

# Surfactant Impregnated Bentonite Clay for the Adsorption of Anionic Dyes

Elvis Fosso-Kankeu, Frans Waanders, and Charissa Laurette Fourie

**Abstract**— Water scarcity is a reality in South Africa due to a number of factors including the presence of invasive foreign plant species and the effects of global warming. It is therefore necessary to develop efficient and cost effective water treatment techniques to protect our already limited water resources. In this study bentonite clay was impregnated with the surfactant hexadecyltrimethylammonium bromide (HDTM) and then used for the removal of anionic dyes from solutions. The clays were characterized using XRD, XRF and FT-IR spectroscopy. The first- and second order kinetic models as well as the Langmuir- and Freundlich isotherm models were used to determine the bentonite's adsorption affinity. The effects of adsorbent dosage, initial dye concentration and contact time were also tested in this study. The natural bentonite (NB) did not adsorb the tartrazine (TAR) or brilliant blue (BB). The HDTM impregnated bentonite performed very well in adsorbing both anionic dyes. The impregnated clay's affinity for BB ( $q_e = 23.47$  mg/g) and TAR ( $q_e = 23.66$  mg/g) are almost the same. HDTM-bentonite can therefore be considered to improve the adsorption capacity of bentonite clay applied for the treatment of water contaminated with anionic dyes.

**Keywords**— Anionic dyes; Adsorption; Bentonite; Surfactant; Brilliant blue; Tartrazine

## I. INTRODUCTION

DYES are more stable due to their artificial origin and their complex molecular structure, they are not easily biodegraded and conventional water treatment methods are proven to be ineffective [1]. Due to an estimated dye production rate of over 10000 tons per year and their extensive industrial use, the environmental pollution increases [2]. When these dyes are introduced into surface waters, it limits sunlight transmission into the water due to its colour intensity. This has a negative effect on aquatic plants and therefore it is hazardous to the aquatic ecosystem [3]. These dyes break down into products that can be toxic, mutagenic or carcinogenic. It is therefore of utmost importance that the dyes be removed from the water to make it safe for human consumption and to protect the environment [4, 5].

Elvis Fosso-Kankeu is with the School of Chemical and Minerals Engineering of the North West University, Bult area-Potchefstroom-South Africa.

Frans Waanders is with the School of Chemical and Minerals Engineering of the North West University, Bult area-Potchefstroom-South Africa

Charissa Laurette Fourie is with the School of Chemical and Minerals Engineering of the North West University, Bult area-Potchefstroom-South Africa.

Various methods exist that can be applied to remove dyes from waste water. Waste water treatment methods can be divided into the following main categories: biological treatment, chemical treatment and physical treatment methods. Adsorption is a physical treatment method and it is a favoured technique due to its removal efficiencies of pollutants that are too stable for conventional techniques. It also produces a product of high quality and it is an economically feasible method [6, 7].

A lot of different dyes can be identified. Dye categorization is done based on the dye's chemical nature and their application. There are three classes of anionic dyes namely: acid dyes, reactive dyes and direct dyes [8]. A previous study has shown that bentonite clay in its natural form hardly adsorbs anionic dyes [9]. The study revealed that bentonite clay has a negative net charge and therefore it can be used for the removal of cationic dyes, such as methylene blue, from water. Bentonite however hardly adsorbs anionic dyes such as methyl orange. It is therefore necessary to use surfactant impregnation to increase the clay's adsorption affinity for these anionic dyes.

In this study the adsorption of anionic dyes onto HDTM-surfactant impregnated bentonite clay is evaluated.

## II. EXPERIMENTAL

### A. Materials

Natural bentonite clay (NB) from Potchefstroom in the North-West region was used as adsorbent during the experiments. The clay was ground and sieved to obtain a particle size of 106  $\mu\text{m}$  and smaller. The clay has a cation exchange capacity (CEC) of 62 cmol/kg.

Anionic dyes such as brilliant blue (BB), obtained from Sigma Aldrich, and tartrazine (TAR), obtained from ACE chemicals, were removed from water with the use of the bentonite clay. The structure of the clay was altered by means of surfactant impregnation because of the clay's natural anionic charge that causes it to hardly adsorb the anionic dyes. The surfactant that was used for the impregnation was hexadecyltrimethylammonium bromide, obtained from ACE chemicals.

### B. Preparation of impregnated clay

The procedure followed for the impregnation of bentonite is as follows. 21 g of bentonite clay was added to 0.54 L of distilled water. The impregnated bentonite was prepared by adding the surfactant (HDTM) to the mass value equivalent to

twice the clay's CEC. The mixture was kept in suspension for 24 hours at 160 rpm and 25°C by using a temperature controlled orbital shaker. The impregnated clay was washed with distilled water and dried at 70°C for 24 hours.

### C. Characterization of the clay

To determine the mineralogical composition of the clay a Philips X'Pert pro MPD X-ray diffractometer (XRD) was used at 40 kV and 30 mA with scan speed: 2 deg/min, 2θ scan range: 3 – 90 deg and the step width: 0.01 deg.

An X-ray fluorometer (XRF) (MagiX PRO & SuperQ Version 4) was used to determine the elemental composition of the clay. The XRF analysis was done at 50 kV and 125 mA.

For the identification of the functional groups in the clay and for the evaluation of the surface activation, the FT-IR spectrum was obtained using the IRAffinity-1S Fourier transform infrared spectrophotometer from Shimadzu with a spectral range from 4000-400 cm<sup>-1</sup>.

### D. Adsorption studies

The equilibrium concentration of each solution was determined using an UVmini-1240 UV-VIS spectrophotometer at the following wavelengths: 425 nm for TAR and 592.5 nm for BB.

The experiments were carried out in a batch system where the temperature, adsorbent particle size, rotation speed and solution volume were kept constant at 25°C, 106 μm, 160 rpm and 0.1 L respectively. The varying parameters that were considered for the experiments were adsorbent dosage (0.01 - 0.3 g), initial dye concentrations (10 - 100 mg/L) and contact time (15 – 90 min).

### E. Isotherm and kinetic models

The adsorption affinity of the natural bentonite clay and impregnated bentonite clay for the removal of different dyes were evaluated using the Langmuir and Freundlich isotherms [10]. The Langmuir isotherm model assumes monolayer adsorption in single solute systems with its linear form given by:

$$\frac{C_e}{q_e} = \frac{1}{k \cdot q_m} + \frac{C_e}{q_m} \quad (1)$$

The Freundlich model is not restricted to monolayer adsorption and it can be applied in heterogeneous systems where its linear form can be expressed by:

$$\log q_e = \log k_f + \frac{1}{n} \cdot \log C_e \quad (2)$$

In the isotherm models  $C_e$  is the concentration of dye at equilibrium in (mg/L),  $q_e$  is the concentration of the dye at equilibrium in (mg/g),  $q_m$  is a Langmuir constant associated with the adsorption capacity in (mg/g),  $k$  is a Langmuir constant related to energy released during adsorption in (L/mg),  $k_f$  is the Freundlich adsorption capacity parameter in (mg/g) and  $n$  is the intensity of adsorption.

To aid in identifying the adsorption rate the pseudo first- and second order models are used [11]. The pseudo first- and second order kinetic models are given by:

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

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

where:  $q_e$  is the concentration of the dye at equilibrium in (mg/g),  $q_t$  is the amount of dye adsorbed at time  $t$  in (mg/g),  $k_1$  is the first order rate constant in (min<sup>-1</sup>),  $k_2$  is the second order rate constant in (g/mg.min<sup>-1</sup>) and  $t$  is the time in (min).

## III. RESULTS AND DISCUSSION

### A. Mineralogical and elemental composition of the clay

The XRD results of natural bentonite clay showed that bentonite is dominant in the clay's composition where quartz and albite are also present. From the XRF analysis alumina and silicate are present which indicates a possible adsorbate species removal by SiO<sub>2</sub> and/or Al<sub>2</sub>O<sub>3</sub>. However other elements including calcium, chloride, iron, magnesium, manganese, sodium and titanium were identified which can have a negative effect on the binding sites available.

TABLE I  
XRD RESULTS OF NATURAL BENTONITE CLAY

Phase name	Figure of merit
Quartz	0.259
Bentonite	1.614
Albite	0.671

### B. FT-IR analyses

The FT-IR results of the natural bentonite (NB) and HDTM impregnated bentonite are shown in Fig. 1. From this figure noticeable differences can be observed as the surfactant influences the structure of NB.

There is a group of adsorption peaks between 3390 and 3610 cm<sup>-1</sup> which is due to stretching bands of the hydrogen bonded O-H groups present in the natural bentonite and HDTM-bentonite. At 3016 cm<sup>-1</sup> there is a peak corresponding to an unsaturated asymmetric stretch vibration of C=C-H that formed after HDTM impregnation. In the region 2918-2848 cm<sup>-1</sup> there are two strong peaks that formed for HDTM-bentonite which indicates the symmetric and asymmetric stretching vibration of methyl (C-H) groups that was not present in NB.

The increasing peak intensities between 1471 and 1487 indicate the bending vibration of N-H of secondary amines. These secondary amines are present in the structure of HDTM before impregnation. It is therefore expected that the HDTM impregnated clay contains this functional group.

The band intensity for NB at 1614 cm<sup>-1</sup> was decreased after HDTM impregnation also confirming the modification of NB.

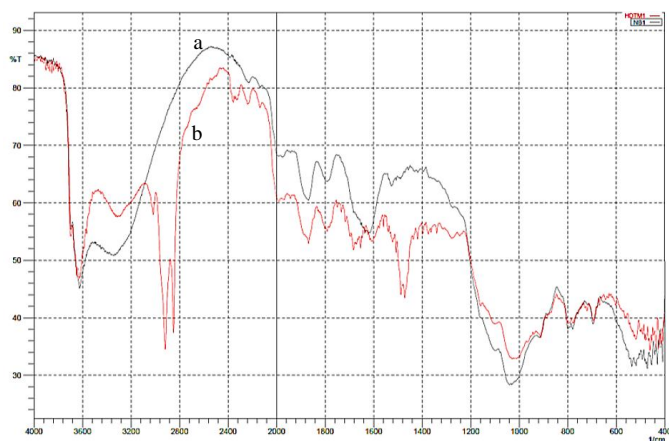


Fig. 1: FT-IR spectra of (a) NB and (b) HDTM-bentonite

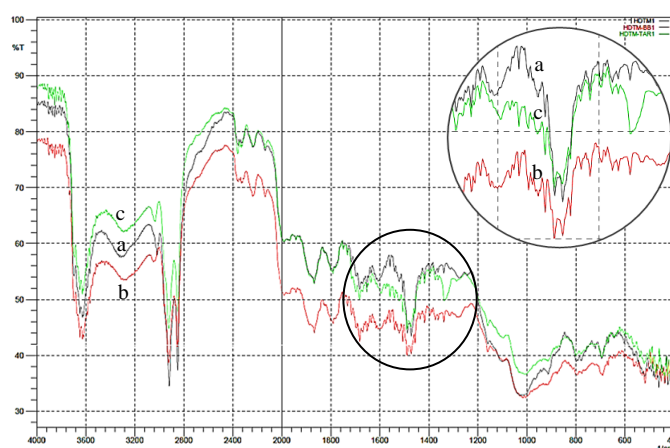


Fig. 3: FT-IR spectra of (a) HDTM-bentonite and of HDTM-bentonite after the adsorption of (b) BB and (c) TAR

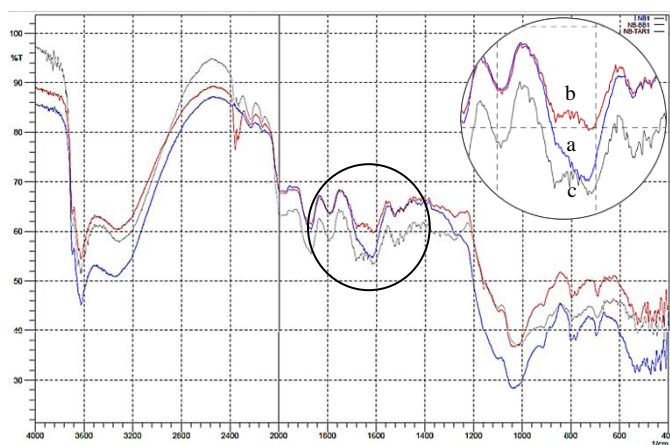


Fig. 2: FT-IR spectra of (a) NB and of bentonite after the adsorption of (b) BB and (c) TAR

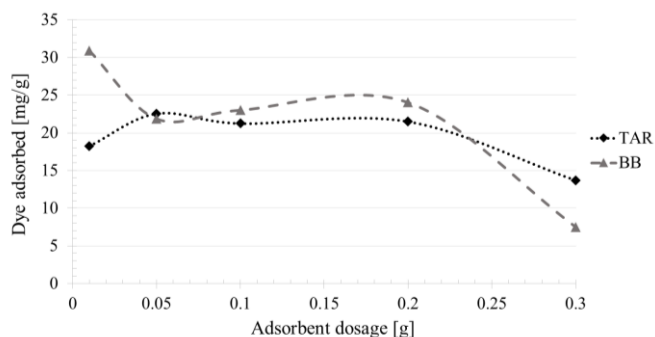
From the FT-IR spectra (see Fig. 2) there is only a small difference is in the band at  $1614\text{ cm}^{-1}$  corresponding to the stretching vibration of  $\text{-C=O}$  in the natural bentonite structure. After adsorption of BB and TAR this peak's intensity reduces slightly.

In Fig. 3 at  $3016\text{ cm}^{-1}$  there is a peak corresponding to an unsaturated asymmetric stretch vibration of  $\text{C=C-H}$  which is reduced after the adsorption of BB. A smaller reduction in this peak is observed for TAR. In the region  $2918\text{--}2848\text{ cm}^{-1}$  there is a change in the band corresponding to the stretch vibration of  $\text{C-H}$ . In the region  $1490\text{--}1470\text{ cm}^{-1}$  there is a change in the band corresponding to the stretching vibration of  $\text{C-C}$  in the aromatic ring. This band diminishes after the adsorption of the different dyes and it can be seen that the change in this band is more evident for BB adsorption.

### C. Adsorption behaviour

The effect of adsorbent dosage (see Fig. 4) was tested where the initial concentration of dyes was kept constant at  $50\text{ mg/L}$  and the contact time was kept constant at  $90\text{ min}$ . The optimum adsorbent dosage for BB and TAR was determined to be  $0.2\text{ g}$ . This optimum dosage was used in further experiments.

For the effect of initial dye concentration (see Fig. 5) the adsorbent dosage was kept constant as determined in the previous experiments and the contact time was kept constant at  $90\text{ min}$ . It can be observed that the adsorption of BB and TAR onto HDTM-bentonite exhibited a sharp increase between  $10$  and  $50\text{ mg/L}$  after which the adsorption did not increase further.

Fig. 4: Effect of adsorbent dosage on the adsorption of dye for a contact time of  $90\text{ min}$

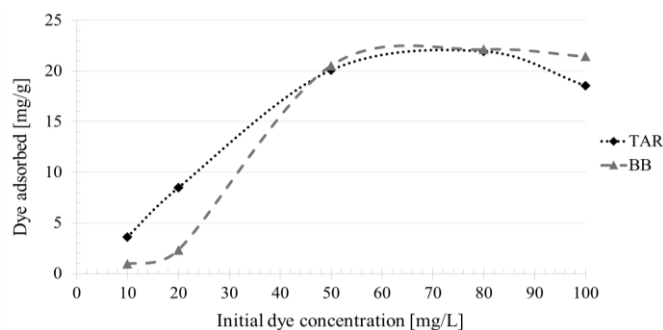


Fig. 5: Effect of initial dye concentration on dye adsorption for a contact time 90 min

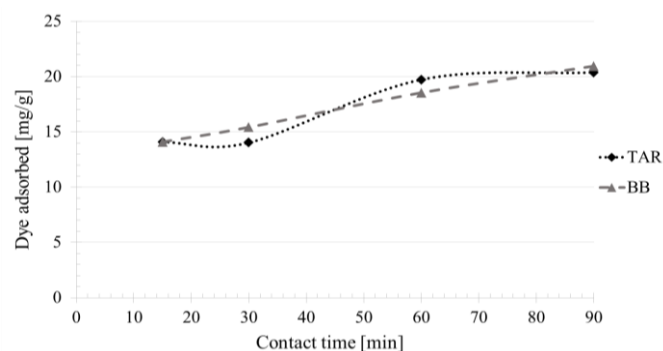


Fig. 6: Effect of contact time on the adsorption of dyes

The effect of contact time (see Fig. 6) on the adsorption of the anionic dyes was investigated at the optimum adsorbent dosage and at a concentration of 50 mg/L. When the contact time was increased, the amount of dye adsorbed was also increased up until 60 min for TAR, after which the adsorption exhibited only a very small increase. For BB the amount of dye adsorbed kept increasing up until 90 min. This suggests that the adsorption of TAR achieves equilibrium faster.

#### D. Isotherm and Kinetic models results

NB did not adsorb the anionic dyes and therefore the isotherm- and kinetic models' constants could not be calculated for NB. The Langmuir isotherm model graph (see Fig 7) for the various dyes were constructed with  $C_e/q_t$  as a function of  $C_e$ . For the Freundlich isotherm model graph (see Fig. 8)  $\log(q_e)$  was plotted as a function of  $\log(C_e)$ .

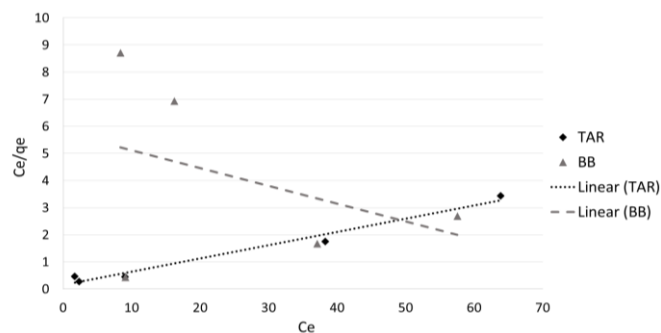


Fig. 7: Linear regression of the Langmuir isotherm model

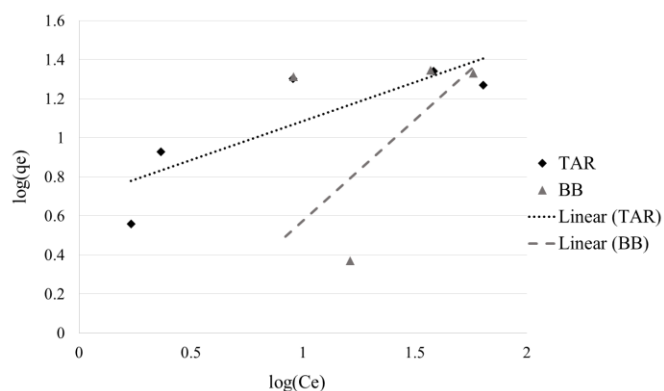


Fig. 8: Linear regression of the Freundlich isotherm model

TABLE I  
CONSTANTS FOR THE ISOTHERM MODELS

	Langmuir isotherm		Freundlich isotherm	
	TAR	BB	TAR	BB
$R^2$	0.7040	0.3511	<b>0.9749</b>	<b>0.7996</b>
$q_m$ [mg/g]	20.53	NF	-	-
$k$ [L/mg]	$315.5 \times 10^{-3}$	NF	-	-
$n$	-	-	2.507	0.968
$k_f$ [mg/g]	-	-	4.849	0.349

\*NF: No fit

From the  $R^2$  values in Table 1 it is clear that the Freundlich isotherm model is a better fit for BB and TAR adsorbed by HDTM-bentonite, with the  $R^2$  values at 0.9749 and 0.7996 respectively.

The pseudo first-order kinetic model graph was plotted where  $\log(q_e - q_t)$  is a function of time (see Fig. 9) and the pseudo second-order kinetic model graph is a graph of  $t/q_t$  as a function of time. The kinetic models are necessary in determining the rate constants corresponding to the adsorption rate.

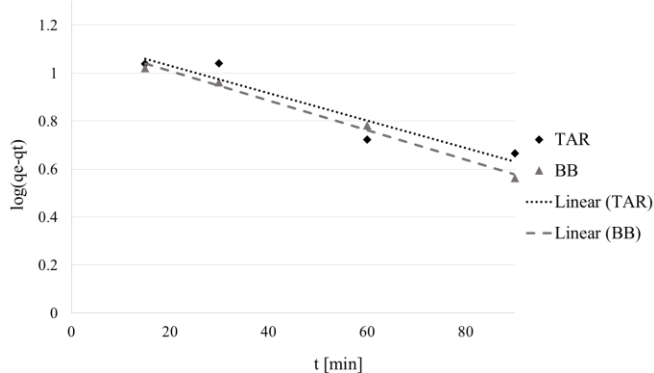


Fig. 9: Linear regression of the pseudo first order kinetic model

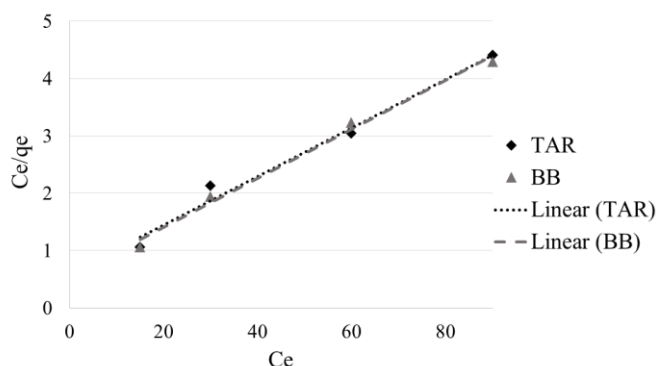


Fig. 10: Linear regression of the pseudo second order kinetic model

TABLE II  
CONSTANTS FOR THE PSEUDO FIRST- AND SECOND ORDER KINETIC MODELS

	Pseudo first order		Pseudo second order	
	TAR	BB	TAR	BB
$R^2$	0.8976	0.9908	<b>0.9817</b>	<b>0.9912</b>
$q_e$ [mg/g]	13.981	13.571	23.66	23.47
$k_1$ [min <sup>-1</sup> ]	$13.2 \times 10^{-3}$	$14.2 \times 10^{-3}$	-	-
$k_2$ [g/mg.min <sup>-1</sup> ]	-	-	$3.00 \times 10^{-3}$	$3.20 \times 10^{-3}$

From the  $R^2$  values in Table 2 it is clear that the experimental data can be represented by the pseudo second-order model as the  $R^2$  values are higher than those of the pseudo first-order model.

The adsorption capacity of HDTM-bentonite for the two dyes are 23.66 mg/g for TAR and 23.47 mg/L for BB where the NB did not adsorb these anionic dyes.

It can be observed from the results obtained in Table 2 that HDTM-bentonite removes BB and TAR from solution. This indicates successful impregnation of NB by using HDTM as a surfactant. Similar results were obtained in previous studies [12, 13].

#### IV. CONCLUSION

This study investigates the removal of anionic dyes from solution with the use of surfactant impregnated bentonite clay. The results obtained throughout this study revealed that bentonite modification with HDTM enhanced the rate at which the dyes were adsorbed. An increase in initial dye concentration in the solution increased the amount of BB and TAR adsorbed onto the HDTM-bentonite, but at an initial dye concentration of 50 mg/L and higher, the adsorption remained more or less constant, which was likely due to the saturation of the binding sites.

The batch kinetic studies revealed that the data corresponded better with the pseudo second-order kinetic model. The isotherm studies revealed that the Freundlich isotherm model is a better fit for BB and TAR adsorbed by HDTM-bentonite.

From the results obtained it can be concluded that HDTM-bentonite is an effective adsorbent in the removal of BB and TAR from solution with an adsorption capacity of 23.66 mg/g for TAR and 23.47 mg/L for BB where NB did not adsorb either of these dyes. HDTM-bentonite can therefore be utilised in industrial wastewater treatment for the removal of anionic dyes.

#### ACKNOWLEDGEMENT

The authors are grateful to the sponsor from the North-West University and the National Research Foundation (NRF) in South Africa. The contribution of Dr O. Ntwampe and Mr N. Lemmer are really appreciated.

#### REFERENCES

- [1] Padmavathy, S., Sandhya, S., Swaminathan, K., Subrahmanyam, Y.V., Chakrabarti, T. & Kaul, S.N. 2003. Aerobic decolorization of reactive azo dyes in presence of various cosubstrates. *Chem. Biochem. Eng. Q.*, 17(2003):147-151.
- [2] Forgacs, E., Cserháti, T. & Oros, G. 2004. Removal of synthetic dyes from wastewaters: a review. *Environment international*, 30(2004):953-971.  
<http://dx.doi.org/10.1016/j.envint.2004.02.001>
- [3] Shen, D., Fan, J., Zhou, W., Gao, B., Yue, Q. & Kang, Q. 2009. Adsorption kinetics and isotherm of anionic dyes onto organo-bentonite from single and multisolute systems. *Journal of hazardous materials*, 172(2009): 99-107.  
<http://dx.doi.org/10.1016/j.jhazmat.2009.06.139>
- [4] Chung, K-T. 2000. Mutagenicity and carcinogenicity of aromatic amines metabolically produced from azo dyes. *Journal of environmental science and health, part C: Environmental Carcinogenesis and ecotoxicology reviews*, 18(2000): 51-74.  
<http://dx.doi.org/10.1080/10590500009373515>
- [5] - Fosso-Kankeu E, Mittal H, Mishra SB, Mishra AK. 2015. Gum ghatti and acrylic acid based biodegradable hydrogels for the effective adsorption of cationic dyes. *Journal of Industrial and Engineering Chemistry*. 22: 171-178.  
<http://dx.doi.org/10.1016/j.jiec.2014.07.007>
- [6] Kharub, M. 2012. Use of various technologies, methods and adsorbents for the removal of dye. *Journal of environmental research and development*, 6(2012): 879-883.
- [7] Robinson, T., McMullan, G., Marchant, R. & Nigam, P. 2001. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource technology*, 77(2001): 247-255.  
[http://dx.doi.org/10.1016/S0960-8524\(00\)00080-8](http://dx.doi.org/10.1016/S0960-8524(00)00080-8)
- [8] Adinew, B. 2012. Textile effluent treatment and decolorization techniques- a review. *Bulgarian journal of science education*, 21(2012): 434-456.
- [9] Fosso-Kankeu, E., Waanders, F. & Fraser, C. 2014. Bentonite clay adsorption affinity for anionic and cationic dyes. Cape Town, 6th Int'l Conf. on Green technology, renewable energy & environmental Engg.
- [10] Okeola, F.O. & Odeunmi, E.O. 2010. Freundlich and Langmuir isotherms parameters for adsorption of methylene blue by activated carbon derived from agrowastes. *Advances in natural and applied sciences*, 4: 281-288.
- [11] Theivasaru, C., Mysamy, S. & Sivakumar, N. 2011. Kinetics, isotherms and thermodynamics studies of adsorption of congo red from aqueous solution onto cocoa shell activated carbon. *Research journal of chemistry and environment*, 15(2011):34-38.
- [12] Gök, Ö., Özcan, A.S. & Özcan, A. 2010. Adsorption behavior of a textile dye of reactive blue 19 from aqueous solutions onto modified bentonite. *Applied surface science*, 256(2010):5439-5443.  
<http://dx.doi.org/10.1016/j.apsusc.2009.12.134>
- [13] Aki, M.A., Youssef, A.M. & Al-Awadhi, M.M. 2013. Adsorption of acid dyes onto bentonite and surfactant-modified bentonite. *Journal of analytical & bioanalytical techniques*, 4(2013):1-7.

The corresponding author is currently a Senior Lecturer in the School of Chemical and Minerals Engineering at the North-West University (Potchefstroom). He is an NRF rated researcher who has published journal articles, book chapters and book.

Dr Elvis Fosso-Kankeu has been the recipient of several merit awards.