Adsorption Potential of Bentonite and Attapulgite Clays Applied for the Desalination of Sea Water

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Abstract—A possible new process for the partial desalination of seawater is to use bentonite clay or attapulgite as an adsorbent. The ion exchange property of these clays, which is a result of the characteristic t-o-t layer structure, enables the use of these materials as adsorbents. This technique has the opportunity to be used as a pre-treatment as current commercial seawater desalination processes are very expensive.

The clay was characterized using XRD, XRF and SEM analyses. To ensure maximum adsorption of all possible elements onto the clay, burnt dolomite (CaO.MgO) was added to the solution to raise the pH. It was found that adsorption of Ca, Mg, K and Na onto bentonite clay and attapulgite follow pseudo-second order kinetics and the Langmuir isotherm model. With the increase in the pH higher adsorption capacities were obtained. FTIR analyses show that the OH - functional group is responsible for the metal adsorption.

Keywords—Bentonite clay, attapulgite, dolomite, seawater, Langmuir isotherm, kinetics.

I. INTRODUCTION

CURRENTLY reverse osmosis is the primary technology used for desalination as it offers effective treatment of water of any salinity [1] and also involves the desalination of brackish water and seawater. Of the total water found on the earth, 97 % is seawater and one percentage is brackish, found in estuaries and underground aquifers [2]. Greenlee *et al*. [1] concluded that there is still a need to find more economical and lower energy consumption techniques for desalination or the development of improved pre-treatment options for current desalination techniques.

Previous research by Enslin *et al*. [3] focused on the removal of heavy metals from acid mine drainage (AMD) with bentonite clay where the success of this research led to the possibility to treat seawater in the same manner. Adsorption is an attractive approach for water treatment, particularly if the adsorbent is cheap and does not require any pre-treatment before its application [4]. Adsorption of heavy metals onto montmorillonite clay has been proven to be successful [5].

Within the South African context, bentonite is made up of sodium and calcium montmorillonite belonging to the smectite group. The smectite group has a trioctrahedral t-o-t structure [6]. Both tetrahedral and octahedral cations are substituted of cations of lower charge which produce an unbalance structure resulting in an overall negative charge that is balanced by exchangeable cations that are absorbed around the edges of the fine clay particles [7]. These cations may be replaced by other cations when the mineral surface is in contact with a liquid, containing cations. Attapulgite (palygorskite) is a hydrated magnesium aluminium silicate mineral and the building blocks are also made of the characteristic t-o-t structure. There is considerable more aluminium replaced by magnesium in the octahedral layer, resulting in a moderate layer charge [8].

Brink [9] claimed a method of treating polluted water by adjusting the pH of the water by adding burnt dolomite as a base and exposing the pH adjusted water to an absorbent clay thereby removing most of the cations from the water to produce at least partially purified water. Dolomite, $CaMg(CO_3)_2$, occurs naturally and deviates relatively from Ca:Mg = 1:1. Dolomite rocks are from secondary origin, formed by the replacement of Ca by Mg in ordinary limestone [7]. When dolomite is heated to 900°C all the CO_2 is driven off from the carbonates to produce CaO.MgO. Dolomite has been proven to be a cost effective alkalizing agent [10].

Monhemius [11] constructed concentration/pH diagrams denoting precipitation limit boundaries, indicating that Mg and Ca are cations that are precipitated at relatively high pH values. Addition of the alkaline mixture will increase the pH to precipitate the metal salts, which will then be adsorbed on the bentonite and removed [9].

The purpose of this study is to investigate the adsorption mechanism of bentonite or attapulgite clay as adsorbent of cations from seawater.

II. METHODOLOGY

In this section the materials used and methods conducted are discussed.

A. Materials

All materials are relatively abundantly available in South Africa and were used without any further purification. The

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bentonite clay, attapulgite and dolomite were milled to a fine powder in a ball mill. The dolomite was heated in a muffle furnace to 900°C to drive off the CO_2 from the carbonate to produce CaO.MgO (burnt dolomite). For adjusting the pH of the seawater a solution of deionised water and burnt dolomite was made by adding 5 g of burnt dolomite to 100 mL of deionized water and this solution was then added to the seawater. The suspension was placed on the shaker table for 30 min and then left in an undisturbed cupboard for 24 hours.

B. Clay characterization

The mineralogical and chemical composition of the clay was determined by X-ray diffraction analysis (XRD) and X-ray fluorescence analysis (XRF), respectively. The diffractometer used was a Philips model X'Pert pro MPD, at a power of 1.6 kW used at 40 kV, programmable divergence and anti-scatter slits; primary Soller slits: 0.04 Rad; 2θ range: 4-79.98; step size: 0.017°. The XRF was used to identify the elements in the clay; it was performed on the MagiX PRO & SuperQ Version 4 (Panalytical, Netherland) with a rhodium (Rh) anode used in the X-ray tube and operated at 50 kV and current 125 mA; at power level of 4 kW. A FEI Quanta 200 ESEM Scanning Electron Microscope, integrated with an Oxford Inca 400 energy dispersive x-ray spectrometer was used for the SEM analyses to identify the compound composition.

The ATR-FTIR (Perkin-Elmer Spectrum 100 spectrometer) was used to ascertain the different functional groups of the clay in the spectral range 4000 – 400 cm^{-1} with a resolution of 4 cm^{-1}.

C. Adsorption experiments

The adsorption experiments were carried out using a batch technique no attempt was made to exclude air. A solution of 100 mL seawater and 1 g of adsorbent, equivalent to 1% adsorbent was used. The conditions under which the effects of contact time, pH and initial concentration were studied and tabulated in table 1.

TABLE 1
EXPERIMENTAL CONDITIONS

Type of study	Conditions
Effect of contact time	30, 40, 50 and 60 min time intervals.
Effect of pH	Samples were taken at a pH of 9; 10 11, 12 and 12.5.
Initial concentration	10, 20 and 30 times dilution of the seawater.

The mixtures containing saline solution and clay in an Erlenmeyer flask were mechanically stirred on an orbital shaker at 200 rpm under constant room temperature and at interval times stated in Table 1, after the require exposure time, the samples were centrifuged at 2 000 rpm for 5 min and filtered with filter paper (4 µm retention). All the samples were stored in polytop tubes sealed under ambient conditions. The concentrations of the salt ions before and after adsorption were determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES) analysis. The spectrometer used was a Agilent 725 Radial ICP-OES

D. Experimental calculations

The adsorption efficiency of the clay was calculated using the following equation [12]:

$$q_e = \frac{(C_0 - C_e)\cdot V}{m}$$

Where q_e the equilibrium adsorption (mg/g), C_0 and C_e are the ions concentrations (mg/L) initially and at equilibrium, respectively, V is the volume of the solution (L) and m is the amount of adsorbent in (g).

The adsorption capacity at a particular time interval was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t)\cdot V}{m}$$

The pseudo-second order is expressed by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \frac{t}{q_e}$$

where k_2 is the rate constant for the second order adsorption in (g/mg.min^{-1}).

The Langmuir isotherm was used to calculate the adsorption affinity of the clays; the linear expression of the Langmuir model is as follows [13]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}}$$

where q_{max} is the maximum adsorption capacity (mg/g) of the adsorbent and b is the Langmuir constant related to the adsorption energy.

III. RESULTS AND DISCUSSION

The results obtained and the discussion of the results will be done under this section.

A. Clay composition

The XRD analysis showed that the mineral content of the bentonite clay was 45% quartz, 45% montmorillonite and the balance kaolinite and bentonite. Attapulgite is composed of 71% montmorillonite and 29% quartz XRF and SEM analyses indicated that the elemental composition of bentonite clay is 59% silicate, 17% alumina, 8% iron(II)oxide, other elements such as K, Mg, Ca, Na and Ti were identified. Attapulgite had a similar composition with less silicate (47%) and alumina (6%) but more magnesium oxide 12%. As expected the dolomite had a composition of 43% CaO and 32% MgO, with 8% silica.

B. Adsorption kinetics

The experimental data for this study was found to fit pseudo-second order kinetics and not first order kinetics. The pseudo-second order plot for the adsorption onto bentonite clay and attapulgite are shown in Figure 1.

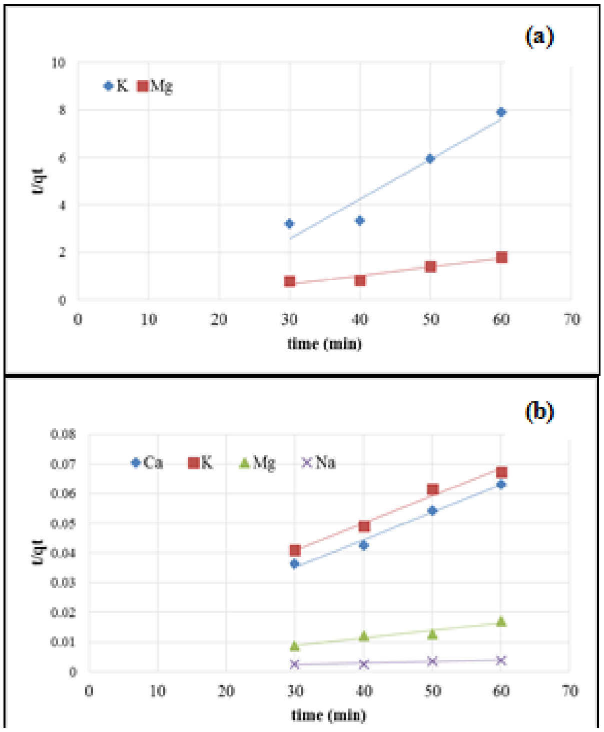


Fig. 1: Pseudo-second order kinetic plots for (a) bentonite clay and (b) attapulgite.

The second order parameters q_e and k_2 were calculated from the intercepts and the slope of t/q_t and the time. The adsorption behaviour of bentonite clay could not be predicted using the Langmuir model because the lack of fitness of the adsorption data, as substantiated by the relatively low R^2 values (Ca, 0.803; K, 0.914; Mg, 0.928 and Na, 0.838). It was found that for the second order rate equation R^2 values for Ca, K, Mg and Na adsorption onto attapulgite were close the unit and confirms that the second order rate model is an appropriate assumption. The adsorption capacity of attapulgite for the removal of Na was relatively high (q_e = 15.221 mg/g), this correlates with the higher concentration of Na in the saline water; it has been stipulated that the adsorption capacity increase with the initial concentration of metal in solution [14]. However, the opposite trend is observed with the adsorption of Ca; in fact Ca is present at lower concentration than K, but the model predicts higher adsorption of Ca than K (q_e equal to 0.952 and 0.8723, respectively). This is likely due to the higher adsorption affinity of the attapulgite for Ca. Calculated values for q_e, k_2 and R^2 are reported in table 2.

TABLE II
CALCULATED PARAMETERS FOR PSEUDO-SECOND ORDER KINETICS.

Adsorbent	Kinetic parameters	Ca	K	Mg	Na
Bentonite	q_e	NF	NF	NF	NF
	k_2	NF	NF	NF	NF
	R^2	0.803	0.914	0.928	0.838
Attapulgite	q_e	0.952	0.872	3.648	15.221
	k_2	0.783	0.523	0.268	0.031
	R^2	0.993	0.985	0.984	0.973

(NF: No Fit)

C. Adsorption isotherms

The relationship between the amount of metal ion adsorbed per unit weight of the adsorbent (q_e) and the equilibrium ion concentration left in the solution (C_e) is studied by the adsorption isotherm. The experimental data for this study was found to fit Langmuir and not Freundlich isotherm models. The Langmuir isotherm model represents the homogenous adsorption on the adsorbent surface with only one type of binding sites and when a molecule occupies an adsorption sites no further adsorption can take place [13]. The Langmuir plot for adsorption of Ca, K, Mg and Na onto bentonite clay and attapulgite is shown in Figure 2.

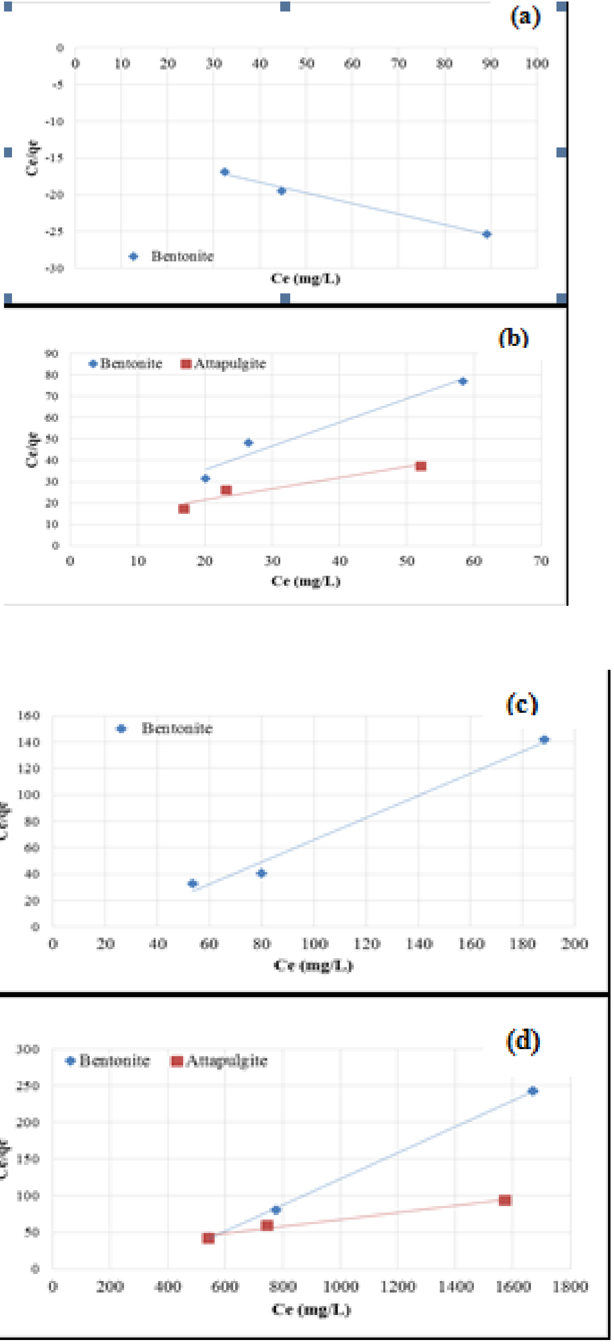


Fig 2 Langmuir isotherm data for the adsorption of (a) Ca, (b) K, (c) Mg and (d) Na.

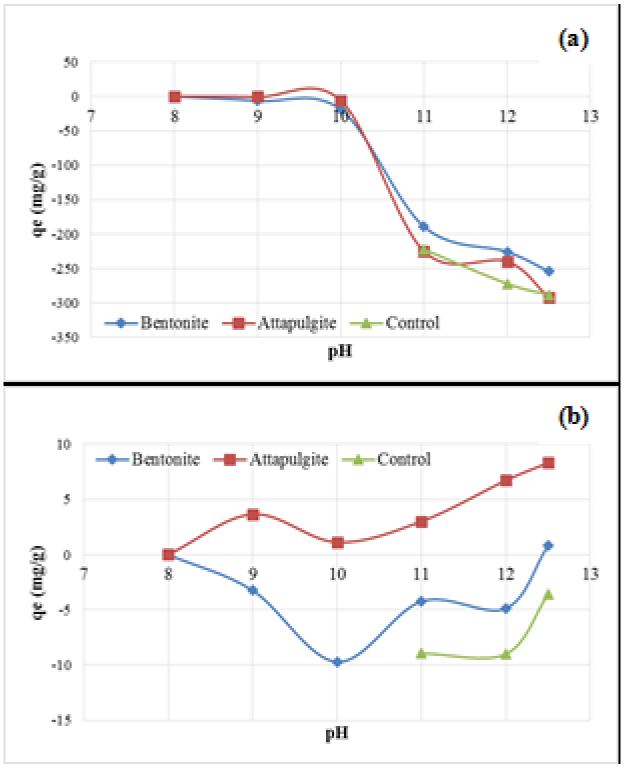
The values of q_{max} and b were calculated from the slope and intercept of the plot between C_e/q_e and C_e. For the adsorption of K, Mg and Na maximum adsorption capacities of 0.909, 1.118 and 5.605 mg/g, respectively, were achieved by the bentonite clay. Attapulgite showed a slightly higher maximum adsorption of Na with a value of 5.698 mg/g. Calculated values for q_{max}, b and R^2 are reported in table 3. The R^2 value for Ca and Mg adsorption onto attapulgite implies that the Langmuir model is not suitable for the prediction of their adsorption potential.

TABLE III
CALCULATED PARAMETERS FOR THE LANGMUIR ISOTHERM

Adsorbent	Isotherm constants	Ca	K	Mg	Na
Bentonite clay	q_{max}	-6.891	0.909	1.188	5.605
	b	1.814	0.08	-0.045	-3.23×10^{-3}
	R^2	0.991	0.956	0.985	0.999
Attapulgite	q_{max}	NF	0.421	NF	5.698
	b	NF	-0.14	NF	-4.79×10^{-3}
	R^2	0.237	0.925	0.495	0.978

D. Effect of pH on the adsorption capacity

Metal adsorption on the adsorbent involves ion exchange and the charge of elements influences the chance of metal uptake significantly. When a pH of 11 was reached, Mg was precipitated and adsorbed, while more Ca was dissolved into the solution due to ion-exchange between Ca and Mg. For both K and Na, attapulgite shows a higher adsorption capacity than for the bentonite. The control done without the addition of clay confirms that the ions were adsorbed. In Figure 3 the effect of pH on the adsorption capacity for Ca, K, Mg and Na are displayed.



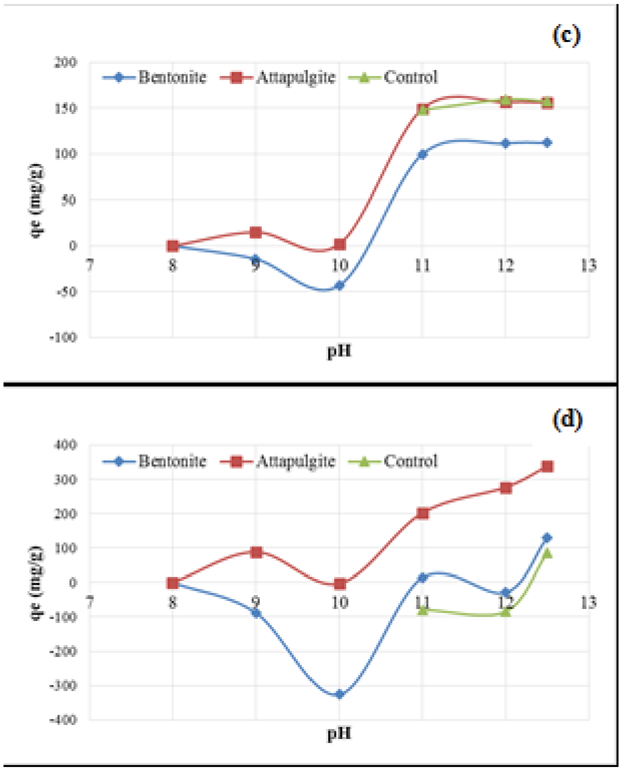
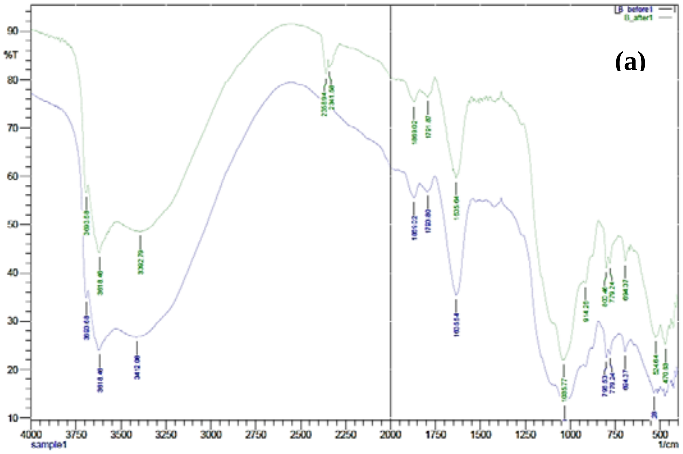


Fig. 3 Effect of pH on the adsorption of (a) Ca, (b) K, (c) Mg and (d) Na

E. Binding sites on the clay

FTIR analyses were done to determine the functional groups responsible for the attachment of metals on the clay. The infrared spectra of the bentonite clay and attapulgite are shown in Figure 4.



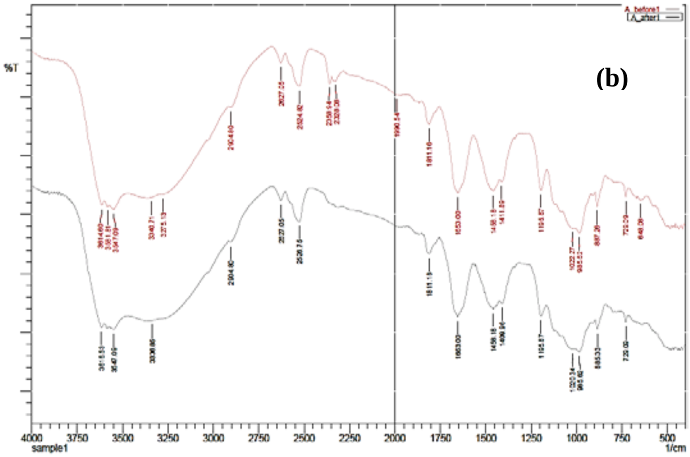


Fig. 4 FT-IR analyses for (a) bentonite clay and (b) attapulgite before and after adsorption

In the region of 3500 – 3200 a small shift in bands is observed, which correspond to the involvement of the OH- group in the binding of metals.

IV. CONCLUSION

Adsorption on both bentonite clay and attapulgite follow pseudo-second order kinetics. Bentonite clay shows a higher adsorption affinity for Mg, while attapulgite shows a higher adsorption affinity for Na. The maximum adsorption capacity of Na onto bentonite and attapulgite are almost equal and fit the Langmuir isotherm model. An increase in pH leads to an increase of adsorption capacity for K, Mg and Na on the bentonite clay and the attapulgite, but K and Na adsorption are much more favourable on attapulgite at high pH levels.

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REFERENCES

[1] Greenlee, L. F., Lawler, D. F., Freeman, B. D., Benoit, M. & Moulin, P. 2009. Reverse osmosis desalination: Water sources, technology and today's challenges. *Water Research*, 43: 2317-2348.

[2] Gleick, P. H. 2006. The World's Water 2006–2007. *The Biennial Report on Freshwater Resources*. Island Press, Chicago.

[3] Enslin, F., Van der Mey, L. & Waanders, F. B. 2010. Acid leaching of heavy metals from bentonite clay, used in the cleaning of acid mine drainage. *The journal of the South African institute of mining and metallurgy*, 110: 187-191.

[4] Gupta, V. K. & Ali, I. 2012. Environmental Water: Advances in Treatment, Remediation and Recycling. Elsevier.

[5] Ayari, F., Srasra, E. & Trabelsi-Ayadi. M. 2005. Characterization of bentonic clays and their use as adsorbent. *Desalination*, 185: 391-397.

[6] Mukherjee, S. 2013. The Science of Clays: Applications in Industry, Engineering and Environment. Springer. India.

[7] Klein, C. & Dutrow, B. 2008. Mineral Science. 23rd ed. Hoboken, NJ: John Wiley & Sons.

[8] Murray, H. H. 2000. Traditional and new application for kaolin, smectite, and palygorskite: a general overview. *Applied Clay Science*, 17: 207-221.

[9] Brink, M. C. 2012. A method of treating polluted water. (Patent: RSA P56169ZA00). Registered on 31 May 2012.

[10] Potgieter-Vermaak, S. S., Potgieter, J. H., Monama, P. & Van Grieken, R. 2006. Comparison of limestone, dolomite and fly-ash as pre-treatment agents for acid mine drainage. *Minerals Engineering*, 19: 454-462.

[11] Monhemius, A. J. 1977. Precipitation diagrams for metal hydroxides, sulphates, arsenates and phosphates. Trans. Inst. Min. metal. Sec. C, p 203.

[12] Mittal, H., Fosso-Kankeu, E., Mishra, S. B. & Mishra, A. K. 2013. Biosorption potential of Gum ghatti-g-poly (acrylic acid) and susceptibility to biodegradation by B. subtilis. *International Journal of Biological Macromolecules*, 62: 370 – 378.

[13] Hameed, B. H. & Foo, K. Y. 2010. Insights into the modelling of adsorption isotherm systems. *Chemical Engineering Journal*, 156: 2-10.

[14] Fosso-Kankeu, E., Mulaba-Bafubiandi, A.F., Mamba, B.B. and Barnard, T.G. 2011. Prediction of metal-adsorption behaviour in the remediation of water contamination using indigenous microorganisms. Journal of Environmental Management, 92 (10), pp 2786-2793.

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