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ORIGINAL RESEARCH

Modern technologies used to treat acid mine drainage by using a polymer-based adsorbent (chitosan and natural fibres)

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The treatment of acid mine drainage (AMD) and the removal of heavy metals and sulphates have remained a challenge for society. This is because it is a serious and life-threatening problem that is encountered worldwide wherever sulphide rocks are exposed to the water and oxygen. Researchers have found that the most effective method when treating AMD is with the use of biodegradable adsorbent membranes, made from chitosan and natural fibres, or chitosan and naturally occurring minerals, e.g. titanium dioxide. The most effective wastewater (acid mine drainage) treatments, using adsorbent membranes are reviewed in this report. This review looks at the cost of installing adsorbent membranes and makes a comparison to traditional treatment technologies used in the treatment of AMD. Polymer-based adsorbents are compared to the traditional treatment technologies used in the treatment of AMD, and the use of polymer-based materials as advanced materials for heavy metal removal and AMD treatment is reviewed. The effect that this new technology has on the environment and human beings is also investigated.

Keywords: acid mine drainage (AMD), polymer, adsorbent, heavy metals, sulphates

Moderne tegnologieë wat gebruik word om suurmyndreinering te behandel deur gebruik te maak van ’n polimeergebaseerde adsorbeermiddel (chitosaan en natuurlike vesels): Die behandeling van suurmyndreinering (SMD) en die verwydering van swaarmetale en sulfate bly steeds ’n uitdaging vir die samelewing. Die rede hiervoor is omdat dit ’n ernstige en lewensgevaarlike probleem is wat wêreldwyd voorkom waar sulfiedgesteentes aan water en suurstof blootgestel word. Navorsers het bevind dat die doeltreffendste metode om SMD te behandel die gebruik is van bioafbreekbare adsorberende membrane, gemaak van chitosaan en natuurlike vesels, of chitosaan en natuurlik voorkomende minerale, bv. titaandioksied. In hierdie verslag word ’n oorsig gedoen van die doeltreffendste behandelings vir afvalwater (suurmyndreinering) wat van adsorberende membrane gebruik maak. Hierdie oorsig kyk na die koste van die installering van adsorberende membrane en tref ’n vergelyking met tradisionele behandelingstegnologieë wat in die behandeling van SMD gebruik word. Polimeergebaseerde adsorbeermiddels word vergelyk met die tradisionele behandelingstegnologieë wat by die behandeling van SMD gebruik word, en daar word ’n oorsig gedoen van die gebruik van polimeergebaseerde materiale as gevorderde materiale vir swaarmetaalverwydering en SMD-behandeling. Die effek wat hierdie nuwe tegnologie op die omgewing en mense het, word ook ondersoek.

Sleutelwoorde: suurmyndreinering (SMD), polimeer, adsorbeermiddel, swaarmetale, sulfate

Introduction to acid mine drainage (AMD) and its effects

Acid mine drainage is toxic waste with a high concentration of metal ions and sulphates present in a water source (Bwapwa, 2018; Bwapwa, et al., 2017). It is created when sulphide-bearing minerals, such as pyrite react with water and oxygen to form sulphuric acid (Bwapwa, 2018; Bwapwa, et al., 2017). The oxidation of pyrite releases ferrous ions and causes the water to become acidic. Acidic water causes heavy metals to be dissolved from the rocks and the conversion of ferrous ions to ferric ions. Consequently, acid mine water is comprised of iron oxides, sulphates, and heavy metals, such as chromium, copper, iron, aluminium, nickel, etc. Industrial activities, such as mining, metal plating and construction have been shown to be the sources of the chemicals found in AMD. AMD poses an environmental and health hazard (Igerase, et al., 2018). The extremely low pH and high ionic content of AMD are responsible for its toxicity and remediation and the disposal methods are costly because the storage of the waste material is usually required.

The removal of these toxic substances is very important and has been performed by using different techniques (Heidari, et al., 2013) including ion exchange, adsorption, chemical precipitation, membrane filtration, chromatography, and electrochemical treatment technologies. These methods have their own advantages and disadvantages.

Chemical precipitation is a widely used method of wastewater treatment because it is a very simple method. The chemicals used to neutralise wastewater in chemical precipitation are: lime, calcium carbonate, caustic soda and soda ash, which results in the formation of sludge. The main disadvantage of this method is that the chemicals used react with the heavy metal ions to form insoluble precipitates (sludge), which must later be processed (Haiming, et al., 2012). The decantation and discharging of the sludge create a secondary environmental problem (Oncel, et al., 2013).

Ion exchange has also been widely used for the removal of heavy metals from waste effluents because of its numerous advantages, such as treatment capacity, better efficiency and high kinetics (Dabrowski, et al., 2004). Materials that are preferred for ion exchange techniques are the synthetic resins over the naturally occurring zeolites, since they have the capacity to effectively take-up the heavy metals from a solution. Their disadvantage is that their effectiveness is short-lived because of certain variables, for example pH, temperature, initial metal concentration and contact time (Daohai, et al., 2014).

The membrane filtration process includes: ultra-filtration, microfiltration, reverse osmosis, nanofiltration and electrodialysis (Fu & Wang, 2011). This type of method has shown great potential in the recovery of heavy metals, but its capacity is affected by fouling of the membranes and enormous energy consumption due to high requirements for the supply of high pressures for pumping and maintenance of the membranes. Membrane fouling is the decline in membrane permeation as a function of time (Robinson, et al., 2016).

Most of these treatment technologies are very difficult to execute and have slow reaction rates, thus causing AMD to be left untreated (Igerase, et al., 2018). The high cost of these traditional treatment technologies has created economic pressure, hence motivating engineers to create inexpensive and environmentally-friendly ways to treat AMD. Wetlands have also been used as an alternative method to remove heavy metals at a low cost (Igerase, et al., 2018).

The adsorption technique has been confirmed to be the most effective technique for heavy metal removal from wastewater. This method is effective and economical. The adsorption process is flexible in operation, easy to install and design. In several cases, it has produced high quality treated effluents. This process is reversible and is responsible for the subtraction and release of the substances. Hence, the use of an adsorbent with good thermal and mechanical properties becomes important. Biosorbents, such as chitosan composites are advantageous since they are effective and efficient in the treatment of wastewater (Chen, et al., 2011).

This review paper describes the ideal method for wastewater treatment, based on cost, effectiveness and efficiency, and compares traditional wastewater treatment technologies to the adsorption technique, which is gaining prominence. Furthermore, this paper reviews the use of polymers, such as chitosan and natural fibres as advanced materials for use in the treatment of wastewater.

Materials and methodology

Selecting processing techniques

It is critical that the most suitable processing technique is selected. Factors which are mostly taken into consideration by researchers, include application, desired properties, shape and size of the final product, nature of the raw materials used and the processing parameters (Ho, et al., 2012). The size of the nanocomposite and parameters used to process the nanocomposite are important factors when choosing the processing techniques. Adsorption was chosen because it has been confirmed to be the most effective technique for heavy metal removal from AMD.

Natural fibre preparation

Natural fibres are made from cells called fibres. They are called fibres because of their relative length. They consist of hemicellulose, cellulose, lignin, pectin, waxes and water-soluble substances. Hemicellulose and pectin play a significant role in the integration of bundle strength, water absorbency, elasticity, swelling and wettability strength. Most matrices are hydrophobic in nature thereby, causing them to have poor adhesion when reinforced with natural fibres.

Natural fibres are known to debond from a matrix when they are not chemically treated, causing poor mechanical properties on the composites formed (Leao, 2005; MacVicar, et al., 1999). Interfacial adhesion between a fibre and matrix is a very important factor, hence the use of chemical modification on the fibre's surface (Matthew, et al.). The mechanical and adsorption properties of a fibre/chitosan nanocomposite, depend on interfacial adhesion holding them together. Good adhesion provides good adsorption capabilities, impact, and tensile properties. In order to obtain a good final product (nanocomposite) with good properties, it is vital to have fibres which are hydrophobic. This is achieved by using chemical, physical, and surface treatments. Chemical treatments include sulphuric acid, alkaline and acetylation. The treatments are used to modify the external properties of the fibre so as to increase the strength of the bond between the fibre and the chitin/chitosan since as it (chitosan) has hydroxyl groups on its structure, which will minimise water absorption of the fibre. Several researchers have carried out studies on the chemical treatment of natural fibres (Kuenen & Robertsen, 1992; Hasan, et al., 2007; Lantzy & MacKenzie, 1979; Guibal, 2004).

In the preparation of sisal fibre, Perry soaked it in liquid nitrogen at room temperature to render it brittle for milling. It was crushed to 200 microns and was kept in an oven at 60 °C until the next process in order to remove moisture (Phiri, 2012). Natural fibres have been grouped according to their origin – bast, seed, leaf, and fruit. Those that are commonly used in the composite application, are the hard types, which are bast and leaf. Their examples include hemp, jute, flax, kenaf, banana and sisal (Leao, 2005).

Chitosan powder preparation

Chitin is a carbon-based polymer found in insects, cell walls of fungi and exoskeletons of crustaceans (Guibal, 2004). Through chemical deacetylation, it is converted to chitosan. Chitosan gets protonated at acidic pH in order to become water soluble. In this protonated state, the anion becomes positively charged and this intercalates with the negatively charged dichromate ions via electrostatic attraction. Chitin contains 2-acetamido-2-deoxy-β-D-glucopyranose residues, while chitosan contains 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glucopyranose residues (Hamdine, et al., 2005). Natural chitosan is chemically or physically treated in order to enhance its adsorption properties. Chitin and chitosan have been shown to be good biosorbents because of their low cost and the amino and hydroxyl functional groups present in chitin and chitosan have shown high adsorption potential (Bhatnagar & Sillanapaa, 2009).

Results and discussion

In several studies, it has been found that a number of functional groups play a significant role in determining if a membrane is suitable for adsorption of AMD. Studies on chitin have shown that it can have an adsorption capacity as high as 14 mg/g for cadmium ions. These studies were done by using the SEM coupled with an X-ray energy dispersion analysis (Benguella & Banaissa, 2002).

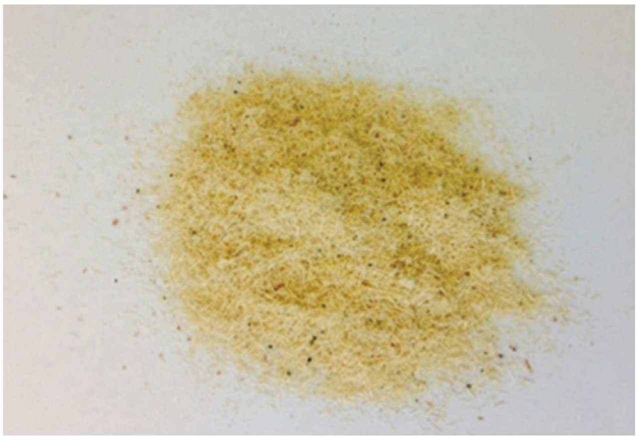

Figure 1: Picture of a treated and milled sisal fibre (Phiri, 2012)

Jha et al. (1988) investigated the efficiency of chitosan when removing cadmium (II) at a pH of between 4.0–8.3. They found that chitosan showed an adsorption capacity of 5.3 mg/g. McKay et al. (1989) reported the fact that chitosan had adsorption maxima of 813, 222, 164 and 75 mg/g for Hg (II), Ni (II), Cu (II) and Zn (II), respectively. The kinetic equilibrium and mass transfer aspects were considered when doing these studies. Aydin and Aksoy (2009) did the equilibrium isotherm studies, which showed that the adsorption of Cu (II) by chitosan or chitin was best described by the Langmuir and Redlich-Peterson models. The adsorption capacity of chitosan for Cu (II) was observed to between 4–5 times higher than that of chitin. Studies have shown that the heavy metal uptake by chitosan was pH-dependent. The rate of removal of heavy metals by chitosan was observed to have increased the pHs of between 4–7.

Kalyani et al. (2005) synthesised a biosorbent chitosan composite, which comprised of chitosan coated on perlite ore, and studied the Cu (II) and Ni (II) removal. A maximum metal uptake was obtained at a pH of 5. The maximum monolayer adsorption capacity of copper ions was found to be 196.07 mg/g, while for nickel ions, it was found to be 114.94 mg/g.

Aydin and Aksoy (2009) studied the removal of chromium (Cr (VI)) by using chitosan. They studied the effect of pH, initial concentration, and adsorbent dose. The pH studies were carried out from a pH range of between 1.5–9.5, the initial concentration varied from 15 to 95 mg/L and the adsorbent dose from 1.8 to 24.2 g/L. The maximum removal was achieved at a pH of 3 at an initial concentration of 30 mg/L and an adsorbent dose of 13 g/L. A maximum adsorption of 102 mg/g was found when using an initial concentration of 100 mg/L. The pseudo second order kinetic model was shown to have the highest correlation with these data.

Perry (2015) conducted a study on the micro-composite made from sisal fibre and chitosan for the removal of chromium and sulphates from AMD. The effect of chromium ion concentration on adsorption was studied by using the adsorption isotherms.

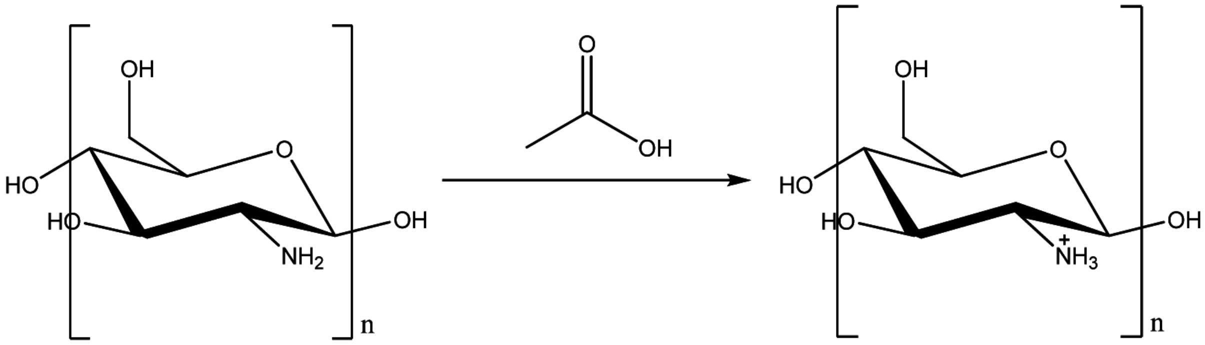

Figure 2: Chemical deacetylation of chitin into chitosan (Guibal, 2004)

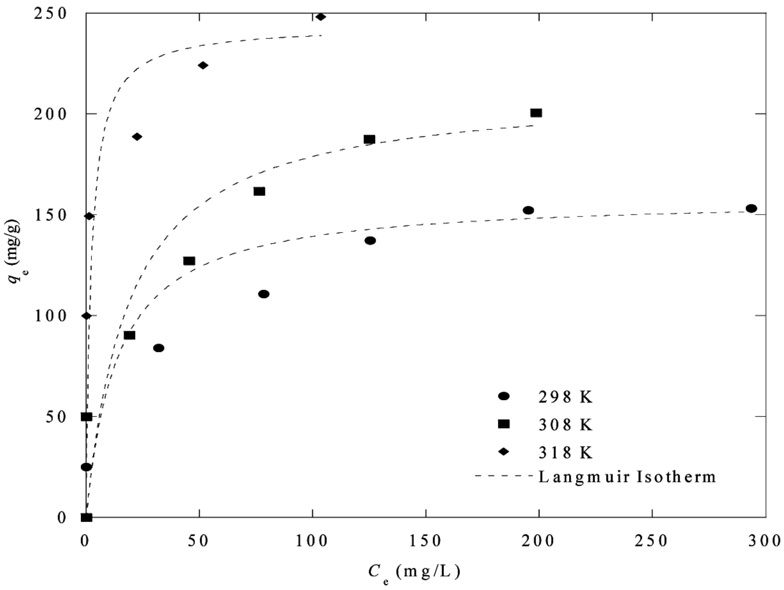

Figure 3: Sorption isotherms for Cr (VI) adsorption onto sisal/chitosan micro composite at varying temperature (Perry, 2015)

It was found that the adsorption capacity increased with an increase in the initial concentration of chromium. An increase in temperature has shown to have increased the mobility of the Cr (VI) ions towards the active sorption sites.

The pH studies that were carried out at different pH values, showed that a 100% removal of chromium was achieved at a pH of 2, meaning that the efficiency of the contaminant's removal was pH-dependent. Thermal studies showed that sisal fibre served as a flame retardant by reducing mass loss (Perry, 2015).

Abou Kana et al., (2013) prepared three (3) chitosan nanoparticles of different sizes (diameters) through the reaction of chitosan with tripolyphosphate (TPP). The diameter of the nanoparticle was found to have been affected by the concentration of TTP solution was therefore, made by dissolving 16 mg of chitosan in 1 litre of 2% acetic acid at a temperature of 60 °C. An amount of 36.7 mg of tripolyphosphate was dissolved in 1 litre of distilled water in order to make 0.1 M solution. The interaction between chitosan and TPP to form nanoparticles was through ionic interaction. There was the stretching and vibrations of the NH and OH groups in chitosan in the FTIR spectra, at a wavenumber of 3440 cm^{-1}. The broadband increased when cross linking in chitosan nanoparticles was introduced. Acetylated amine appeared near the 1650 cm^{-1} wavenumber. The band at 1065 cm^{-1} wavenumber is due to the combined effects of C-N stretching vibrations of the primary amine and C-O stretching vibrations from the primary alcohol in chitosan (Abou Kana, et al., 2013).

The studies of the X-ray diffraction patterns of the chitosan nanoparticles with different sizes have shown the peak of the semi-crystalline structure of a reformatted chitosan, and it was considerably reduced at a diffraction angle of 10°. The smaller the diameter of the adsorbent, the higher the adsorption capacity. Large surface areas of the effective sites, gave the maximum uptake capacity (Abou Kana, et al., 2013).

The size and dosage are the most important parameters for the adsorption process; because they determine the adsorption capacity of the adsorbent or the effectiveness of the adsorbent. The results have shown that the dosage of 16 and 24 mg/L of chitosan nanoparticles were the most effective dosages for the maximum removal of heavy metals and other impurities. Chitosan nanoparticles have been found to have high charge density. The charge density increased with an increase in adsorption. On the other hand, the dosages of 32 and 40 mg/L, performed poorly due to the excess polymer leading to saturation, whereby there were no active sites available for the impurities to settle on, as shown in Figure 5. The optimum dose was reached at 24 mg/ℓ, which removed ~88.5% for the ratio 1:1 of TTP. The total suspended solid (TSS) removed was 95.2%. The maximum removal of TSS was achieved at a ratio of 1:5 TPP and at a dose of 16 mg/L (Abou Kana, et al., 2013).

Conclusion

The use of chitosan and its derivatives is continually gaining significant attention in the treatment of AMD because of its outstanding adsorption capacity, especially for metal ions and because the material is cheap, non-toxic, biocompatible, and biodegradable. However, there are gaps in the treatment of AMD which need to be filled. Despite the various AMD treatment technologies and materials, natural polymeric materials have been proven to be the most effective when dealing with AMD. This is because of their excellent properties and conservation of the environment, animals, aquatic life and humans. Most treatment technologies are limited by their high cost, difficulty in execution, non-biodegradability, negative impact on the environment and the threat to human life. It is urgent and highly

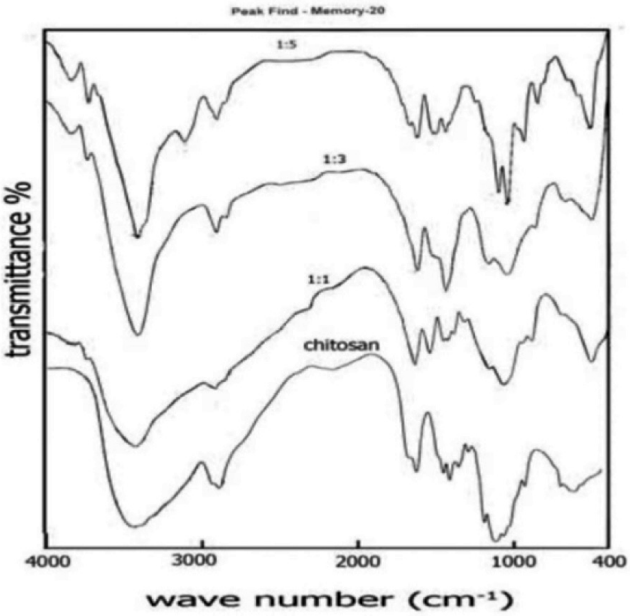

Figure 4: FTIR spectra of chitosan and its nanoparticles of different degree of cross linking (Abou Kana, et al., 2013)

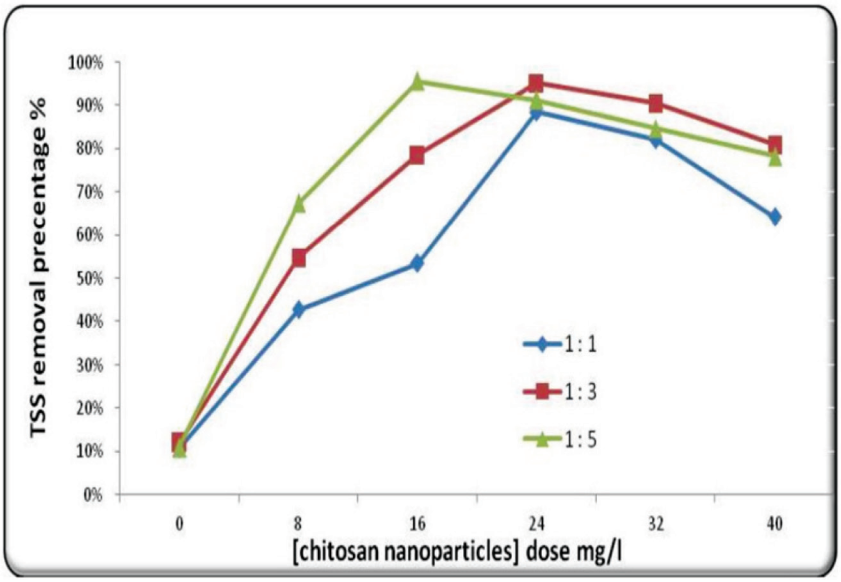

Figure 5: Effect of different doses and sizes of nano-chitosan on percentage of total suspended solid (TSS) removal (Abou Kana, et al., 2013)

pertinent to design and develop an adsorbent material from chitosan and a natural fibre, which can solve this AMD problem. Some of the important issues concerning the AMD treatment with chitosan are summarised below:

- Selection and identification of the types of chitosan for maximum metal and sulphate uptakes.
- Regeneration studies to recover the metals, sulphates and the appropriate adsorbents, needed to enhance the economy.

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