

Evaluation of Chitosan-Bentonite Composite Performance towards Remediation of Sulphate Containing Effluent

S. Mbakop, N.H Mthombeni, T.Y Leswifi, M.S Onyango

Abstract— Urbanization and industrialization in developing countries play a great role in exacerbating water scarcity by driving up the water demand as well as polluting natural water resources. Nanomaterials have recently been on the spotlight of many research studies in environmental remediation due to their exceptional physicochemical properties. Consequently, this work is part of a wider project aimed at developing a large scale production process of chitosan-bentonite composite for real field application as most adsorption media development are limited to laboratory scale synthesis. This paper discusses the adverse effects of sulfate anions on living organisms and the existing and potential techniques for removal of this pollutant from industrial wastewaters. Moreover chitosan-bentonite composite was prepared as an adsorbent and characterized. Preliminary adsorption experiments were conducted and the effects of solution pH and adsorbent dosage on the removal of sulfate from aqueous solutions were investigated. The adsorption capacity achieved so far provides a strong motivation to further develop the material for industrial application.

Keywords—Adsorption, nanomaterials, wastewaters, sulfate.

I. INTRODUCTION

Sulfate naturally originates mostly from the processes of chemical weathering of sulfur containing minerals and the oxidation of sulfides and sulfur [1]. Thus it is a major anion present in natural water resources and industrial effluents from acid mines and inorganic chemical industries [2]. Unlike arsenic, nitrate and certain notorious heavy metals, sulfate has a low toxicity level and therefore no primary standard for drinking water or aquatic life [3]. However, increased sulfate concentrations in public water supplies present a potential health hazard. Prolonged human exposure to high sulfate concentrations through excessive ingestion via the food chain or water uptake could cause catharsis, dehydration and gastrointestinal irritation [4]. Consequently sulfate concentrations in water bodies have come under increasing scrutiny from regulatory authorities over the past two decades [5].

Conventional techniques regarding sulfate removal from aqueous solutions include biological treatment [6], ion exchange [7], electrodialysis [8], reverse osmosis [9], chemical precipitation [10] and sorption [11]. Most of these

technologies have limitations such as small-scale application, large consumption of reagents, space and energy requirement, high operational and maintenance costs and huge volume of sludge generation [12]. Recently researchers have focused their attention on the removal of sulfate via adsorption [13]. As a result several adsorbents such as γ -Al₂O₃ [14], chitin based shrimp shells [15], goethite [16] and polypyrrole-grafted granular activated carbon [17] have been used to remove sulfate from aqueous solutions. However most of these studies have reported low sorption capacities due to the high solubility and stability of this anion in aqueous solutions [18].

The application of nanotechnology in wastewater treatment has been regarded as the platform of the 21st Century. The development and application of nanotechnologically engineered materials has improved the efficiency of adsorption technology in solving crisis involving drinking-water quality and wastewater treatment [19]. The unique and novel properties of nanoparticles such as accessible active sites, very large surface area and short diffusion length which result in high adsorption capacity, rapid extraction dynamics and high adsorption efficiencies make them well suited for treating industrial wastewaters [20].

Nanoclays have been reported as one of the emerging adsorbents used in wastewater treatment due to their ability to adsorb a wide range of contaminants such as organics, inorganic cations and anions. Moreover, the surface properties of nanoclays can be altered through chemical modification to create new adsorption sites that have affinity for targeted ions in solution [21]. Biopolymers as adsorbents have been on the spotlight of current studies due to their low cost, high capacity, non-toxicity, biodegradability and efficiency. Among these biopolymers, chitosan, a deacetylated derivative of chitin appears to have several desirable characteristics relevant to adsorption [22]. The electrostatic attraction between chitosan and anions has been extensively investigated and has been reported to occur at low pH due to the protonation of the amine groups [23]. However high cost, low density and low chemical stability are drawbacks associated with the use of pure chitosan as an adsorbent [24]. Fortunately, immobilizing chitosan on a low-cost material such as natural clays would result in less amount of biopolymer being used without affecting the overall anion uptake capacity [25].

In this review, a critical evaluation of the various sulfate removal technologies is reported. Thereafter, in-situ chemical preparation and characterization of the chitosan-bentonite

Mbakop, S., Nthombeni, N., Onyango, M.S., Department of Chemical Engineering, Tshwane University of Technology (phone: +27712501423; e-mail: sandrine.mbakop@ymail.com).
Leswifi, T.Y., Department of Chemical Engineering, Vaal University of Technology.

composite is discussed. Finally a match between the material properties and its performance towards sulfate removal in preliminary batch adsorption experiments is established. For preliminary batch sorption experiments, the effects of solution pH and adsorbent dose on the adsorption of sulfate onto chitosan-bentonite composite are evaluated. The synergy of the unique chemical selectivity of protonated chitosan towards anions and the functional groups present in nanoclays as well as their suitable density is expected to provide improved capacity and fast kinetics for remediation of sulfate containing aqueous solution.

II. SULFATE

A. Occurrence of Sulfate

Sulfur occurs in different oxidation states of which only the -2 (sulfide), 0 (native sulfur) and +6 (sulfate) are considered stable in nature. Sulfate is known as the dominant aqueous sulfur species found in most aerobic geochemical systems [26]. Sulfate ion is a polyatomic anion with the chemical formula SO_4^{2-} . The oxidation of iron sulfide also known as pyrite (FeS_2) is the most common source of sulfate release into the environment. During mining operations, pyrite generates the acidity of the waters and simultaneously supply large quantities of Fe and sulfate. The sulfide weathering process can either release all sulfate or only a portion, and form secondary salts, such as halotrichite. These minerals because of their high solubility become immediate source of sulfate containing waters through dissolution and hydrolysis activities [27].

B. Toxicity of Sulfate, Health effects and Guidelines

Although it is one of the anions with the least toxicity, studies have reported concentrations above 600 mg/L in drinking water to cause cathartic effects resulting in purgation of the alimentary canal [28]. Dehydration and laxative effects have also been reported where high magnesium or sodium concentrations are associated with high sulfate concentrations [29]. The accumulation in waters of salts such as calcium sulfates hampers the number of cycles of reuse of waters on the mining sites and creates ecological problem if decanted [30]. This has increased the concern on sulfate concentrations in water bodies and led to the introduction of recommended guideline values, rather than standards, for sulfate and TDS in groundwater and effluent discharges of several countries (see Table 1). These typical guideline values are based on USEPA or WHO guidelines which recommend that the maximum concentration of sulfate in drinking water or water utilized by livestock or for irrigation and generally should not be more than 500 mg/L [31]-[35].

TABLE 1

Recommended maximum Sulfate levels, in mg/l [31-35]

Country	Sulfate
USA effluent	500
Canada effluent	1500
EU guide limit	100
DWAF effluent (South Africa)	600
Australia	100

WHO guidelines for drinking water

250

III. TREATMENT TECHNIQUES FOR SULFATE REMOVAL

Various treatment techniques for sulfate removal from aqueous effluents are presented in literature under two broad categories; membrane removal and Sulfur precipitation [36]. These techniques are reverse osmosis, electrodialysis, ion-exchange, chemical precipitation and biological treatment. The last two decades researchers have been increasingly interested on the adsorptive removal of sulfate from aqueous solution.

A. Reverse Osmosis

Reverse osmosis process consists of separating a highly concentrated sulfate solution from a dilute solution using a semi-permeable membrane as medium [37]. The higher the concentration gradient across the membrane, the greater the tendency for water to permeate to the concentrated solution. This hydraulic force is the osmotic pressure of the system. To reverse the osmosis process, an external hydraulic pressure is applied to the saline, therefore forcing water through the membrane against osmotic pressure [38]. Traditional reverse osmosis can be used at moderate concentrations. At higher sulfate salts concentrations, fouling and the corrosion of the membrane walls will occur [39]. Despite the development of improved RO techniques such as seeded and modified RO [40], high cost, high energy consumption, and poor control of process parameters represent drawbacks for this technology [41].

B. Electrodialysis

This technique utilizes the principle of applying direct electrical current across a pile of alternating cation and anion selective membranes [42]. During the process anions are attracted to the anode but cannot penetrate through anion-impermeable membranes and are therefore concentrated. Meanwhile, cations move in opposite direction and are blocked by anion-permeable barriers. This mechanism removes all salts dissolved in the aqueous solution and provide clean water for collection [43]. Although reduced cost could be achieved during this process, by periodically reversing the process and inducing membrane self-cleaning, several disadvantages including fouling, energy consumption are associated with this method [44].

C. Ion-exchange

The process of removal of sulfate ions through ion exchange involves interchange between the anion present in aqueous solution and the hydroxyl ion on a positively charged resin (an anionic resin). Ion exchange resins contain various polar exchange groups bound together by a three dimensional network [45]. Once the sulfate ions are extracted from the aqueous solution they are attached to the resin structure in exchange for another ion therefore, immobilizing the polluting species. Like the techniques previously mentioned, fouling and high operating costs are common issues in this process [46].

D. Chemical Precipitation

Sulfate removal through chemical precipitation have been the center of many research studies in the past [47]. The process is made of three stages consisting of initially removing metals as hydroxides through lime addition (at pH 12) as a pre-treatment step, then seed crystallization technique is used to precipitate the gypsum. Finally, aluminum hydroxide is added to form insoluble ettringite. Afterwards the ettringite can either be considered as secondary waste or it can be dissolved in sulfuric acid to recycle $\text{Al}(\text{OH})_3$. The subsequent effluent can be seeded with gypsum to enhance the gypsum precipitation step [48]. The advantage of this removal technique is the additional. However secondary waste generation and solid waste disposal are crises resulting from this method [48].

E. Biological Treatment

Biological treatment consists of extracting sulfate as stable sulfides minerals from aqueous solutions under anoxic conditions, the stability of sulfides minerals under these circumstances is a result of their low solubility [49]. Open and flooded underground mine workings pits that are anoxic, are identified as a suitable environment for sulfate biological reduction systems. A properly designed biological reactor could also represent a good alternative. During the biological reduction process, two specialised and strictly anaerobic bacteria *desulfovibrio* and *desulfotomaculum* are used. These bacteria use their respiratory metabolism during which sulfate, acting as final electron acceptors are reduced to hydrogen sulfide [50]. Although efficient under appropriate treatment conditions, this technology faces several difficulties including, high energy consumption and operating costs, availability of efficient bacteria and efficient control of process parameters [51]. Therefore there is an urge to develop a technology that is highly efficient with minimum residence time. On the other hand, such a process should be environmentally friendly, economically feasible.

F. Adsorption

Recently, adsorptive remediation of sulfate containing wastewater have become more popular among research studies and it has been reported to be a simple and robust technique, and also efficient and environmentally friendly [52]. There are two types of adsorption processes: physical and chemical adsorption. Physical adsorption takes place when weak interparticle bonds like Van der Waals, dipole-dipole and hydrogen bonds are formed between the adsorbate and adsorbent. Generally, physical adsorption is easily reversible. Chemical adsorption is the result of strong interparticle bonds forming between the adsorbate and the adsorbent due to the exchange of electrons; such bonds are covalent and ionic bonds. In this case, separation occurs due to the differences in molecular polarity, shape and mass causing some molecules to be held more strongly on the surface than others [53]. Various adsorbents such as $\gamma\text{-Al}_2\text{O}_3$, chitin based shrimp shells, goethite and polypyrrole-grafted granular activated carbon have been used to remove sulfate from aqueous solutions. However most of these studies have reported low sorption capacities due to the high solubility and stability of this anion in aqueous solutions [54].

G. Nanomaterials and Water Purification

The potential of nanostructured materials regarding water and wastewater treatment have been demonstrated in many research studies over the years. The application of nanotechnology to conventional adsorption process could have result on result on tremendous improvement of this technique. With nanomaterials used as adsorbents, the adsorption process can take place at ionic/atomic/molecular scale in a very selective manner with high efficiency [55]. The sulfate uptake capacity could be enhanced to many fold thanks to the nano-dimension and significant increased surface- to volume ratio. Moreover nanomaterials possess two exceptional properties relevant to adsorption. They have far much larger surface areas compare to bulk particles. Additionally they can be tailored with various chemical functional groups to increase their affinity towards specific pollutants. As a result, nanomaterials exhibit high adsorption capacities and display stronger affinities towards heavy metals and anionic compounds [18].

IV. MATERIALS AND METHODS

A. Materials

Natural bentonite was obtained from the Council for Scientific and Industrial Research (CSIR) South Africa-Pretoria. Sodium sulfate (NaSO_4) for use as a salt for synthetic wastewater preparation, hydrochloric acid 32% (HCl), sodium hydroxide (NaOH) and deacetylated chitosan were supplied by Merck Schuchardt (Pty) Ltd-South Africa and used as received without further purification. Deionized water was used to prepare synthetic sulfate stock solutions and for all dilution purposes based on experimental requirements.

B. Preparation of Bentonite-Chitosan Composite

The chitosan coated bentonite composite was prepared by dissolving 5 g of deacetylated chitosan into 200 ml of 5 % (v/v) hydrochloric acid. The solution was stirred for 24 hours. Afterwards 20 g of bentonite was added slowly and the mixture was stirred for 3 hours. In order to precipitate the dissolved chitosan into bentonite, 1 M of sodium hydroxide aqueous solution was added dropwise until a pH7.0 was obtained. The mixture was vacuum filtered and the cake dried in an oven overnight at 60°C . The dried cake was crushed and milled to particles size between 160 μm to 53 μm .

V. RESULTS AND DISCUSSION

A. Characterization of Bentonite –Chitosan Composite

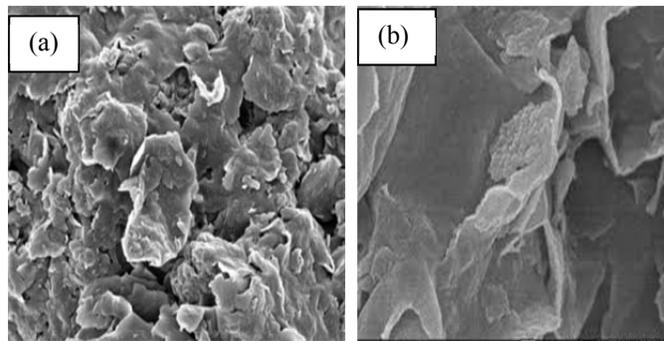


Figure 1: SEM images of raw bentonite (a) and chitosan-bentonite composite (b)

The scanning electron microscopic analysis (SEM) is a common technique for characterization of the surface morphology and physical properties of the adsorbent. It is primarily used to determine the particle shape, size distribution and porosity. Figure 1 displays SEM pictures of raw bentonite and chitosan-bentonite composite before adsorption process. The roughness, and irregular surface morphology of the raw bentonite illustrated on the left side of figure 1 shows a more porous material. Upon modification to form chitosan-bentonite, the sharp edges observed on the raw bentonite material are smoothed and the distinguished gray areas have darkened. This could be an indication of a successful coating of the chitosan onto the bentonite material. The overall structure could be a good indication for effective sulfate anions removal from aqueous solution.

B. Equilibrium Studies

1) Effect of pH

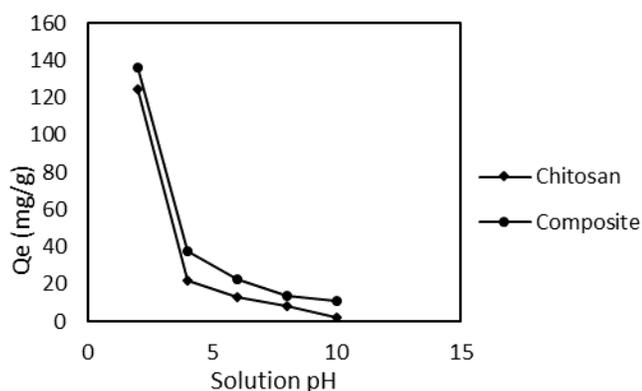


Figure 2: Effect of initial pH on sulfate adsorption onto chitosan-bentonite composite. (Initial conc. 224 mg/L, Temp. 298K, sorbent mass 50 mg)

The efficiency of the adsorption process is significantly influenced by the system pH as it affects not only the dissociation and ionization of the adsorbate molecule, but also the surface properties of the adsorbent. The effect of initial pH on the removal of sulfate by chitosan-bentonite composite are shown in figure 2. It is evident that the sulfate adsorption onto the composite is higher at lower pH and gradually decreases as the pH of solution increases. The abundance of hydroxyl ions could be the reason for the lower adsorption capacity at alkaline pH, as these negatively charged ions compete with sulfate anions for the same adsorption sites. Moreover, the protonation of the amine groups of the chitosan at lower pH has also contributed to the higher adsorption capacity obtained at lower pH. Experimental data (see figure 2) indicated that combination of chitosan and bentonite exhibited only slightly higher capacity of adsorption also at lower pH. However combining both material overcome the disadvantages of high cost and very low material density related to the use of pure chitosan. Immobilizing chitosan onto an abundantly and relatively low cost material such as bentonite does not affect

the overall performance of the composite. Moreover the highest performance obtained at pH 2 represents an advantage for the remediation of acid mine drainage as the pH is generally low and hence pH adjustment may not be required.

2) Adsorbent dosage

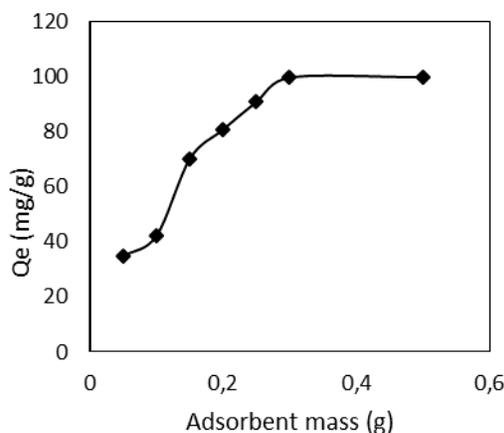


Figure 3: Effect of adsorbent dosage on sulfate adsorption onto chitosan-bentonite composite. (Initial conc. 2000 mg/L, Temp. 298K, pH = 2)

TABLE 2

Various adsorbents with respective adsorption capacities at optimum dosage for sulfate removal from aqueous solution [17]; [56]-[59]

Adsorbents	Qe (mg/g)
Chitosan-bentonite composite	100
Polypyrrole-grafted granular activated carbon	44.7
Coconut choir pith	4.5
Modified rice straw	74.76
Organo-nano-clay	20.15
poly(m-phenylenediamine)	108.5

The effect of sorbent mass on the remediation efficiency of the sulfate aqueous solution was explored at 298 K, with sorbent dose between 0.05-0.5 g and an initial pH 2. Figure 3 illustrates the effect of adsorbent mass on sulfate removal uptake increases with increasing adsorbent mass. This could be the result of more available active sites for sulfate sorption since the number of available active sites is proportional to the adsorbent mass. However, 0.3 g and 0.5 g of adsorbent were noted to exhibit similar adsorption capacities. This could be due to overlapping of the available active sites and congestion of particles which hindered the adsorption of sulfate ions. This may also be due to the excess availability of sorption sites. Table 2 presents the adsorption capacities obtained at optimum mass (0.5 g) with chitosan-bentonite composite and several materials used as adsorbents for sulfate removal from aqueous solution. Based on the active functional groups on the adsorbents and their affinity towards anions pollutants the results are relatively comparative.

VI. CONCLUSION

This study proposed adsorption as a robust technique for sulfate ions removal from aqueous solution. Adsorption process requires a robust media of known kinetics and equilibrium capacity. Consequently, this study explored the use of chitosan-bentonite composite. The media was synthesized, characterized and test in sulfate removal from aqueous solution. Results revealed that the magnitude of adsorption was primarily dependent on the solution initial pH and the sorbent dosage. In particular, performance was favored at pH 2. This is consistent with the fact that amine groups from the chitosan are protonated at very low pH. Meanwhile, a maximum media dosage in the range of 0.3-0.5 g of chitosan-bentonite composite was found to be required for approximately 100 mg/g adsorption. Though these results are only preliminary in a wide study still to be conducted, they give the indication that chitosan-bentonite composite is a potential material for sulfate removal. There is a need to conduct more adsorption kinetics, equilibrium and fixed-bed dynamic studies to generate enough data for adsorber design.

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