

Surfactant Impregnated Bentonite Clay for the Removal of Heavy Metals from Solution

Elvis Fosso-Kankeu*, Frans Waanders, Nico Lemmer and Ruben H. Steyn

Abstract—The increasing level of water scarcity is a significant issue in South Africa. This is due to many factors such as global warming, population growth as well as water pollution. There is thus a great need for the development of effective, affordable and readily available resources for water treatment in order to sustain the presently limited resources. During this study, Bentonite clay was subjected to impregnation with the anionic surfactant, Sodium dodecyl sulfate (SDS) for the purpose of removing heavy metals from solution. Characterization of the Bentonite clay was executed by making use of XRD-, XRF- as well as FT-IR spectroscopy. Pseudo first-order and Pseudo second-order kinetic models were used for the purpose of modelling the adsorption kinetics. The parameters that were tested and varied in this study were adsorbent dosage and contact time. The natural Bentonite clay (NB) adsorbed some of the copper(II) and lead(II) in solution; the adsorption affinity of all adsorbents for lead(II) was higher than that of copper(II). The bentonite clay that was impregnated with SDS (SDS-B) showed a greater effectivity in adsorbing both copper(II) and lead(II) as compared to NB. The SDS impregnated clay's affinity for copper(II) and lead(II) was 21.5 mg/g and 28.6 mg/g, respectively. The impregnation of Bentonite with SDS may thus be considered to increase the adsorption capacity of the adsorbent by increasing the number of binding sites available for ion exchange on the surface of the natural Bentonite.

Keywords—Adsorption; Bentonite; Copper(II); Lead(II); Kinetics; Sodium dodecyl sulfate; Surfactant

I. INTRODUCTION

It is predicted that South Africa will inevitably reach a state of water scarcity by the year 2025 in accordance with the International Water Management Institute (IWMI). An adequate intervention with regards to water pollution is required [1].

Symptoms related to acute heavy metal exposure may include headaches and abdominal pain. Long-term exposure may be carcinogenic, mutagenic, teratogenic and even toxic, depending on the specific metal [2]. In conjunction, heavy metal pollution

poses a serious cause for alarm regarding the aquatic environment [3-11].

Over the years, many conventional techniques have been introduced for this purpose. The methods include: chemical precipitation, chemical oxidation/reduction, evaporation, filtration as well as electrochemical treatment. There are a variety of detrimental aspects regarding these methods which include: low removal efficiency, high energy related costs as well as the production of toxic waste byproducts that require additional means of disposal [12-17].

Bentonite clay consists of a layered silicate structure which contributes to its effective cation exchange capacity. Consequently, it is known to be a relatively good adsorbent of specific heavy metal ions. This is due to the presence of hydrated cations such as K^+ , Ca^{2+} and Fe^{3+} in the interlayer surfaces. During an ion exchange reaction, these ions can be exchanged quite easily by heavy metals which may substitute the appropriate charge. This cation exchange reaction is known to be a reversible process which is dependent on the specific metals present, the solution concentration, pH as well as the presence of additional ions which compete with the heavy metals for adsorption sites [18-23].

An additional step is the consideration of surfactant impregnation of the clay, which leads to a modified clay with a higher adsorption affinity. The adsorption between metal ions such as copper(II) and lead(II) and natural clays displays relatively weak binding strengths. The addition of a surfactant leads to much greater binding strengths between the negatively charged clay and cationic metal ions in solution. This is facilitated by the formation of a surface-cation complex [24]. Metal ions are cationic in nature; furthermore, an anionic surfactant, Sodium dodecyl sulfate, is chosen.

The purpose of this study is to evaluate the adsorption capacity of copper(II) and lead(II) onto SDS-impregnated Bentonite.

II. EXPERIMENTAL SETUP AND MODELLING

A. Materials

Sodium dodecyl sulphate (SDS) was bought from ACE chemicals, South Africa. Natural bentonite clay (NB) obtained from NWU's School of Chemical- and Mineral Engineering

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was used as an ingredient in the production of modified clay and as an adsorbent.

The natural bentonite clay used has a cation exchange capacity of 62 cmol/kg. The clay was modified by surfactant impregnation for the purpose of altering the structure of the clay in order to increase the adsorption capacity of the clay.

Lead nitrate and copper nitrate obtained from NWU's School of Chemical- and Mineral Engineering were used as the respective adsorbates. Distilled water was used as ingredient during the preparation of the modified clay as well as a medium for adsorption and -ion exchange.

B. Modification of the Bentonite

A sample of bentonite clay was weighed in order to obtain twenty-one grams of clay. The sample was added to 0.5 litres of deionised water. The mass equivalent of SDS which is equal to twice the Bentonite's cation exchange capacity was added to the mixture of clay and deionised water for impregnation. For optimal modification, the resulting mixture was put in an orbital shaker at room temperature and 160 rpm for 24 hours. Finally, the mixture was centrifuged, washed, dried in an oven and then crushed by a mortar and pestle.

C. Adsorbent Characterization

A Philips X'Pert pro MPD X-ray diffractometer (XRD) was utilised to do a mineralogical analysis of the NB. It is operated at 40 kV and 30 mA and the speed at which the sample is scanned is 2 degrees/min. Furthermore, the range at which the scan is performed (2θ) is between 3 degrees and 90 degrees. The step width is 0.01 degree.

A MagiX Pro & Super Q X-Ray Fluorometer was utilized in performing a mineralogical analysis of the NB. The analysis was performed at 50 kV and 125 mA.

An FTIR analysis was performed to identify the functional groups of the NB and SDS-B for the purpose of determining the degree of surface activation. An IRAffinity-IS Fourier transform infrared spectrophotometer was used. The spectral range is between 4000 cm^{-1} and 400 cm^{-1} [25].

D. Batch Adsorption

The concentration of the copper(II) and lead(II) at equilibrium was established by means of an ICP Expert II, Agilent Technologies 720, inductively coupled plasma optical emission spectrometer.

The adsorption took place in a closed system; the initial metal concentration, the particle size of the clay, the rotation speed, the volume of the solution and the solution temperature were fixed at 60 mg/l, 6 μm , 160 rpm, 0.1 L and 25°C , respectively. The experimental parameters that were tested included adsorbent dosage (0.050 g – 0.300 g) and contact time (10 min – 130 min).

E. Modelling of Kinetics

The adsorption kinetics may be described by the Pseudo First-Order model [26].

In linearized form it is written as the mathematical expression:

$$\log(q_e - q_t) = q_e - \frac{k_1}{2.303} t \quad (3)$$

q_t represents the capacity of copper(II) or lead(II) uptake after t minutes (mg/g)

k_1 represents the Pseudo first-order rate constant (min^{-1})

t denotes the adsorption contact time (min)

The Pseudo Second-Order model is described as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} \quad (4)$$

k_2 denotes the Pseudo second-order rate constant ($\text{g/mg}\cdot\text{min}$)

III. RESULTS AND DISCUSSION

A. X-Ray Diffractometry and X-Ray Fluorometry

An XRD analysis was performed for the purpose of evaluating the mineralogical composition of the clay. Natural clay is rarely composed of pure Bentonite; other minerals are present which have an influence on the purity of the Bentonite as well as the adsorption capacity of the clay.

The XRD results revealed that the NB is mainly composed of pure Bentonite. Furthermore, there is a small portion of albite and quartz present which also form part of NB's make up.

An XRF analysis was performed to obtain insight regarding the elemental composition of the NB.

The analysis revealed the presence of calcium, iron(II), magnesium and manganese which may be substituted by copper(II) and lead(II), facilitating adsorption. However, sodium and titanium were also present which might have a detrimental effect on the number of binding sites and thereby restrict adsorption.

B. FTIR Results

An FTIR analysis was performed to identify functional groups that are present in a specific compound. In Fig. 1 the FTIR spectra of NB and SDS-B is compared; numerous changes in structure are present which confirms the surface activation of NB.

The adsorption peaks in the 2800 cm^{-1} – 3000 cm^{-1} region correspond to an asymmetric- and symmetric stretch vibration of the H-C-H groups that are not present in NB and appeared after SDS impregnation.

In the spectral region between 1400 cm^{-1} and 1500 cm^{-1} there is a bending vibration of the H-C-H groups that formed after SDS modification.

Between 1625 cm^{-1} – 1750 cm^{-1} there is a vibrational stretch of the C=O functional group after impregnation, depicted by the difference in peak intensity.

Sulfate forms part of the structure of SDS; an SO_2 asymmetric vibration is observed between 1300 cm^{-1} and 1400 cm^{-1} which reveals a successful impregnation of NB [27].

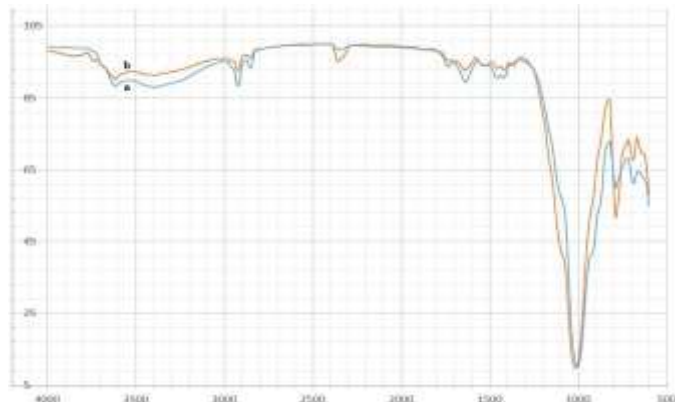


Fig. 1: FTIR Analysis of (a) NB and (b) SDS-B

In the spectral range between 2800 cm^{-1} and 2850 cm^{-1} it may be observed that a stretching vibration of C-H in the NB occurs. After adsorption of copper(II) and lead(II) has taken place, the formation of adsorption peaks is observed in Fig. 2.

Furthermore, a variety of noticeable differences before and after adsorption may be observed, confirming the successful ion exchange of copper(II) and lead(II) cations into the interlayer regions of NB.



Fig. 2: FTIR analysis of (a) NB and NB after (b) lead(II) and (c) copper(II) is adsorbed

For SDS-B, the spectral range between 2800 cm^{-1} and 2850 cm^{-1} reveals a stretching vibration of C-H. After adsorbing copper(II) and lead(II), the formation of adsorption peaks is notable.

In the spectral region between 1440 cm^{-1} and 1500 cm^{-1} , associated with the bending vibration of the H-C-H groups, the peak intensity significantly decreases after the adsorption of copper(II) and lead(II).

Other visible differences in the spectral region may be observed, confirming the successful adsorption of copper(II) and lead(II) onto SDS-B.

This is illustrated in Fig. 3.

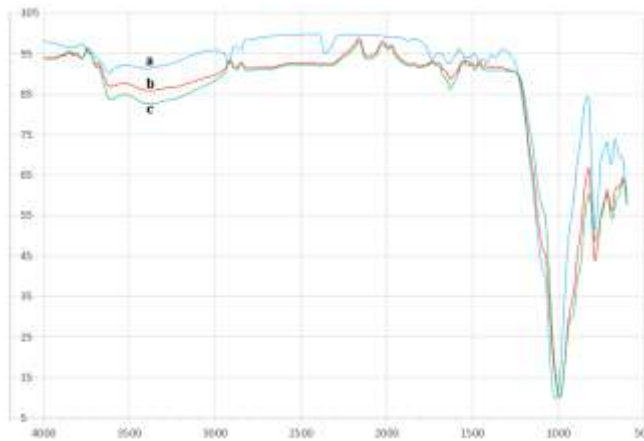


Fig. 3: FTIR analysis of (a) SDS-B and SDS-B after (b) lead(II) and (c) copper(II) is adsorbed

C. Effects of Adsorbent Dosage and Adsorption Time

The parameter of NB dosage was varied whilst the initial concentration of copper(II) and lead(II) remained constant at 60 mg/l . The adsorption contact time was fixed at 150 min . The solution temperature and volume was held constant at 25°C and 0.1 L , respectively.

It is illustrated in Fig. 4 that there is a sharp decline in the adsorption affinity of NB for both metals as the NB dosage increases; the rate at which NB becomes saturated with lead(II) is significantly higher than -copper(II). The rate, for both metals, stabilises with an increase in NB dosage.

The optimal dosage is determined to be 0.2 g .

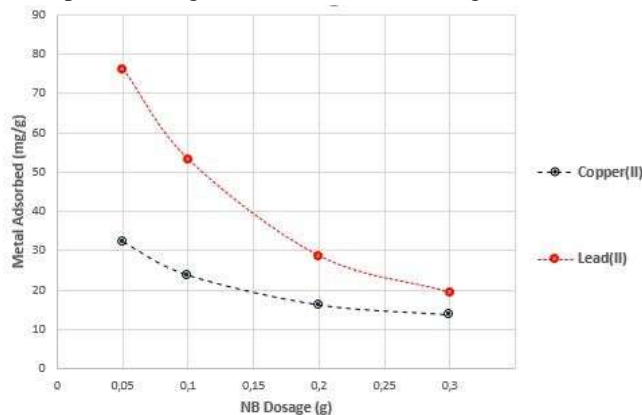


Fig. 4: Effect of NB variation on copper(II) and lead(II) adsorption

It is clear from Fig. 5 that the rate of adsorption affinity decrease for SDS-B is slightly higher than -NB for lead(II) at dosages lower than 0.2 g . The rate for both adsorbents is equal for copper(II).

The adsorption affinity of SDS-B for copper(II) is higher than that of NB. The adsorption affinity of SDS-B for lead(II) is higher than that of NB for dosages less than 0.2 g .

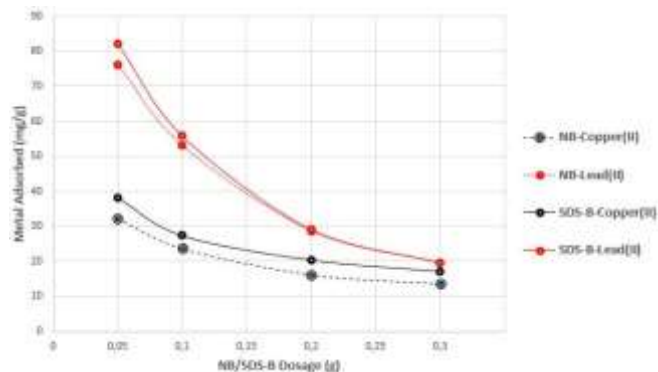


Fig. 5: A comparison of NB- and SDS-B variation on copper(II) and lead(II) adsorption

The parameter of contact time was varied between 10 min and 130 min whilst the initial concentration of copper(II) and lead(II) remained constant at 60 mg/l. The adsorbent dosage (SDS-B) was fixed at 0.2 g. The solution temperature and volume was held constant at 25°C and 0.1 l, respectively. This is depicted in Figure 5.

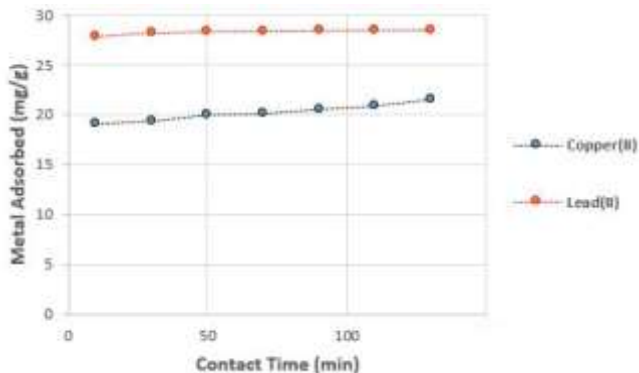


Fig. 6: Effect of Contact Time on Copper(II) and Lead(II) adsorption

The amount of lead(II) that is adsorbed throughout the contact time range is fixed at 28 mg/g. This reveals that lead(II) reaches its equilibrium concentration very rapidly at an adsorbent dosage of 0.2 g.. Previous studies have reported higher affinity of adsorbents for lead [28-30].

The adsorption affinity of SDS-B for copper(II) slightly increases over the contact time range and is expected to stabilise as the equilibrium concentration is reached.

D. Adsorption Kinetics

For the purpose of kinetics, the linearized form of the Pseudo first-order kinetic model is utilised. The model of SDS-B adsorption for copper(II) and lead(II) is depicted in Fig. 7

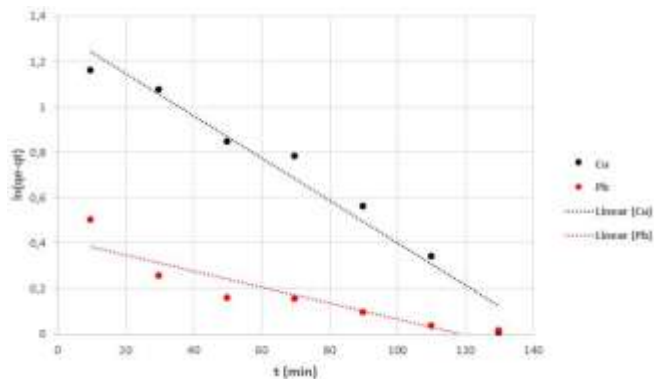


Fig 7: Linearized form of the Pseudo First-Order Kinetic Model

The linearized form of the Pseudo second-order kinetic model is illustrated in Fig. 8. It is evident that this model has a far better fit for the kinetic data of copper(II) and lead(II) adsorption onto SDS-B as compared to the Pseudo first-order model.

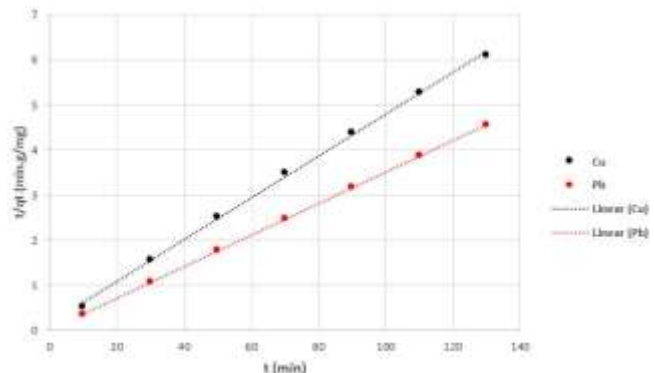


Fig. 8: Linearized Form of Pseudo Second-Order Kinetic Model

It is evident from the R^2 values from Table 1 that the Pseudo second-order model is better equipped to represent the kinetic data for SDS adsorption of copper(II) and lead(II).

The adsorption capacity of SDS-B for copper(II) and lead(II) is determined to be 21.5 mg/g and 28.6 mg/g, respectively.

TABLE 1: PSEUDO FIRST-ORDER- AND PSEUDO SECOND-ORDER CONSTANTS

| Model | Parameters | Pb(II) | Cu(II) |
|---------------------|---|---------|---------|
| Pseudo First-Order | q_e (mg/g) | 1,52 | 3,10 |
| | k_1 (min^{-1}) | 0,00350 | 0,00930 |
| | R^2 | 0,835 | 0,963 |
| Pseudo Second-Order | q_e (mg/g) | 28,6 | 21,5 |
| | k_2 ($\text{g/mg}\cdot\text{min}^{-1}$) | 0,00972 | 0,00781 |
| | R^2 | 0,999 | 0,999 |

IV. CONCLUSION

The purpose of this study was to evaluate the adsorption capacity of copper(II) and lead(II) onto SDS-modified Bentonite. The successful impregnation of Bentonite is evident throughout the study, confirmed by FTIR analysis as well as the relevant adsorption studies.

The adsorption affinity of SDS-B for both metals is higher than that of NB and decreases with adsorbent dosage as the excess adsorbents in solution interact.

The total amount of lead(II) that is adsorbed throughout the contact time range stays constant whilst that of copper(II) increases; this reveals that lead(II) reaches its equilibrium concentration very rapidly at an SDS-B dosage of 0.2 g.

From kinetic studies, the rate of lead(II) adsorption is faster than that of copper(II) for all adsorbents.

SDS-B proves to be an effective adsorbent for the removal of heavy metals and can be utilized for wastewater purification.

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