

Chitosan-graft-Polyacrylamide adsorbent for Sulphate removal from water

Elvis Fosso-Kankeu, Frans Waanders, and Bennie Steyn

Abstract — The extensive mining activity in South Africa has resulted in the constant release of solid and liquid wastes into the environment which contributes to the accumulation of sulphates in water sources. Adsorption has become a very attractive technology for the purification of water from pollutants, but the removal of sulphate is yet to be tested. Chitosan graft polyacrylamide copolymer has shown strong cationic adsorbent qualities and thus would be ideal in removing the sulphates. Characterization of the copolymer was done using FTIR and SEM analyses, then the grafting ratio was determined by weighing. Adsorption tests were then done, with sodium sulphate, to observe the optimal adsorption conditions required for the sulphate removal. Parameters investigated during the adsorption tests included pH, copolymer dosage, initial concentration of sulphate and time. Isotherm and kinetic studies were carried out to determine the adsorption behavior of the synthesized copolymer. The adsorption tests showed that 3g/L copolymer dosage is ideal, while higher sulphate removal was achieved at pH below 4. The optimal adsorption capacity was found to be 226 mg sulphates/g copolymer. From these tests it was proven that the copolymer adsorbs and removes sulphate from the water, making it a viable solution for acid mine water remediation.

Keywords— Sulphates; acid mine water; chitosan; chitosan graft polyacrylamide; adsorption

I. INTRODUCTION

MINING operations across the world are one of the main producers of heavy metal and mineral salt pollutants that flow into the water system [1, 2, 3]. Among these mineral salts, sulphates have been studied very little and because of the danger they pose to the environment their removal is of the utmost importance [4]. The traditional methods of removal of sulphates either take very long or are extremely expensive, thus a need exists to find a cheaper and faster way of removing the sulphates [5]. Adsorption has thus become one of the more attractive ways of dealing with these salts, but the materials generally used, like aluminum salts, are dangerous in that they may cause Alzheimer's disease when consumed or other health effects.

Recently chitosan has received significant attention in the adsorption and removal of pollutants in water because of its

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low price, fast removal, and bio-degradability [6]. Chitosan also shows strong bonding capability with synthetic polymers, specifically polyacrylamide, that significantly increase the adsorption potential of the copolymers [7]. This study will investigate the adsorption behaviour of the grafted chitosan-g-polyacrylamide (C-g-PAM) in removing sulphates from water.

II. METHODOLOGY

A. Materials

De-acetylated chitosan (high molecular weight) and the sodium sulphate, were used as received from Sigma-Aldrich. The acrylamide was purchased from Merck Chemical Co. Ltd., and the ammonium ceric nitrate initiator was purchased from ACE Pty. Ltd., both of which were used as received.

B. Grafting of the copolymer

The grafting of the PAM onto the chitosan backbone was done by the ceric ammonium initiation method [7]. 100mL of a 1% acetic acid solution was prepared in a 250mL Erlenmeyer flask, into which, 0.4g of chitosan was added and shaken at 100 rpm for 30 minutes. The same weight of ceric ammonium nitrate was added with a pre-determined amount of PAM and the mixture was allowed to react for 3 hours. After the 3 hours, the mixture was precipitated in acetone and the white, jelly like copolymer was washed with more acetone two more times, to remove any homopolymer. All the copolymer was added into a single beaker and this was dried in a vacuum oven at 50°C for 24 hours.

C. Characterization of the copolymer

1) Grafting ratio tests

The first set of test was to find the optimal grafting ratio which was determined by weighing and the calculation was done as in Eq. 1. The object of the test was to determine the best ratio of PAM to chitosan added to produce the best copolymer. The tested ratios were 1:1, 3:1, 5:1, and 7:1 of chitosan to polyacrylamide weight.

$$\text{Grafting Ratio } \%G = \frac{W_1 - W_0}{W_0} \times 100\% \quad \text{Eq. 1}$$

Where W_1 is the weight of the copolymer and W_0 is the weight of the chitosan added.

2) FTIR

A KBr method, Fourier Transform Infrared Spectroscopy (FTIR) analysis was carried out on the pure chitosan, copolymer that had not been used for adsorption and copolymer that had been used to adsorb sulphates.

3) SEM

A scanning electron microscope (SEM) was used to take enhanced photographs of the pure chitosan and unused copolymer particles to reveal any structural differences among them as a result of successful copolymerization.

D. Adsorption of sulphates

The adsorption experiment was carried out in a batch system. Sodium sulphate was added to 100 mL of de-ionized water and shaken lightly until the sulphates were dissolved. The copolymer was then added and allowed to adsorb the sulphates before a small sample of the solution was removed and centrifuged. 1 mL of the centrifuged liquid was mixed with 10 mL of a 1% nitric acid solution and sent for ICP-OES analysis to find the concentration of sulphur still present in the water. For the tests, four different parameters were tested, one at a time with the others kept constant.

The parameters that were tested was the copolymer concentration (0.1 g/100 mL, 0.2 g/100 mL, 0.3 g/100 mL, 0.4 g/100 mL), pH (2, 4, 6, 8), sulphates concentration (500 mg/L, 1000 mg/L, 2000 mg/L, 3000 mg/L) and adsorption time (15 min, 30 min, 60 min, 90 min). While one parameter is being varied the others are kept constant.

E. Isotherm and Kinetic Models

The Langmuir and Freundlich isotherms were used in their linear forms to calculate the adsorption affinity of the copolymer for the sulphates. The linear Langmuir equation is as in Eq. 2.

$$\text{Linear Langmuir} \quad \frac{C_e}{q_e} = \frac{1}{q_m k} + \frac{C_e}{q_m} \quad \text{Eq. 2}$$

Where C_e is the equilibrium concentration of the sulphates in (mg/L), q_e is the adsorbance of the copolymer at equilibrium (mg sulphates/g copolymer), q_m is a Langmuir constant related to the adsorption capacity in (mg sulphates/g copolymer), and k is a Langmuir constant related to the energy released in adsorption in (L/mg).

The Freundlich isotherm's linear form follows in Eq. 3.

$$\text{Linear Freundlich} \quad \log q_e = \log k_f + \frac{1}{n} \log C_e \quad \text{Eq. 3}$$

Where C_e is the equilibrium concentration of the sulphates in (mg/L), q_e is the adsorbance of the copolymer at equilibrium (mg sulphates/g copolymer), n is the intensity of adsorption and k_f is related directly to the adsorptive capacity in (mg sulphates/g copolymer).

The kinetics of adsorption was calculated using the pseudo-second order equation as in Eq. 4.

Where q_e is the adsorbance of the copolymer at equilibrium (mg sulphates/g copolymer), q_t is the adsorbance of the copolymer at time t (mg sulphates/g copolymer), and k_2 is the rate constant of the adsorption in (g/mg.min)

III. RESULTS AND DISCUSSION

A. Characterization Results

1) Graft Ratio

The grafting ratio tests were completed as described before and from **Fig. 1** it is clear that at a weight ratio of 7:1 PAM added to chitosan the grafting ratio was the highest and thus this was used for all further grafting.

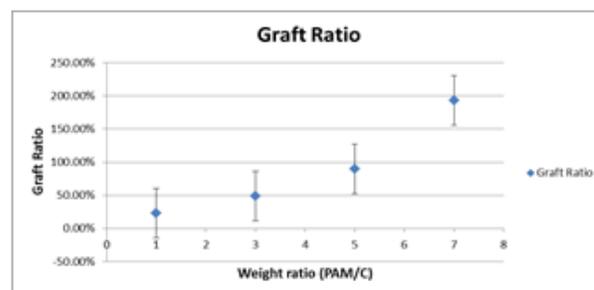


Fig. 1: Graft Ratio Test Results

2) FTIR

The FTIR results in **Fig. 2** show the characteristic peak of the C=O group at 1700 cm^{-1} , with amino groups peaking at 3600 cm^{-1} , 1560 cm^{-1} , and 1160 cm^{-1} . Literature [7, 8] commonly has additional peaks around $900\text{-}1100 \text{ cm}^{-1}$ because of acetyl groups on untreated chitosan but these do not apply since the chitosan is already de-acetylated.

The grafted copolymer shows many of the same bands but the one at 1700 cm^{-1} is much stronger due to more groups being created and open for adsorption on the unused copolymer. When the used and unused copolymer is compared it is easy to see the lowered intensity of the 2800 cm^{-1} , 1700 cm^{-1} , and $1560\text{-}1400 \text{ cm}^{-1}$, bands. This is most likely caused by the sulphates molecules filling the copolymer sites that would otherwise absorb more light energy.

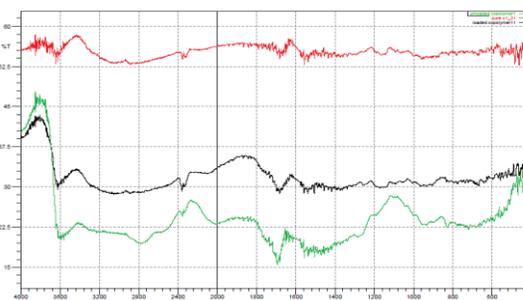


Fig. 2: FTIR spectra of the pure Chitosan (red), unused C-g-PAM (green), and adsorbed C-g-PAM (black)

3) SEM

$$\text{Pseudo-Second Order} \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Eq. 4}$$

The SEM images in **Fig. 3** and **Fig. 4** show the pure chitosan and C-g-PAM at 800x magnification, respectively. The main difference that indicates successful grafting is the tiny dots and particles on the surface of the copolymer which is where the PAM has grafted to the chitosan backbone. These

images compare very well with other SEM images from literature [9, 10]

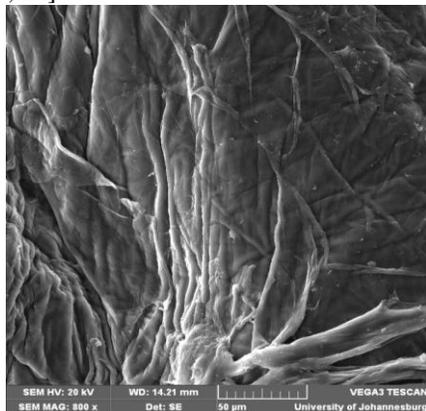


Fig. 3: 800x Magnification SEM image of pure chitosan

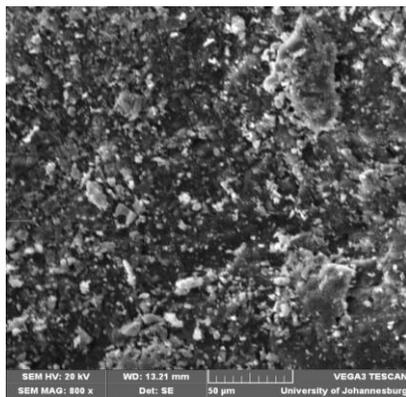


Fig. 4: 800x Magnification SEM image of C-g-PAM

B. Adsorption Results

1) Effect of copolymer dosage on sulphate removal

The adsorption experiments were carried out as mentioned above, it was possible on the basis of the ICP results to determine the impact of the parameters considered. Changing the copolymer concentrations but keeping the other values constant showed that the optimal concentration was at 0.3g/100mL because it removed more sulphates from the water as can be seen in Fig. 5. At the optimal concentration the adsorbance of the copolymer was calculated to be 224.52 mg sulphates removed/g copolymer added.

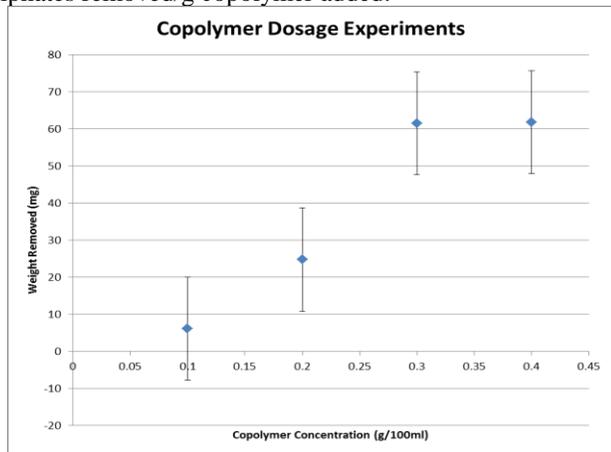


Fig. 5: Sulphate removal as a function of copolymer dosage.

2) pH Tests

The pH tests results showed that at a pH of 4 or less the adsorption was much stronger as can be seen in Fig. 6. The weight of sulphates removed is shown plotted vs. the pH in the solution. The average adsorbance at the lowered pH was 283.63 mg sulphates removed/g copolymer added.

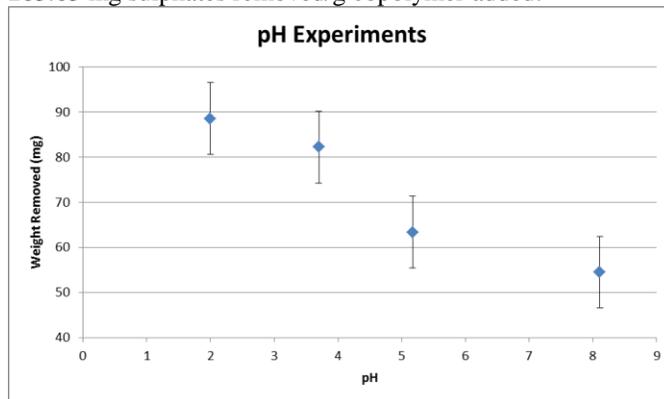


Fig. 6: Sulphate removal as a function of pH

C. Isotherms and Kinetic Model

The Langmuir and Freundlich isotherms were fit with the data from the sulphates concentration tests and the resulting graphs are shown in Fig. 7 and Fig. 8, respectively.

The Langmuir graph was made by plotting C_e/q_e vs. C_e where the slope = $1/q_m$ and the intercept = $1/K_L q_m$. From this plot the value of q_m was 277.78 (mg/g) and K_L was 0.00349. Because the R^2 value was relatively close to unity, the plot seems to be acceptable, implying that the adsorption occurs mainly on the monolayer surface.

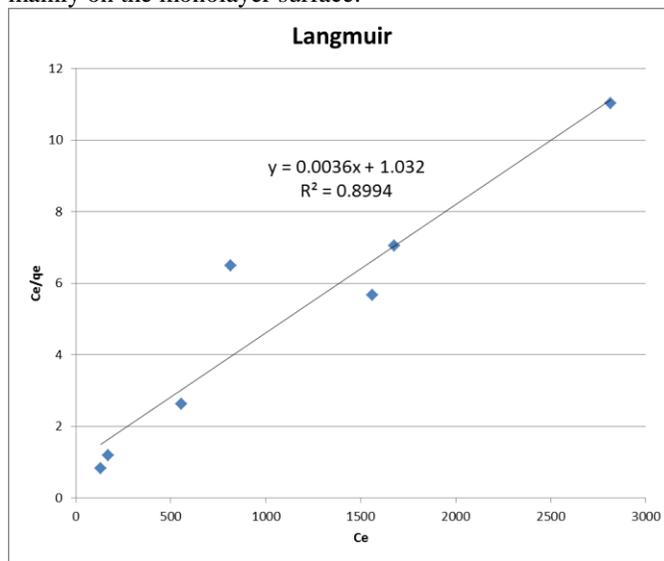


Fig. 7: Langmuir Isotherm graph

The Freundlich isotherm graph, plotted as $\ln q_e$ vs. $\ln C_e$, had a much worse fit with the very low R^2 value indicating the poor fit. Thus the values that could be calculated from this method will be disregarded.

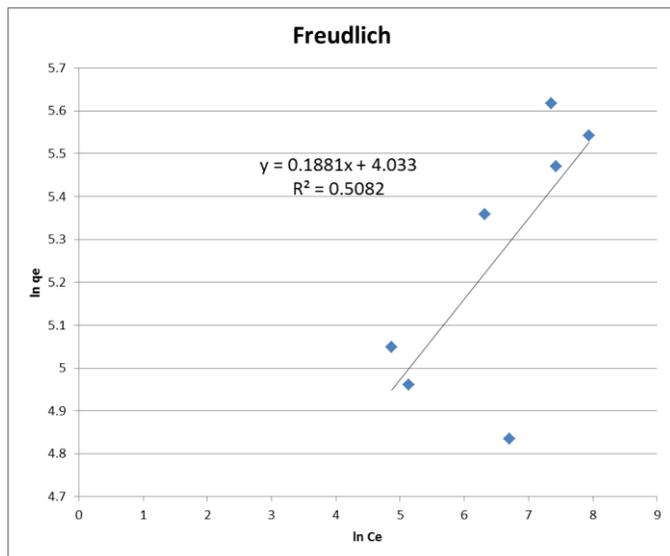


Fig. 8: Freundlich Isotherm Graph

The values from the time tests were used to plot the pseudo-second order graph, by plotting t/q_t vs. t , as in Fig. 9. The graph has a R^2 value closer to unity which indicates the suitability of the model to predict the adsorption behaviour of the copolymer and thus the K_2 value of -0.00092 (g/mg min) and q_e of 128.21 (mg/g) were calculated.

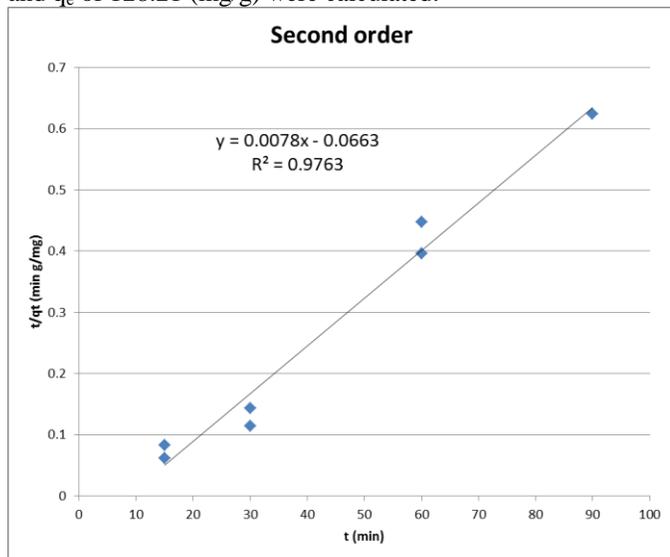


Fig. 9: Pseudo-Second Order Kinetic Model Graph

IV. CONCLUSION AND RECOMMENDATIONS

The chitosan-graft-polyacrylamide was successfully synthesized in this study and exhibited different physiochemical characteristics to the pure chitosan. The adsorption capabilities of the newly grafted copolymer was thus thoroughly investigated and shown to be adequate in removal of sulphates. The Langmuir isotherm model was found suitable to predict the adsorption behaviour of the copolymer, implying that the adsorption mainly occurred on the monolayer surface. Because of the high rate of adsorption there exists the possibility of industrial use of the copolymer in sulphate removal from acid mine water systems. The particles also remain solid and large enough that they may be filtered

out of the system easily, which opens the door for them to be used in a constant flow system in a water treatment facility.

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