Synthesis and Application of Hydrogel-Silica Composite for the Removal of Lead from Aqueous Solution

Elvis Fosso-Kankeu, Frans B. Waanders, Inecke M. Grobler and Nico Lemmer

***Abstract*—** Due to the individual qualities of hydrogel and silica the aim of this study is to synthesize hydrogel-silica. The hydrogel and hydrogel-silica composite will be synthesized, characterised and tested as adsorbents for the removal of lead in the water. The adsorption capacity of hydrogel and the composite was examined at different adsorbent dosages and time to determine the optimum conditions. The kinetic models were employed to determine the adsorption behaviour of hydrogel and hydrogel-silica composite. It was therefore found that lead adsorption on the various adsorbents occurred through chemisorption mechanism. While the adsorption capacities were 28.496 mg/g and 27.812 mg/g for hydrogel and the hydrogel-silica composite respectively**.**

***Index Terms*—** Hydrogel, hydrogel-silica, composite, metal, kinetic, adsorption, lead.

I. Introduction

The resources of water in South Africa have decreased drastically, and that is a major concern due to the fact that the water demand will exceed the supply in the next decade, in accordance to the authorities and specialists in this field [1]. Due to the chronic water shortage in South Africa, a deficiency which is attributed to climate change, industrial and population expansion, it is important to derive an approach which will address the usage of all available water resources effectively and economically [1].

The emphasis relating to efficient use of available water resource lies mostly along the treatment of wastewater effluent in order to re-use it in various processes. The treatment includes the removal of heavy metals and turbid materials from the wastewater in order to improve its quality so that it may not be detrimental to equipment, living organisms and the environment [2].

The occurrence of heavy metals in raw water is usually attributed to weathering of rocks and earths, volcanic eruptions and human activities. Industrial activities such as mining is another source of heavy metals in freshwater. Acid mine drainage (AMD) has been identified as one of the main attributes to water pollution [3]. AMD is caused by sulphuric acid (H2SO4) which is derived from the oxidation of geologically formed FeSx, mostly pyrite (FeS2) in aqueous medium as shown in Equation 1:

$$2FeS2 + 7O2 + 2H2O \cdot 2Fe2+ + 4SO42- + 4H+ \quad (1)$$

Elvis Fosso-Kankeu is with the School of Chemical and Minerals Engineering of the North West University, Potchefstroom; South Africa

Frans B. Waanders is with the School of Chemical and Minerals Engineering of the North West University, Potchefstroom; South Africa.

Inecke M. Grobler is with the School of Chemical and Minerals Engineering of the North West University, Potchefstroom; South Africa.

Nico Lemmer is with the School of Chemical and Minerals Engineering of the North West University, Potchefstroom; South Africa..

The AMD is an unavoidable phenomenon because it is generated in both abandoned and active mines. The sulphuric acid formed (Eq.1) sinks down to underground water.

There are several techniques that were developed to remove heavy metals and turbid materials from waste water, i.e. distillation, reverse osmosis, carbon nanotubes, Fenton's reagent, wet oxidation, advanced oxidation, coagulation-electro oxidation. These techniques are complex, incur high costs and do not cover a wide range of the wastewater poor quality [4].

Chemical precipitation techniques have been extensively researched and a conclusive optimal approach is still a challenge, hence there is a need for diversification. Other processes produce waste materials that can also act as reagents in the production of undesired products and also a large amount of slit that is produced [5]. Reverse osmosis incurs water wastage which also includes electricity (due to pressurized process). Its main disadvantage is that it does not accommodate highly turbid wastewater with coarse particles; where bacteria and chemicals can also pass through the membrane [6].The disadvantages associated with ion exchange are iron and calcium sulphate fouling, adsorption of organic matter and bacterial contamination [7, 8]. The disadvantage of electro-dialysis is the fact that bacteria and viruses are not removed due to their neutrality [9].

Adsorption is one of the most effective techniques to employ, for the removal of metals in water. Adsorption lowers the concentration of impurities due to the adhesion of molecules to a surface (the adsorbent). Thus adsorption is a surface based process which is inexpensive and effective. The adsorbents that are used in this project include hydrogel and silica to form a hydrogel-silica composite.

Using hydrogel adsorbents has many advantages which include; easy loading and cations capturing with simple elements, reusability and the fact that it can be a semi-continuous operation. The use of hydrogel-silica composite for the removal of metal pollutants from water has become attractive because hydrogels are chemically stable, stable in fluctuating temperatures, react to variations in environmental stimuli, adsorb huge amounts of biological fluids and swell, have unique biocompatibility, flexible methods of synthesis, have a range of constituents and desirable physical characteristics [10, 11].

The goal for this project is to synthesize and characterize hydrogel-silica and to use kinetic studies to determine the adsorption behaviour of hydrogel-silica.

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II. METHODOLOGY

A. Synthesis of adsorbents

1) Hydrogel

The adsorbents were synthesised by using the free radical graft co-polymerization technique. The initiator (20 mg) and crosslinker (30 mg) each was added to 50 mL of deionised water. K-carrageenan (1 g) was now dissolved in deionized water (20 mL) in the reaction vessel and stirred robustly by using a magnetic stirrer, 5 mL of the initiator solution and two minutes later 5 mL of the crosslinker solution was also added during this stirring process, 1 g Acrylonitrile (1.24 mL) was added to the solution and stirred again. The vessel was then placed into the oven for 2 hours at 60 °C and the reaction was now able to take place. After the reaction was done, the vessel was left to reach room temperature, after which the unreacted homopolymer, monomers, crosslinkers and initiators was washed off with deionised water at 85°C. Lastly the hydrogel was left to dry for 24 hours in the oven at 40 °C and crushed.

2) Hydrogel-silica composite

The exact process was followed to synthesise the hydrogel-silica composite, the only difference being that 600 µL TEOS was added to the 20 mL deionised water in the beginning and stirred for 2 min. Then the rest of the above mentioned procedure was followed.

3) Reagents

The correct amounts of the compound containing lead, was dissolved in deionised water to prepare the adsorptive solution.

B. Scanning Electron Microscopy (SEM) analysis and Energy-dispersive X-ray spectroscopy (EDS)

Scanning electron microscopy (SEM) photography (TESCAN, VEGA SEM) was used to determine the surface morphology of each adsorbent under a 20-kV electron acceleration voltage coupled with energy-dispersive x-ray spectroscopy (EDS) for elemental analysis[12].

C. Adsorption experiments

1) Determining optimum dosage of adsorbents

The optimum dosage experiment was conducted by preparing a 100 mL metal solution of 30 ppm at temperature of 30° C. A 0.1 g of adsorbent was added and mixed at 160 rpm for an hour. The above mentioned steps were then repeated for 0.2, 0.3 and 0.4 g of adsorbent.

The whole process was repeated for hydrogel and the composite respectively for the adsorption of lead.

2) Determining the optimum time

This was done by preparing a 100 mL metal solution of 30 ppm concentration, considering optimum conditions obtained from previous experiments. The mixture was then stirred at 160 rpm for 10 min. The above-mentioned steps were then repeated at 10, 20, 30, 40, 60, 80, 100 and 120 min for the adsorption of lead.

Inductively coupled plasma (ICP) atomic emission spectroscopy (Agilent Technologies, USA) analysis was used to measure the remaining metal ions in the supernatant.

D. Mathematical modelling

1) The adsorption capacity determination

The equilibrium concentration is determined before the adsorption capacity is determined using Equation 2:

$$q_i = \frac{(C_0 - C_i)V}{m} \quad ; \qquad i = e, t \tag{2}$$

Where q_i is the amount of metal adsorbed per unit mass of adsorbent (mg/g); C_0 is the initial metal ions concentration in the solution (mg/L); C_i is the metal ion concentration (mg/L); m is the amount of adsorbent (g) and V is the solution volume (L). The subscript *"i"* denotes the state either of the system, equilibrium (*e*) or at a time interval (*t*).

2) Kinetics modelling

The adsorption capacity at different times needs to be calculated before the kinetic models are applied. This is done by using equation 2:

The pseudo first-order kinetic rate law is indicated by equation 3:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

The pseudo second-order kinetic rate law is indicated by equation 4:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{4}$$

Where the rate constants for the first and second order kinetics are k_1 and k_2, respectively, q_e is the equilibrium amount of metals adsorbed (mg/g) and q_t the amount of metals adsorbed at a specific time *t* (mg/g). The rate constants were determined by using non-linear regression methods.

III. RESULTS AND DISCUSSION

A. Effect of adsorbent dosage

TABLE I
EFFECT OF ADSORBENT DOSAGE ON LEAD ADSORPTION

Adsorbent	Dosage of adsorbent (g)	Average adsorption capacity (mg/g)
Hydrogel	0.1	24.688255
	0.2	13.443775
	0.3	8.608908333
	0.4	6.4755225
Hydrogel-silica	0.1	25.97112
	0.2	13.2822625
	0.3	8.88066
	0.4	6.90148

It is clear from Table I that hydrogel delivered an average adsorption capacity of 24.688 mg/g at the optimum dosage of 0.1 g and hydrogel-silica delivered an average adsorption capacity of 25.971 mg/g at the same dosage. This means that hydrogel-silica has a better adsorption affinity to lead when compared to hydrogel.

B. Scanning Electron Microscopy (SEM) analysis

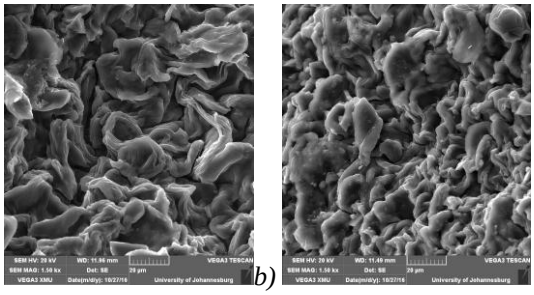

Fig. 1 SEM image of hydrogel before adsorption of lead (a) and hydrogel after lead adsorption (b) at 1500 magnification.

The surface texture of the Hydrogel after lead adsorption is smoother than before adsorption. Before adsorption the hydrogel is much flakier. This might be due to the swelling abilities of hydrogel, as considerable amount of water was adsorbed, including lead.

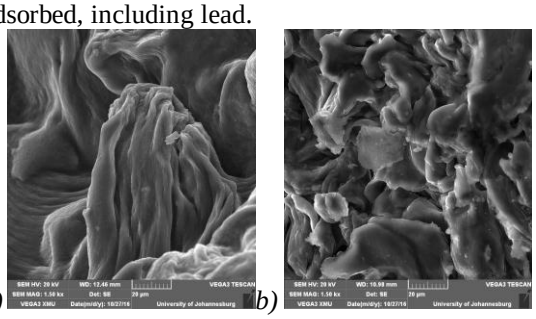

Fig. 2 SEM image of hydrogel-silica before adsorption of lead (a) and hydrogel-silica after lead adsorption (b) at 1500 magnification.

The surface of the hydrogel-silica before lead adsorption is much smoother compared to the surface after lead adsorption. This might be due to the fact that the hydrogel-silica composite is very strong and tough before adsorption, and after lead adsorption it become more brittle or flaky.

C. Energy-dispersive X-ray spectroscopy

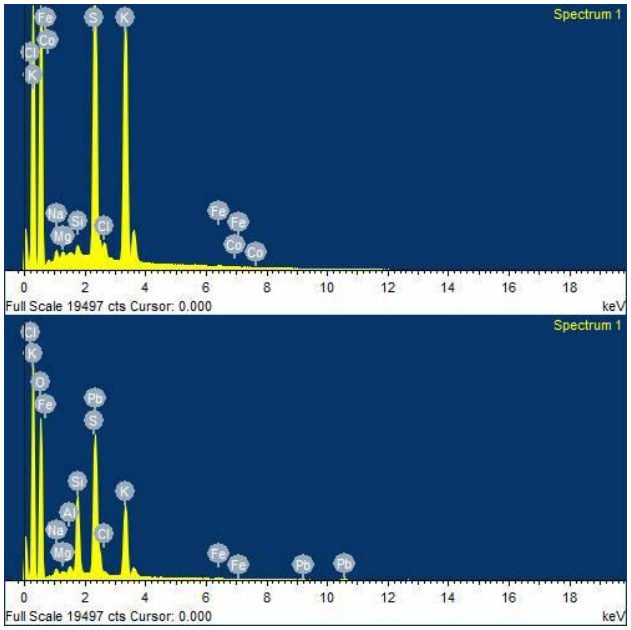

Fig. 3 EDS graph of the elements present in hydrogel before lead adsorption (a) and after lead adsorption (b).

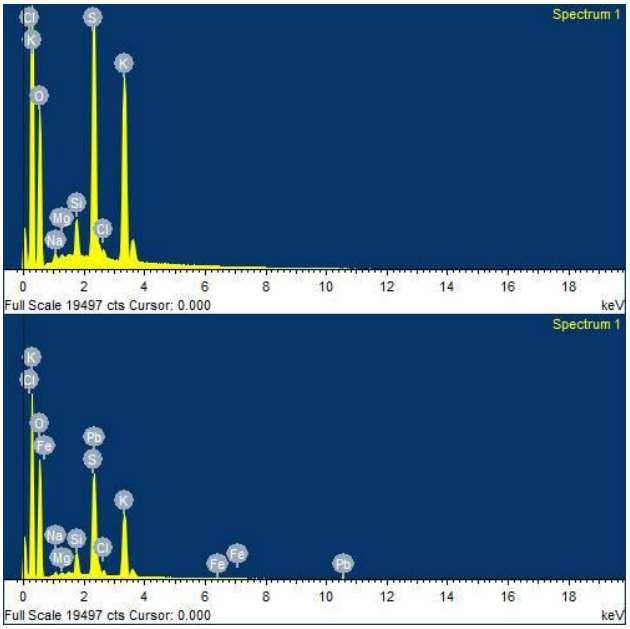

Fig. 4 EDS graph of the elements present in hydrogel-silica before lead adsorption (a) and after lead adsorption (b).

The figures above shows the elements that is present in the adsorbent before and after lead adsorption. It can be clearly seen that lead is not present in the adsorbents before adsorption, while it is observed on the exposed adsorbents; furthermore the peak of lead seems to be more pronounced for the loaded hydrogel than the loaded composite.

D. Kinetic study

To fit the experimental data both the pseudo-first and pseudo-second order kinetic models were used. The intercept $(1/k_i q_e^2)$ and the slope $(1/q_e)$ of the plot t/q_t *vs.* t (Figure 5) were used to calculate the values of k_i, $i=1,2$ and $q_{e,cal}$. The R^2 values for the kinetic models as seen in Table II are close to each other, but in both cases this value indicates that the pseudo-second order model is more favourable due to the higher R^2 values. The adsorption capacity ($q_{e,exp}$) of hydrogel is relatively similar to that of hydrogel-silica. This means that both adsorbents have equal affinity for lead. However, hydrogel-silica provide the advantage of being more stable and could therefore be easily regenerated.

TABLE II
KINETIC MODEL PARAMETERS FOR THE ADSORPTION OF LEAD

Adsorbent	Kinetic Model and Parameters				
	$q_{e,exp}$	Pseudo 1st order		Pseudo 2nd order	
Hydrogel	28.496	q_{e1}	27.340	q_{e2}	28.046
		k_1	0.250	k_2	0.030
		R^2	0.965	R^2	0.989
hydrogel-silica composite	27.812	q_{e1}	27.070	q_{e2}	27.572
		k_1	0.267	k_2	0.042
		R^2	0.991	R^2	0.997

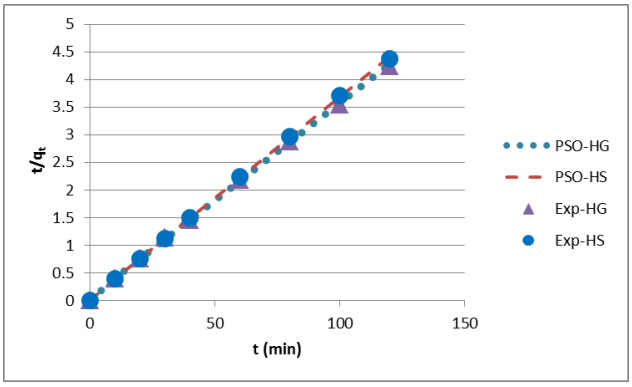

Figure 5: Kinetic data to pseudo-second-order rate model fit for the adsorption of lead onto hydrogel and hydrogel-silica

IV. Conclusion

The hydrogel and hydrogel-silica composite were synthesized, characterised and tested as adsorbents for the removal of lead in the water. The adsorption capacity of hydrogel and the composite was examined at different adsorbent dosages, which revealed that both adsorption were effective at relatively low dose, providing an advantage on the cost. The kinetic models were used to determine the adsorption behaviour of hydrogel and hydrogel-silica. It was found that the pseudo-second order model suits better to adsorption equilibrium data, implying that lead was adsorbed through a chemisorption mechanism. It was also observed that hydrogel and hydrogel-silica had similar affinity for lead, implying that hydrogel-silica could be the ideal adsorbent based on its stability.

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The corresponding author is currently an Associate Professor in the School of Chemical and Minerals Engineering at the North-West University (Potchefstroom). He is an NRF rated researcher who has published journal articles, book chapters and book.

Prof Elvis Fosso-Kankeu has been the recipient of several merit awards