------|-----------|-----------|
| Chromium      | 80        | 61             | 19.00        | 23.75     | 0.67      |
| Manganese     | 14.01     | 0.021          | 13.99        | 99.86     | 0.4663    |

Table 6: Removal Efficiency and Peak Adsorption Performance of the Sisal–Chitosan Composite SC3

| AMD Substance | Co (mg/L) | SC3: Ce (mg/L) | Co-Ce (mg/L) | % Removal | qm (mg/g) |
|---------------|-----------|----------------|--------------|-----------|-----------|
| Chromium      | 80        | 2.70           | 77.3         | 96.62     | 2.57      |
| Manganese     | 14.01     | 0.04           | 13.97        | 99.71     | 0.46      |

Table 7: Removal Efficiency and Peak Adsorption Capacity of the Sisal–Chitosan Composite SC4

| AMD Substance | Co (mg/L) | SC4: Ce (mg/L) | Co-Ce (mg/L) | % Removal | qm (mg/g) |
|---------------|-----------|----------------|--------------|-----------|-----------|
| Chromium      | 80        | 63             | 17           | 21.25     | 0.56      |
| Manganese     | 14.01     | 0.021          | 14.80        | 100.50    | 0.46      |

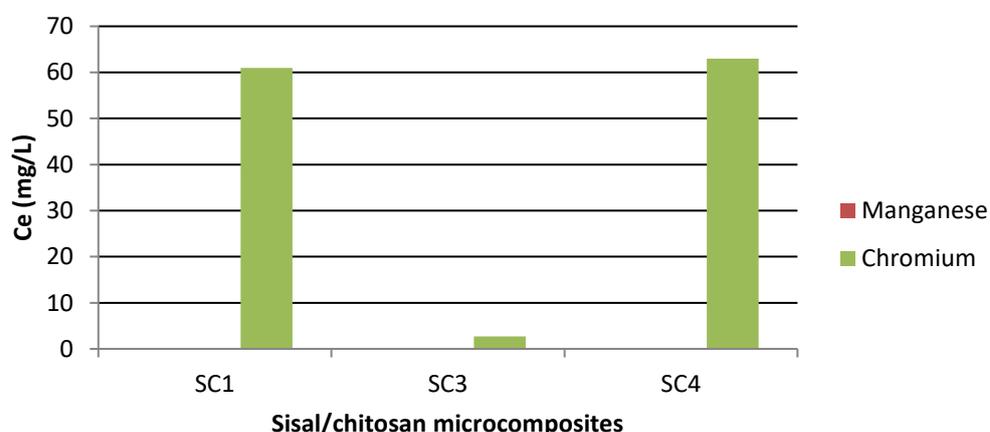
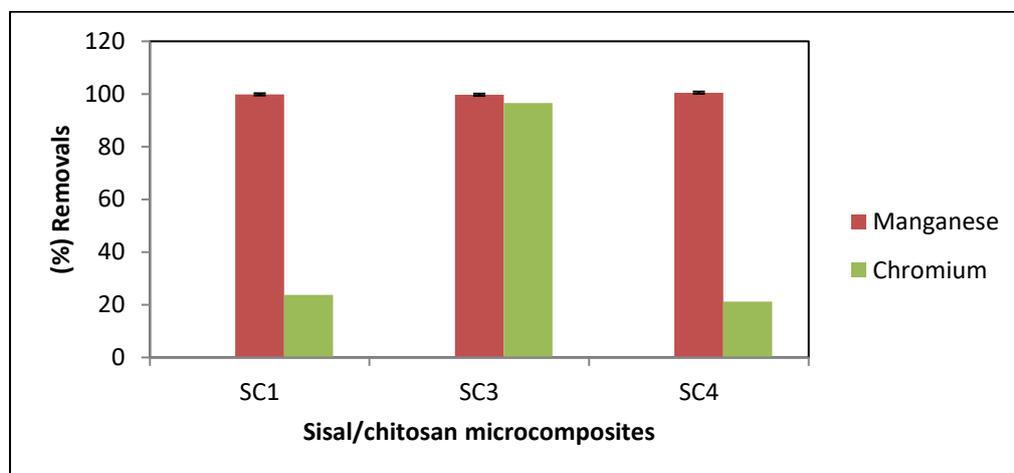


Figure 4: Influence of Sisal–Chitosan Composite Dosage on Cr<sup>6+</sup> and Mn<sup>2+</sup> Uptake at the Initial Metal Concentration

The spectra in Figure 4, together with the data presented in Tables 5–7, illustrate how the sisal/chitosan composites influence the initial concentrations of Cr<sup>6+</sup> and Mn<sup>2+</sup> during adsorption. The results clearly indicate that SC3

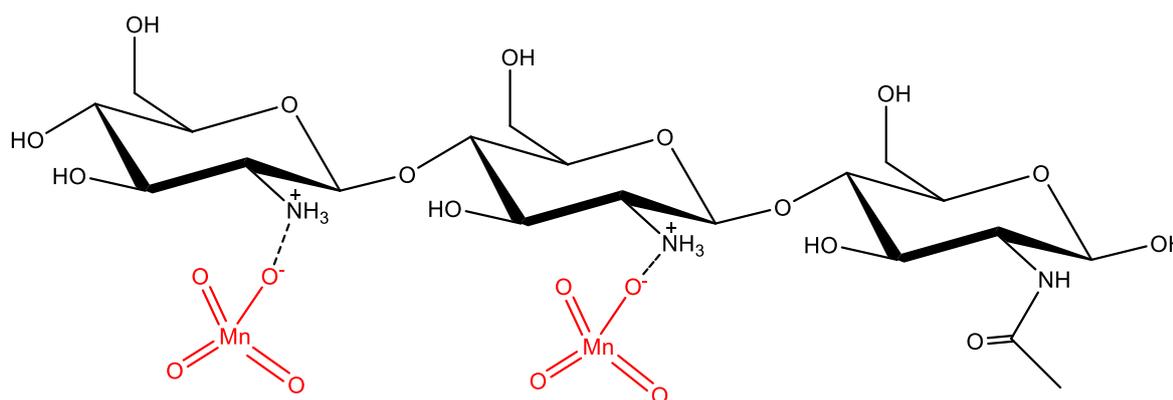
achieves the greatest reduction in chromium levels compared with SC1 and SC4. This behaviour is expected, as SC1 consists entirely of chitosan, which on its own exhibits limited adsorption capacity due to its relatively closed pore structure [24]. Incorporating sisal into the polymer matrix enhances porosity and surface accessibility, resulting in improved adsorption efficiency.



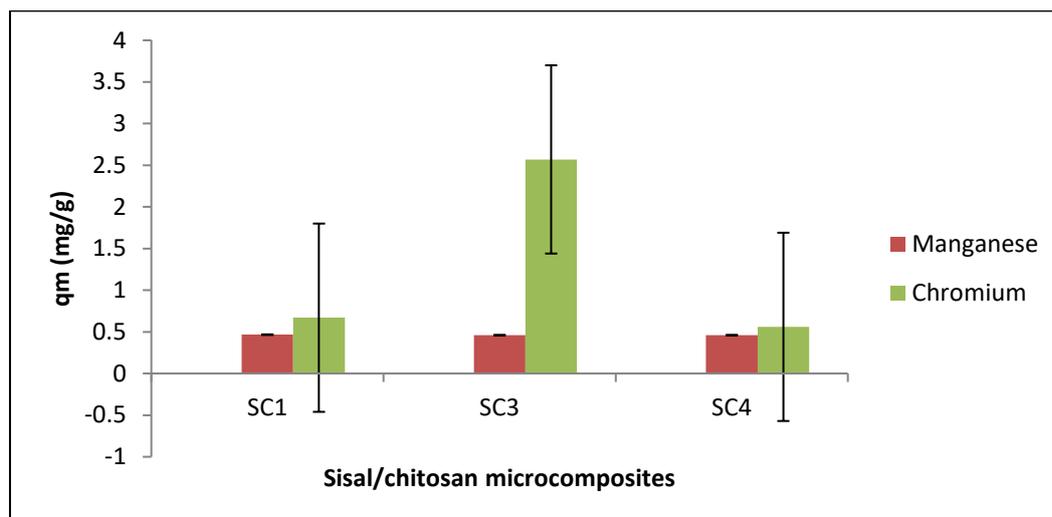
**Figure 5: Influence of Sisal–Chitosan Composite Dosage on the Removal Efficiency of Cr<sup>6+</sup> and Mn<sup>2+</sup>**

The extent of heavy-metal removal differed depending on the composite used. Figure 5 and Tables 5–7 illustrate how varying the dosage of the sisal–chitosan microcomposites influenced the percentage removal of Cr<sup>6+</sup> and Mn<sup>2+</sup> for SC1, SC3, and SC4. Among the tested materials, SC3 consistently demonstrated the strongest affinity for both chromium and manganese.

Across all experiments, an average removal efficiency of approximately 97% was achieved for the metals examined. As illustrated in Figure 6, this behaviour is largely attributed to the protonation of chitosan under acidic conditions, which enhances its electrostatic attraction to metal ions present in AMD. Chitosan is a heteropolymer made up of 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose units, produced through the alkaline deacetylation of chitin sourced from crustaceans, fungi, and other organisms. The polymer becomes soluble and more structurally open under low pH, increasing its porosity and capacity to bind contaminants.



**Figure 6: Illustration of the adsorption mechanism showing how the sisal–chitosan microcomposite binds Mn<sup>2+</sup> ions**



**Figure 7: Influence of Sisal–Chitosan Composite Dosage on the Adsorption Capacity for Cr<sup>6+</sup> and Mn<sup>2+</sup>**

Acid mine drainage (AMD) remains a major source of environmental contamination in regions with both active and legacy mining operations. As shown in Figure 7 and Tables 5–7, the SC1 and SC3 composites displayed the highest adsorption capacities, reaching approximately 2.5 mg/g for both chromium and manganese. Despite this, the overall adsorption capacities of all tested composites (SC1–SC4) were generally low for these metals. The reduced performance of SC4 can be attributed to its lower chitosan content relative to SC1 and SC2, which limits the availability of functional groups required for efficient metal uptake.

## CONCLUSION

The objective of this work was to develop and evaluate polymer-based microcomposites capable of extracting chromium and manganese from acid mine drainage. Kinetic modelling showed that the adsorption behaviour closely followed a pseudo-second-order mechanism. ICP analysis of the raw AMD sample confirmed metal concentrations of 14.01 mg/L for manganese and 80 mg/L for chromium. To enhance performance, the adsorbent dosage was optimised, with 1.5 g of the SC3 composite giving the most efficient removal of both metals.

The batch experiments provided valuable insight into the influence of operating conditions particularly pH and adsorbent dosage on metal uptake. Maximum adsorption of Cr(VI) and Mn<sup>2+</sup> occurred under highly acidic conditions, with pH 2.0 giving the best results. The SC3 formulation displayed the strongest affinity for both target metals, achieving an average removal efficiency of approximately 97%.

As anticipated, EDX analysis of the treated composites (SC1, SC3, and SC4) showed clear evidence of chromium and other metal species attached to the material surface, confirming successful adsorption.

## ACKNOWLEDGEMENT

1. The University of Johannesburg
2. Tshwane University of Technology

## REFERENCES

- [1] Annie kamala Florence J, Gomathi T and Sudha P N. Equilibrium adsorption and kinetics study of chitosan-dust kenaf fibre composite, Archives of applied science research (2011); 34:366-376.
- [2] Cho J, Heuzy, M Bégin, A Carreau, P.J. Viscoelastic properties of chitosan solutions: effect of concentration and ionic strength, Journal of Food Engineering (2006). 74:500-515.
- [3] Desbrieres J. 2002. Viscosity of semi flexible chitosan solutions: Influence of concentration, temperature and role of intermolecular interactions. Bio-macromolecules (2003); 3:342-349.
- [4] Edday N.O, Odoemelan, S.A, Mbaba, A, Elemental composition of soils in some dump sites, Electtonical Journal of Environmental Agriculture and food Chemistry (2006); 5:1399-1465.
- [5] USEPA. Technical document of acid mine drainage prediction, Office of Solid Waste, Washington, USA (1994); 1:48.
- [6] Peppas A, Komnitsas K, Halikia I. Use of organic covers for acid mine drainage control. Minerals Engineering (2000); 13:563-74.
- [7] Morrissey C. Mining's malignant menace, Review Magazine, St James' Square, London: Rio Tinto (2003); 6:68-108.
- [8] Diz H.R. Chemical and biological treatment of acid mine drainage for the removal of heavy metals and acidity, Ph.D. thesis, Virginia Polytechnic Institute and State University, USA (1997); 6:65.

- [9] ATSDR (2000) Toxicological profile for manganese. Atlanta, GA, United States Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.
- [10] IPCS (1999) Manganese and its compounds. Geneva, World Health Organization, International Programme on Chemical Safety (Concise International Chemical Assessment Document 12).
- [12] USEPA (1984) Health assessment document for manganese. Cincinnati, OH, United States Environmental Protection Agency, Environmental Criteria and Assessment Office (EPA-600/8-83- 013F).
- [13] Setshedi K.Z, Bhaumik M, Songwane S, Onyango M.S, Maity A. Exfoliated polypyrrole-organically modified montmorillonite clay composite as a potential adsorbent for Cr (VI) removal, *Chemical Engineering Journal*, 222 (2013) 186-197.
- [14] Balaguru P.N & Shah S.P. Development and evaluation of Biocure obtained from bacterial cellulose and standardized extract of propolis (EPP-AF) for the treatment of burns and/ or skin lesions, Brazil, São Paulo Research Foundation – FAPESP (1992); 41:234-260.
- [15] Korkina L.G, Phenyl propanoids as naturally occurring antioxidants from plant defence to human health, *Cell and Molecular Biology* (2007); 53: 15-25.
- [16] Silver M Control of acid mine drainage including coal pile and ash pond seepage. *Constructed Wetlands for Wastewater Treatment*, Lewis Publishers, Chelsea, Michigan (1989); 21:753–760.
- [17] Johnson D.B. Acidophilic microbial communities: candidates for bioremediation of acidic mine effluents. *Int. Biodet. & Biodeg* (1995); 1:41-58.
- [18] Robb G.A. Environmental consequences of coal mine closure, *The Geographical Journal* (1994); 106:33-40.
- [19] Pronk J.T & Johnson D.B. Oxidation and reduction of iron by acidophilic bacteria, *Geomicrobiology Journal* (1992); 10:153–171.
- [20] Kuenen JG & Robertsen LA. The use of natural bacterial populations for the treatment of sulphur containing wastewater, *Biodegradation* (1992); 3: 239–254.
- [21] Gadd G.M & White C Microbial treatment of metal pollution working biotechnology, *TIBTECH* (1993); 11: 353-359.
- [22] Barton L.L & Tomei F.A. Characteristics and activities of sulphate-reducing bacteria, *Sulphate Reducing Bacteria* Plenum Press, New York (1995); 3:1-22.
- [23] Abideen Idowu Adeogun, Andrew E. Ofudje, Mopelola Idowu and Sarafadeen O. Kareem, Equilibrium, kinetic, and thermodynamic studies of the biosorption of Mn(II) ions from aqueous solution by raw and acid treated corncob biomass, *BioResources* (2011) 6:4117-4134.
- [24] Madihally S.V, Matthew H.W.T. Porous chitosan scaffolds for tissue engineering *Biomaterials* (1999), vol. 20, no. 12, pp. 1133-1142.
- [25] Mehta P.K, Monteiro P.J.M. *Concrete: Microstructure, Properties, and Materials*. New York, McGraw-Hill (1993).
- [26] Salata, L.A, Craig G.T Brook I.M. In-vivo evaluation of a new membrane (Gengiflex) for guided bone regeneration (GBR), *Journal of Dental Research* (1995); 74: 825.
- [27] Van Zyl H.C. Environmental systems in Amcoal, *Mining Environment management*, March issue (1996):18-21.
- [28] Younger P.L, Curtis T.P, Jarvis A, Pennell R Effective passive treatment of aluminium-rich acidic colliery spoil drainage using a compost wetland at Quaking Houses, County Durham. *J* (1997).