

# The removal of $Mg^{2+}$ and $Ca^{2+}$ and turbidity from aqueous solution employing copolymerization of ethyl acrylate onto guar gum

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## Abstract

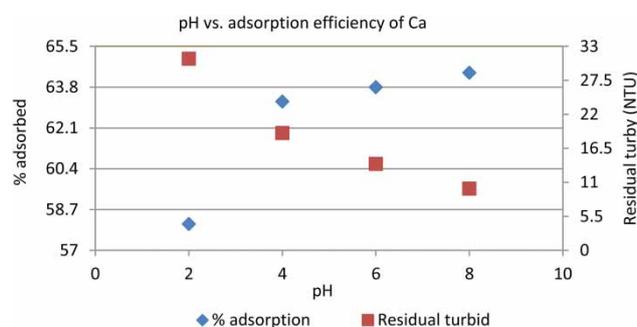
Acid mine drainage collected from decant in Krugersdorp, South Africa, was treated in a series of laboratory experiments using synthesized copolymer of guar gum-g-polymer (GG) for the removal of calcium and magnesium and turbidity. 250 mL of sample and 25 mL distilled water were added into 16 Erlenmeyer flasks. The samples were irradiated in a micro-oven at 900 W for 3 min and the mixtures were placed in a soxhlet extractor for homopolymerization, after which they were dried and crushed. The results showed an exponential increasing adsorption efficiency of calcium removal with increasing pH range 2–4, and a slight increase between the pH range 4–8. On the other hand, the results showed a continuous increasing adsorption removal efficiency of magnesium with increasing pH in a range 2–8. The results showed a slight increasing adsorption efficiency of calcium removal with increasing dosage between 15 and 25 mg/L of GG, an exponential increase between 15 and 35 mg/L and resuming a slight increase between 45 and 55 mg/L dosage. On the other hand, the results showed an exponential increasing adsorption efficiency of magnesium removal between 15 and 54 mg/L dosage and slight increasing trend between 45 and 55 mg/L dosage.

**Key words:** AMD, copolymer, gum-g-polymer, irradiated

## Highlights

- Treatment using waste materials.
- AMD treatment without pH adjustment.
- Treatment using sorption mechanism.

## Graphical Abstract



## INTRODUCTION

African countries are relatively rich in mineral resources, representing almost 40% of the minerals global reserves with coal, gold and copper as significant minerals. On the other hand, they are main contributors to acid mine drainage (AMD), a main source of water and environmental pollution. The environmental degradation attributable to AMD is an undesirable and uncontrollable phenomenon as production of AMD occurs in both active and ceased mining operations (Duan & Gregory 2002). Generation of AMD in gold, copper and coal mining operations is periodically discharged directly into local streams, thus exacerbating the quality of water. Notwithstanding the origin of the mine water, i.e. sand or slime dumps, flooded mines or direct discharge of effluents still contribute to environmental degradation (Naicker *et al.* 2003). The poor quality of AMD such as acidity, high concentration of toxic metals and sulphates prohibits discharge directly into public streams as it is a serious threat to marine life (Feng *et al.* 2004). Treatment of complex wastewater such as AMD requires appropriate selection of the reagents with high reactivity to be able to destabilize equilibrium force such as of van der Waals attractive and electrostatic repulsive forces that maintain water stabilization (Swartz & Ralo 2004). The reactivity of the reagents (coagulant/flocculant) is determined by the ability to reduce electrostatic forces of repulsion and reduce the diffuse layer (double layer compression). Commercial polyelectrolytes have been widely utilized as reagents in spite of a common problem of causing re-stabilization when overdosed (Swartz & Ralo 2004). Another disadvantage is their ability to operate effectively within a limited pH range. The complexity of AMD attributable to chemical composition; that is, inorganic matter, dissolved and suspended materials, colour, odour and toxic metals, is a main contributory factor perturbing physico-chemical leading to effective removal of contaminants. There are other reagents which have been exploited for the treatment of AMD such as in the neutralization process. Maree (2004) conducted studies on AMD using a neutralization process employing dosage and contact time as parameters. Despite attractive results shown by the process (Maree 2004), treatment of AMD has shown to be unaffordable and that renders effluent treatment in developing countries a serious challenge. The reaction rate of limestone when added as neutralizing agents proved to be dependent upon the quantity and surface area of the material, chemical composition of the colloid and contact time.

The removal of the turbid materials was obtained at pH values of 7.4 and 7.8, respectively. Other studies conducted by Ntwampe *et al.* (2015a, 2015b) used a combination of natural minerals and neutralizing agents with great success. However, their studies were circumstantial as they were focusing on the removal of the pollutants, unlike the present study, which focuses on specific toxic metals. Some of the studies were conducted on the removal of turbid materials using ferric salts without pH adjustment (Ntwampe *et al.* 2015c, 2016). The results revealed that ferric ions are easily removed from the wastewater (AMD) because they precipitate at a pH below 3.0. Research studies on this subject still continued where researchers exploited various technologies to improve removal efficiency of turbidity from the AMD (Wei *et al.* 2008; Sibrell *et al.* 2009; Buzzi *et al.* 2011). Some other researchers such as Bolto & Gregory (2007) employed technologies for wastewater clean-up, an approach which is also applicable to AMD. Buzzi *et al.* (2011) employed electrodialysis to treat AMD whereas others obtained fly ash from coal combustion (Gitari *et al.* 2008a, 2008b; Madzivire *et al.* 2009). The treatment of AMD with lime has been explored mainly for pH adjustment, although some use the technology as a main process for precipitation of toxic metals. Some of the profound applications that were introduced include controlling AMD at the source; such techniques included the use of thiocyanate compounds and phosphate derivatives (Mudder *et al.* 2005). Apart from commercial reagents explored in wastewater treatment, natural minerals have always been used as the main reagents (Waanders & Brink 2010; Gitari *et al.* 2011; Ntwampe *et al.* 2013a, 2013b).

As has been indicated, AMD contains a variety of pollutants ranging from minerals, toxic metals, sulphates, iron, inorganic matter, colour and odour, and it has been noticed that there is a

considerable amount of calcium and magnesium contributing to water hardness. The use of natural polymers for the remediation of water pollution is an eco-friendly process. Activated carbon, silica gel and alumina are the most common technologies considered to be effective industrial adsorbents; however, they were considered unaffordable particularly in developing countries. Application of plant materials produced or extracted from plants has been considered as an alternative approach mainly due to low cost implications, and that include chitosan, tannin, *moringa oleifera*, plantagoovata, starch, cactus, mize, *prosopis juliflora*, and mustard Bazanella *et al.* 2012; Beltran-Heredia & Sanchez-Martin 2009; Bodlund *et al.* 2013; Gunaratna *et al.* 2007; Jadhav & Mahajan 2014; Mandloi *et al.* 2004; NabiBidhendi *et al.* 2009; Pal *et al.* 2005; Szygula *et al.* 2008), among others. On the other hand, grafting of natural polymers has also been exploited due to their ability to increase adsorption capacity for the removal of metal pollutants present in water; an approach embarked upon in this present study. The study investigates copolymerization of guar gum-g-poly (ethyl acrylate) dosed to AMD for the removal of calcium and magnesium metals. Ethyl acetate is used primarily as a solvent and diluent, being favored because of its low cost, and low toxicity; it is an ideal adsorbent due to its characteristics such as being gel-like, adhesive, hardener and odourless. It is commonly used to clean circuit boards and in some nail varnish removers; in coffee, beans and tea leaf production it is used as a decaffeinator (Tan *et al.* 2018), which can be extended in paint manufacturing as an activator or hardener. On the other hand, guar gum is a galactomannan polysaccharide extracted from the guar bean, consisting of the sugars galactose and mannose. Its solubility provides it with an ability to react well with other compounds and considerable swelling property. Low pH of the AMD is attributable to its high rate of hydrolysis and loss of viscosity, including rapid swelling when pulverized to minute particle size. It is a thickening agent in various applications, and can also be used for weight loss by humans (Chapman 2012). It has almost eight times water thickening ability compared to other agents such as cornstarch; and is considered as an effective emulsifier, becoming a hydrocolloid used in producing thick pastes and thickening liquids or hot gels.

The aim of this study is to remove calcium, magnesium, and turbidity from the AMD in order to meet the required specification for various applications, using a copolymer (guar gum-g-poly (ethyl acrylate)) prepared by graft copolymerization under microwave irradiation in aqueous solution. The overall objectives of this study were to optimize the removal of the concentration of  $Mg^{2+}$  and  $Ca^{2+}$  ions and turbidity from the aqueous solution.

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## MATERIALS AND METHOD

### Preparation of adsorbent

10 g of guar gum (GG) was poured into 1 L of water and stirred for 10 min using a magnetic stirrer until a homogeneous solution was obtained. 2.5 g of ethyl acrylate was added to the mixture and stirred for another 10 min. 1.8 g potassium peroxydisulphate (initiator) was added to the mixture and stirred for 15 min. The optimum conditions for the synthesis of the copolymer were irradiation in a domestic microwave with a power of 900 W and an exposure time of 3 min. The grafted samples were placed in a Soxhlet extractor to dissolve all the homopolymer. The samples were dried and crushed.

### AMD sampling and characterisation

The samples were collected from the Western Gold Mine in Krugersdorp in a 25-litre plastic drum. The sample was air-tight and stored at room temperature. The pH, conductivity and turbidity (turbid materials) of the AMD sample before mixing were 2.78, 4.94 mS/cm, 147 NTU. Table 1 shows the chemical composition of the AMD sample.

**Table 1** | Chemical composition of raw AMD sample

Element	Conc (ppm)
Al	8.12
Co	6.72
Cu	8.37
Fe	36.1
K	6.79
Mn	34.4
Ni	5.46
Pb	6.22
Sb	4.78
Se	6.36
Zn	5.47

### Preparation of calcium and magnesium solutions

An additional amount of calcium and magnesium was added to the AMD; this was accomplished by preparation of 88 mg/L of hard water by diluting a mixture of 0.711 g of  $\text{CaCl}_2$  and 0.325 g of  $\text{MgCl}_2$  to a litre of distilled water as one of the protocols for preparation of hard water.

### pH measurement

A SensoDirect Multimeter (made in South Africa) pH/ORP/DO/CD/TDS meter with an electrode filled with silver chloride solution and an outer glass casing with a small membrane covering at the tip was used. The equipment was calibrated with standard solutions at pH of 4.0 and 7.0 before use.

### Conductivity

A similar Multimeter instrument to that described in sub-section 3.3.1 was used. The CD probe was connected and the measurement was selected using the appropriate button, and the CD reading was displayed.

### Turbidity measurement

A Merck Turbiquant 3,000 T Turbidimeter (made in Japan) was used to determine the turbidity of the suspended particles in the supernatant, using NTU as a unit of measure. It was calibrated with 0.10, 10, 100, 1,000 and 10,000 NTU standard solutions.

### Scanning electron microscopic analysis

A KYKY-EM3200 digital scanning electron microscope (model EM3200) equipment (China) was used to produce the SEM photomicrographs.

### Inductively coupled plasma (ICP-OES)

A Perkin Elmer Optima DV 7000 ICP-OES optical emission spectrometer (USA) was used to determine the metals (calcium and magnesium) in the supernatant of the AMD samples. It was calibrated with a standard solution between 2 and 50 mg/L of the salts mentioned above.

### X-ray diffractometric analysis

The X-ray diffraction (XRD) patterns of the samples were analysed using a Rigaku Miniflex II Desktop X-ray diffractometer (Japan) with Cu  $K\alpha$  radiation. A step size of  $0.02^\circ$  at a speed of  $4^\circ (2\theta)/\text{min}$  over  $10\text{--}80^\circ$  was applied. The minerals in VM treated between 950 and  $1,300^\circ\text{C}$  were quantified by Siroquant software.

### Adsorption capacity

First and second-order models are applied to investigate adsorption kinetics of an adsorbate onto adsorbent, i.e. turbid materials onto the flocculant. The models are common models, as shown by Equations (1) and (2).

Pseudo first order model

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

Pseudo second order model

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

where  $q_e$  is the adsorbed amount of the dye at equilibrium (mg/g),  $q_t$  is the adsorbed amount of turbid materials at a certain time  $t$  (mg/g) and  $k_1$  and  $k_2$  is the rate constant for the first and second order adsorption kinetics, respectively. Non-linear regression methods were used to determine these rate constants.

### Adsorption isotherm

#### Freundlich isotherm

The Freundlich model is applied to explain the adsorption of the turbid materials onto a heterogeneous surface of an adsorbent (GG flocculant). The model is applied for multilayer adsorption on the surface of a heterogeneous adsorbents; it is applied to plot  $\ln q_e$  vs.  $\ln C_e$  graph for the best-fit line that determines the  $R^2$  values for each pollutant adsorbed onto the copolymer, and a well-known logarithmic form of Freundlich is defined by the following equation:

$$\text{Log } q = \text{log } K_F + \frac{1}{n} \text{log } C \quad (3)$$

where  $K_F$  is the parameter related to the strength of the sorbed ion adsorbent binding,  $q$  is the saturation sorption capacity,  $K_F$  is a parameter related to the sorption capacity, and  $n$  is a measure of the sorption intensity.

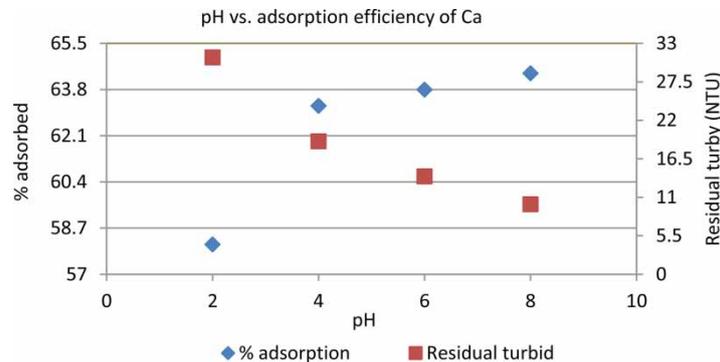
## EXPERIMENTAL PROCEDURE

The experiment was done in duplicate due to the large number of samples to be carried out. An amount of 0.025 g of the copolymer was added to each of the sixteen 250 mL Erlenmeyer flasks and thereafter 25 mL of distilled water was added. The calculated amount of 1,000 mg/L metal solution was added to each of the samples. The samples containing the metal ions were mixed in the temperature-controlled orbital shaker at 200 rpm for 10 min. 20 mL of each sample was transferred into a centrifugal tube and the samples were centrifuged at 4,000 rpm for 60 min. 15 mL of supernatant was transferred into poly top glass vials for ICP analysis. The samples were then taken away for various analyses.

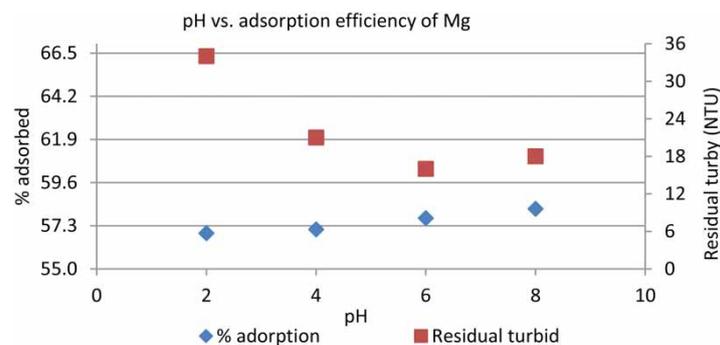
## RESULTS AND DISCUSSION

The study was to investigate the removal efficiency of the calcium and magnesium ion, turbid materials and toxic metals present in the AMD sample using synthetic copolymer prepared by grafted ethyl acrylate and guar gum. The experimental results showed a considerable removal of the pollutants in the AMD sample using the copolymer, also showing a better removal efficiency of calcium ions compared to magnesium ions. The results showed a best fit in the pseudo first order and Freundlich models. The grafted copolymers increased particle size compared to GG, which is evidence that ethyl acrylate was grafted successfully onto GG. The particles also differ in shape.

Figures 1 and 2 show the removal efficiencies of calcium and magnesium and residual turbidity in supernatant of the AMD treated with GG, respectively.



**Figure 1** | pH vs. removal efficiency of calcium and residual turbidity in the supernatant.



**Figure 2** | pH vs. removal efficiency of magnesium and residual turbidity in the solution.

The results show an increasing trend of removal efficiency of calcium with increasing pH in a range of 56.9–58, 2%. Increasing pH abates solubility of calcium and proliferates the rate of precipitation, assisting sorption by the flocculant. Calcium is a mineral salt which is required in water at a particular level as it forms part of the vital constituents required by plants and humans for specific functions; hence the removal efficiency is satisfactory because more than 60% constitutes to the deficiency of basic natural minerals. The complex mineral content of the AMD can cause high ionic strength and zeta potential due to the content of various minerals, hence strong destabilizing reagents are required to compress the diffuse and Stern layers' compression; a precursor of sorption for optimal removal of turbidity (pollutants), copolymer exhibits similar sorption performance to that shown by bentonite clay (Ntwampe *et al.* 2016), which can also be associated with high ion exchange capacity and physico-chemical reactivity.

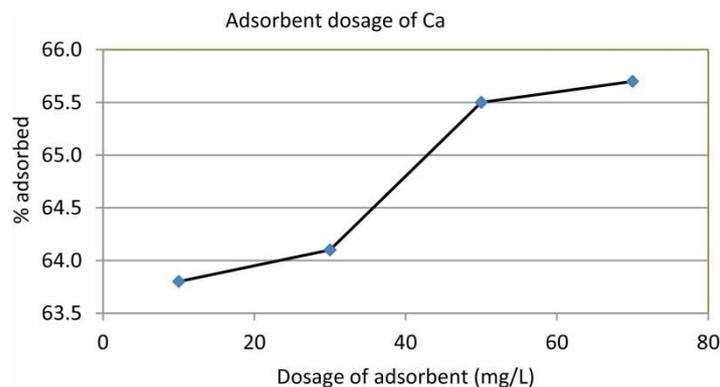
On the other hand, the residual turbidity showed a decreasing trend with increasing dosage from 147 NTU to a range of 35–16 NTU; however, the trend is non-linear, i.e. higher at pH 2 and decreasing significantly between pH 4 and 8 (21–16 NTU). Removal efficiency of the pollutants at pH 2 is 77.7%, a relatively positive removal efficiency; this confirms that the removal of the pollutants from treated wastewater is not entirely dependent upon the pH, but the destabilizing strength of a reagent (Flynn, 1984; Ntwampe *et al.* 2013b, 2016). The removal of the pollutants was ameliorated by extra synthesized calcium, particularly at higher pH values. Its solubility was abated at higher pH to form precipitates, which act as secondary flocs for emerging smaller flocs referred to as primary flocs during the nucleation process. The rate of hydrolysis also increases with increasing pH, improving the removal efficiency of pollutants. The residual turbidity at pH 4 is slightly higher compared to that of 6 and 8, which is almost identical at both pH values. The observation shows that the copolymer reached maximum efficiency. It is suggested that the flocculant reached equilibrium point at pH 8. Figure 2 shows the relationship between the pH and the removal efficiency of calcium and turbid materials present in the AMD sample.

Taking in consideration the chemical structure of ethyl acetate,  $\text{CH}_3 - \text{COO} - \text{CH}_2 - \text{CH}_3$ , a double bond between the second carbon and oxygen atoms provides the compounds with higher reactivity. The compound has a glue-like property, which makes it an ideal adsorbent of adhesive property; it can also be considered as an ester of ethanol and acetic acid mostly used a solvent. The removal efficiency of turbid materials in general (Figure 2) is an direct representative of the characteristics of ethyl acetate, invoked by its use as a hardener and adhesive as afore-mentioned. The results show increasing removal efficiency of magnesium with increasing pH by 58.1–64.4%; efficiency slightly higher than that of calcium as afore-mentioned. Magnesium, as much as calcium, is a mineral salt which is required in water at a particular level as it forms part of the vital constituent in water bodies. The pH range under which the experiment was conducted is a suitable range for reactivity of magnesium. According to Metcalf & Eddy (2003), the advantage of dosing  $\text{Mg}(\text{OH})_2$  in the solution at elevated pH is attributed to its ability to adjust to a maximum pH of 9.0, acting as a buffer that controls the pH of the wastewater within active range. Such a property is not common with  $\text{Ca}(\text{OH})_2$ , which is able to raise the pH of the wastewater until it reaches a maximum of 12.0. Magnesium salts form  $\text{Mg}(\text{OH})_2$  precipitates when the pH is raised above 9.5, and precipitates are not complete until the pH reaches 11 (Metcalf & Eddy 2003). Increasing trend of adsorption efficiency can also be explained as being effected by the decreasing concentration of hydronium ions ( $\text{H}^+$ ) with increasing pH, resulting in competing effect for the adsorption sites that are abated.

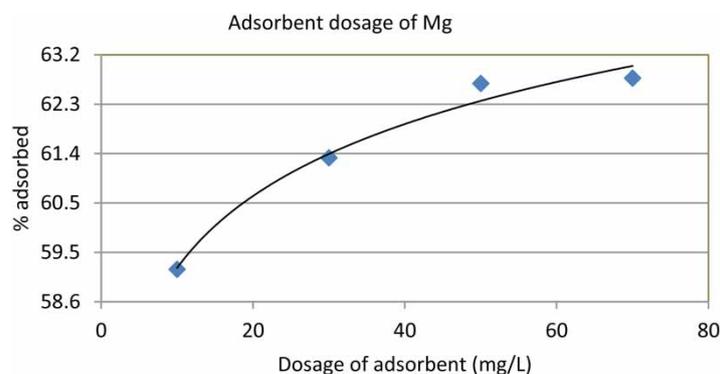
Residual turbidity showed a decreasing trend with increasing dosage from 147 NTU to a range of 31–10 NTU, the trend is also non-linear. Sorption with ethyl acetate is influenced by a series of reactions occurring in aqueous solution such as hydrolysis resulting in acetic acid and ethanol. Based on a basic state, it has an accelerating capacity for hydrolysis, which is subject to the formation of metal precipitates, these being calcium, magnesium, toxic metals and other hydrolysable materials present in the wastewater in this study. The resultant ethyl esters are typically hydrolyzed in a two-step process

starting with a stoichiometric amount of a strong base such as a metal hydroxide, ameliorating the turbidity removal performance.

The removal of magnesium at pH 2 is higher compared to that of the samples between pH 4 and 8 (19–10 NTU), including the removal of calcium at pH 2 (Figure 1). The removal efficiency of the pollutants at pH 2 is 78.9%, relatively positive removal efficiency. Figures 3 and 4 show the removal efficiencies of calcium and magnesium in a supernatant of the AMD treated with 20–60 mL of a flocculant. Apart from the removal efficiencies of calcium and magnesium, the copolymer also exhibited optimal removal of other metals and metalloids. The removal efficiency of toxic metals such as Co, Cu, Ni, Pb, Sb, Se and Zn was reduced from 6.72, 8.37, 5.46, 6.22, 4.78 and 6.36 to 0.258, 0.347, 0.675, 0.189, 0.270, 0.395 and 0.415 mg/L respectively (Table A2). Figure 3 shows the relationship between the adsorption efficiency of calcium in the solution and the dosage of the copolymer.



**Figure 3** | Dosage of copolymer vs. adsorption efficiency of calcium in the solution.

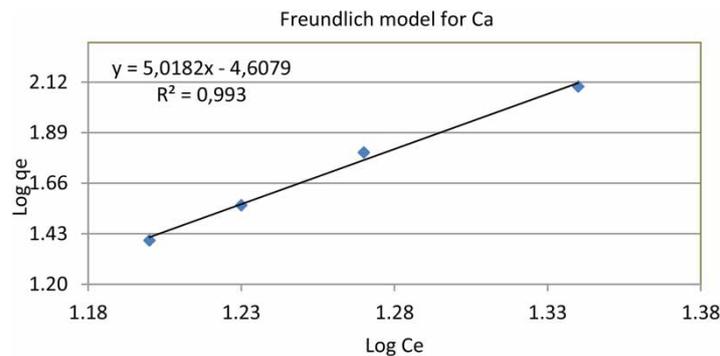


**Figure 4** | Dosage of copolymer vs. adsorption efficiency of magnesium in the solution.

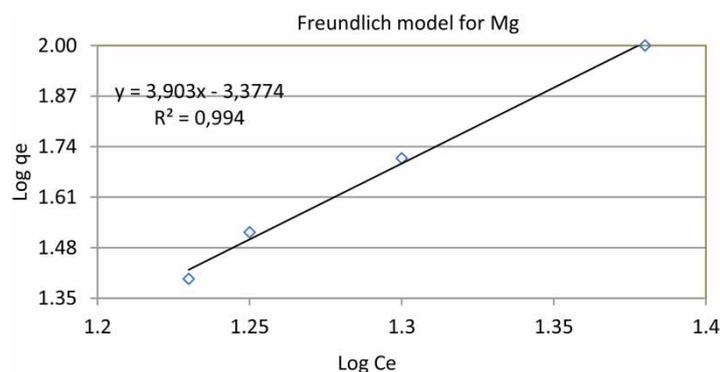
It is a fact that a selection of an adsorbent is based on certain properties such as surface area, adsorption capacity, ionic exchange, cationic exchange capacity, selectivity, and so on, a treatment system showing high removal efficiency is indicative of association to almost all of those properties. The changing trend of the adsorption capacity of calcium is not linear, but exhibits a zig-zag pattern which shows that there is a sudden increasing rate of reactions taking place between each dosage. The trend shows the adsorption capacity of copolymer during both chemical and physical reactions that occurred since its addition until the final stage. Figure 4 shows the relationship between the adsorption efficiency of magnesium in the solution and the dosage of the copolymer.

The adsorption changing trend of magnesium increases with increasing dosage in a similar manner as calcium, but its curve is slightly linear compared to that observed with calcium. The observation

shows that magnesium reacted consistently with dosage, which is also indicative of the effect of pH on the removal of magnesium. The inference is based on the fact that increasing dosage elevated the pH of the system, which suggests that both the pH and the quantity of the copolymer influenced the removal efficiency of magnesium consistently. The concept is also applicable to calcium removal efficiency, but the reaction rate varies with increasing pH and the quantity of the copolymer. Figures 5 and 6 show the experimental data fitted in the Freundlich model to determine the thermodynamics of the processes.



**Figure 5** | Freundlich model showing adsorption capacity of calcium onto copolymer.



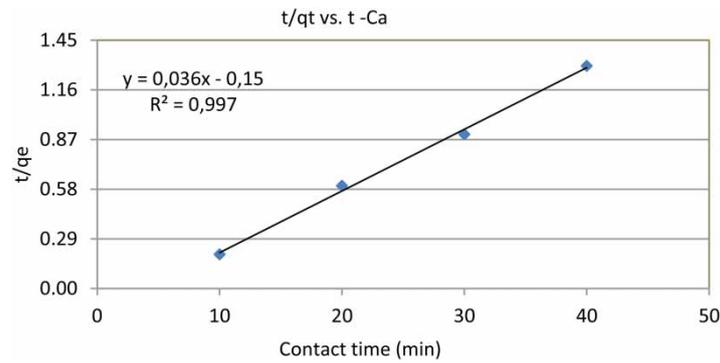
**Figure 6** | Freundlich model showing adsorption capacity of magnesium onto copolymer.

It is observed that the value of the determination coefficient is close to unity, implying that the Freundlich model is suitable for prediction of the adsorption behaviour in this study. The correlation regressions between  $\log q_e$  and  $\log C_e$  in both removal efficiencies of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions are close to unity, 0.993 and 0.994 respectively, which indicates that the adsorption process was favourable under prevailing conditions, and the thermodynamic process revealed that the processes by copolymerised GG were spontaneous and the adsorption was both endothermic and physical in nature.

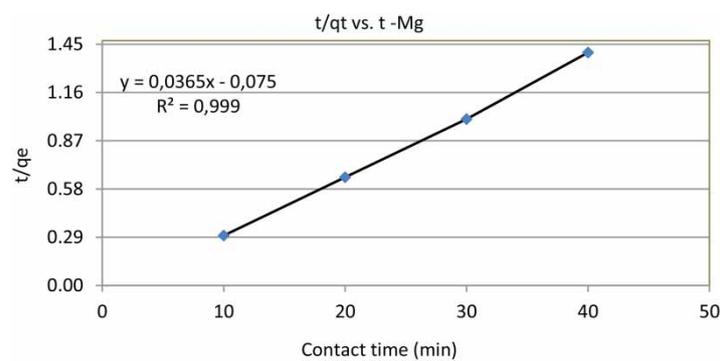
Figures 7 and 8 show graphs representing the pseudo first order model in order to illustrate the trend of the experimental results using the ratio of time and adsorption vs. contact time; the correlation regression ( $R_2$ ) was determined using both x and y values.

The pseudo second order model was also applied for the kinetic study of the adsorption of the concentration of  $\text{Ca}^{2+}$   $\text{Mg}^{2+}$  ions. The  $R^2$  values for the adsorption of both metal ions are similar to those observed with Freundlich; that is, close to unity, equal to 0.997 and 0.999 respectively. The observations suggest that the pseudo-second order rate model is an appropriate assumption for experimental data.

Figure 2 A1 and A2 show the XRD graph of the substances appearing in the sludge of the sample dosed with copolymer and the SEM micrographs of the sludge of the sample dosed with the



**Figure 7** | Pseudo first order plot for calcium onto copolymer.



**Figure 8** | Pseudo first order plot for magnesium onto copolymer.

copolymer respectively. The intensity of the peaks of the copolymer is greater than that of the polymer, which is evidence of ethyl acrylate being grafted on the polymer backbone. The SEM micrograph of grafted copolymers (a) shows increased particle size compared to GG (b), which is evidence that ethyl acrylate was grafted successfully onto GG. The micrograph shows a grafted copolymer morphological structure exhibiting tightly fragmented flocs joined together leaving less than 8% area with voids which resulted during the grafting process; on the other hand, the micrograph showing the GG morphological structure reveals isolated dense flocs surrounded by voids occupying more than 50% of the area. The micrograph showing the copolymer is an ideal representative of optimal metal adsorption or removal from the solution, with prospects of high adsorption capacity attributable to their small size and large surface area. The double bond between the carbon and oxygen of ethyl acetate in the copolymer breaks during physico-chemical reactions in the system. A lone pair of electrons makes it an electron donor, increasing nucleophilicity of the polymer, which then behave as a convenient linker between the ions of the turbid materials and the copolymer. As [Yaghoubi & Ramazani \(2018\)](#) explained, in the adsorption mechanism between the functional groups of amine and the carbon nanotubes, the lone pairs of the ethyl acetate makes it an electron donor, a special chemical feature that characterizes a copolymer as an appropriate nucleophile ([Yaghoubi & Ramazani 2018](#)). The adsorption characteristics of ethyl acetate also include the physico-chemical properties attributed to guar gum, mainly its ability to form a gel and act as a thickener, an attribute to high sorption capacity of turbid materials. Its larger surface area, when pulverised to small particle size, created a larger surface area that optimized sorption of calcium ions and other turbid materials. It also increases the hydroxyl ions during hydrolysis in its primary form as sugar molecules to form metal hydroxyl species, which during nucleation formed larger settleable agglomerates, hence the low residual turbidity in treated effluent (supernatant). The physico-chemical properties of a combination of ethyl acetate and

guar gum (copolymer) provide it with a high sorption capacity, as reflected by high removal of calcium, magnesium, toxic metals and other pollutants.

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## CONCLUSION

The results showed an exponential increasing adsorption efficiency of calcium with increasing pH range of 2–4, and a slight increase in the pH range of 4–8. On the other hand, the results showed a continuous increasing adsorption removal efficiency of magnesium with increasing pH in a range of 2–8. The results showed a slight increasing adsorption efficiency of calcium removal with increasing dosage between 15 and 25 mg/L of a copolymer, an exponential increase between 15 and 35 mg/L and a slight increase resuming between 45 and 55 mg/L dosage. On the other hand, the results showed an exponential increasing adsorption efficiency of magnesium removal between 15 and 54 mg/L dosage and a slight increasing trend between 45 and 55 mg/L dosages. The data also fitted the pseudo second order model for the prediction of the binding capacity; it was therefore found that the copolymer had a higher adsorption capacity for calcium compared to magnesium. The copolymer showed high removal efficiency of turbid materials (turbidity). It is observed that the value of the determination coefficient is close to unity, implying that the Freundlich model is suitable for prediction of the adsorption behaviour in this study. The values of  $1/n$  are bigger than 1.0, this indicated that the adsorption process is favourable at higher concentrations. The results obtained from the experimental data show a correlation regression ( $R^2$ ) of 0.993 and 0.994 for calcium and magnesium using the pH vs. adsorption efficiency applying Freundlich adsorption isotherms; the data then exhibited 0.997 and 0.999 correlation regression using the dosage vs. adsorption efficiencies of calcium and magnesium respectively.

Although a perception is created that metal hydroxides are water softeners, the principal process occurring during the process is mainly promotion of the hydrolysis process for adsorption after being added to wastewater containing toxic metals and hydrolysable turbid materials. They suppress solubility of hydrolysable materials to form precipitates of metal hydroxides; where the rate of the production of  $\text{Ca}(\text{OH})_2$  precipitates was faster compared to that of  $\text{Mg}(\text{OH})_2$  precipitates, an inference invoked by the removal efficiencies of both metal ions. The copolymer showed a high removal efficiency of other toxic metals and turbid materials. The results show increasing trend of removal efficiency of calcium with increasing pH in a range of 56.9–58.2%. Increasing pH abates the solubility of calcium and proliferates the rate of precipitation, assisting sorption by the flocculant. The observation shows that magnesium reacted consistently with dosage, which is also indicative of the effect of pH on the removal of magnesium. The inference is based on the fact that increasing dosage elevated the pH of the system, which suggests that both the pH and the quantity of the GG influenced the removal efficiency of magnesium. The SEM micrographs of the copolymer is identified more by moderate size flocs joined together to form a sponge-like structure, indicating that the removal of turbid materials was a physico-chemical phenomenon.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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