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Evaluation of N-terminated siloxanes grafted onto lignocellulose as adsorbent for the removal of phenol red from water

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Abstract This study reports the chemical modification of lignocellulose (from Kikuyu grass) with N-terminated siloxanes and its utilisation as adsorbent for the removal of phenol red from aqueous media. The stability of the bond between lignocellulose and siloxane was assessed after Soxhlet extraction of unreacted siloxanes in tetrahydrofuran for 5 h, as well as soaking the materials in water for 24 h. Adsorption tests showed the prepared materials to be good candidate for the removal of phenol red (dye) from water, with adsorption capacity from 1.454 to 3.312 mg of phenol red adsorbed per gram of adsorbent. The kinetics of adsorption was found to follow a pseudo-second-order equation indicating chemisorption rather than simple forces of association. The linearised form of adsorption isotherms matched with the Langmuir model.

Keywords Lignocellulose · N-terminated siloxane · Chemical modification · Phenol red · Adsorption · Kinetics · Isotherms

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Introduction

Lignocellulose is the most abundant renewable resource on the planet. Its utilisation has recently gained considerable attention in many applications (Belgacem and Gandini 2005; Iqbal et al. 2013). Sustainability, eco-efficiency and cost-effectiveness of lignocellulose are directing the development of the next generation of materials, products and processes (Xie et al. 2007; John and Anandjiwala 2008; Mulinari et al. 2010). Although waste from mowing grass is considered as useless after it had served to embellish yards, this material can be of great importance because of its numerous functional groups content. Lignocellulose functional groups have shown good capacity in adsorbing various pollutants (heavy metals, persistent pollutants and dyes) from aqueous media (Rege et al. 2000; Aleksandrova et al. 2004). However, lignocellulose functional groups are more active after release from intermolecular bonds (Nguyen 1982). A range of techniques including silane treatment, acetylation and benzoylation (Gadhe et al. 2006; Baltazar-Y-Jimenez and Bismarck 2007; Kekalo et al. 2008; John and Anandjiwala 2008) are used for chemical modification of lignocellulose. Such modification can avail the lignocellulosic material to be used as adsorbent for the removal of pollutants from water.

Among different water pollutants, phenol red (dye) has attracted a lot attention. Researchers (Mittal et al. 2009) have used deoiled soya for the removal and recovery of phenol red from wastewater; the adsorption capacity was found to be 2.6×10^{-5} mol g⁻¹. When using activated charcoal for the removal of phenol red, Iqbal and Ashiq (2007) found that its adsorption was favoured at low temperatures, and the dye was chemisorbed on activated charcoal. Laccase from microorganism (Trametes versicolor, CBS100.29) growth was used by Moldes et al.



(2004) to investigate the decolourisation of phenol red; their results were 36 % in 24 h and 40 % after 48 h. Adsorption of phenol red was assessed by Abdullah et al. (2012) on silica-filled epoxidized natural rubber (ENR)/ polyvinyl chloride (PVC) Beads; 2.67 mg of dye per g of phenol red were adsorbed onto beads. Vala and Tichagwa (2013) investigated the removal of phenol red from water using clinoptilolite modified with N-terminated siloxanes; 0.32 mg of phenol red was removed per g of adsorbents. Ghaedi et al. (2014) used gold and titanium dioxide nanoparticles loaded on activated carbon for the removal of phenol red.

To the best of the authors' knowledge, no report was found in the literature on the grafting of N-terminated siloxanes onto lignocellulose for the preparation of adsorbent for the removal of dyes. Most of the previous works used carbonyl-terminated siloxanes for the chemical modification of lignocellulosic materials. Therefore, this study reports the chemical modification of lignocellulose from grass and its investigation as adsorbent for the removal of phenol red from aqueous solution. The study was carried out from February 2010 to November 2012 as part of PhD study, in the Department of Pure and Applied Chemistry, University of Fort Hare, South Africa.

Materials and methods

Materials and chemicals

Grass (Pennisetum clandestinum, Kikuyu grass)

Grass (*Pennisetum clandestinum*, Kikuyu grass) was collected from gardens within the University of Fort Hare (Eastern Cape, South Africa) and used as source of lignocellulose.

Chemicals: Dibutyltin dilaurate (DBTDL)

Chemicals: Dibutyltin dilaurate (DBTDL) was supplied by Sigma-Aldrich and phenol red by Hopkin & Williams Ltd. Three siloxanes: 3-aminopropyl-terminated polydimethylsiloxanes (NH15D, NH40D and NH130D, Mw = 1,000, 2,600, and 11,000 g/mol, respectively) were supplied by Wacker Chemie AG/Germany.

Methods

Grass: treatment and chemical modification

The plant material was milled into powder and soluble substances were extracted by decoction. The solid residue (lignocellulose) was oven-dried to constant weight at 105 °C overnight. The lignocellulose powder was then



hydrolysed in 2 % w/v H_2SO_4 by refluxing at 97.5 °C for 5 h (Shibazaki et al. 1995; Curreli et al. 2002). After filtration, the residue was thoroughly washed and overnight oven-dried at 105 °C.

After hydrolysis, lignocellulose was chemically modified with siloxanes according to the procedure of Matías et al. (2000) and Le Digabel et al. (2004) carried out as follows: in a 3-neck round bottomed flask, 10 ml of 3-aminopropylterminated polydimethylsiloxane were added to 1.5 g of hydrolysed lignocellulose mixed with 30 ml of dimethylformamide (DMF). The mixture was then refluxed for 5 h at 130 °C under a nitrogen atmosphere, in the presence of 200 µl of dibutyltin dilaurate (DBTDL). The unreacted siloxanes were Soxhlet extracted with 100 ml tetrahydrofuran (THF) for 5 h. The resulting modified lignocellulosic materials were designated as: LNH15D, LNH40D and LNH130D (lignocellulose modified with siloxane NH15D, NH40D and NH130D, respectively). It is important to indicate that a pungent smell of ammonia was noticed during the chemical modification of lignocellulose with N-terminated siloxanes and litmus paper tested positive.

Adsorption studies

A phenol red stock solution of 100 mg/l was prepared in de-ionised water and dissolution was achieved through *ultrasonication*. All solutions were prepared from the stock solution. Adsorption experiments were carried out by adding 100 ml solutions of different concentrations (0.25, 0.50, 1.0, 1.5 and 2.0 mg/l) of phenol red into 500 ml Erlenmeyer flasks containing 0.1 g of adsorbent, at pH 7.1. The flasks were shaken on an orbital shaker (mrc Orbital shaker, Israel) at 160 rpm and at room temperature. Aliquots of the shaken solution were taken after 5, 10, 20, 30, 60, 120, 180, 240, 300 and 360 min, filtered through a 0.45 µm syringe filter (Supor® Membrane, from Pall Corporation-USA), and then the phenol red concentrations measured using the UV-Vis spectroscopy at 433 nm. The amount of phenol red adsorbed by the lignocellulosic materials was determined by Eq. 1.

$$Q_{\rm t} = \frac{V(C_{\rm o} - C_{\rm t})}{m} \tag{1}$$

where Q_t is the adsorbed amount of phenol red at time, t; C_o and C_t are concentrations of phenol red (initial and at time, t, respectively); m is the mass of adsorbent, and V is the volume of adsorbate solution used.

Characterisation of the prepared adsorbents

Untreated, H₂SO₄-treated and chemically modified lignocellulose were characterised by different techniques. Material samples were dispersed in KBr matrix for Fourier



Fig. 1 FT-IR of untreated and modified lignocellulosic materials

Transform Infra Red (FTIR), using Perkin Elmer Lambda 25 spectrophotometer (Shelton, USA). The X-ray diffraction (XRD) patterns were obtained with a Bruker D8 diffractometer with Advance Cu-Ka radiation $(\lambda K\alpha 1 = 1.5406 \text{ Å})$ at 40 kV and 40 mA. The surface morphology was examined by scanning electron microscopy (SEM) with a Joel JSM-6390 LV scanning electron microscope (Tokyo, Japan) at voltage of 15 kV (materials were sputter coated with gold to prevent charging and improve surface resolution before observation). The thermogravimetric analysis (TGA) was evaluate on TGA-7 Perkin Elmer Pyris (heating rate of 20 °C/min at the temperature range of 20-900 °C in static atmosphere, weight of samples taken in the range of 7.6-9.8 mg).

Results and discussion

The materials obtained after grafting N-terminated siloxanes onto lignocellulose appeared to be light and fluffy compared with the raw material. Based on solid state *nuclear magnetic resonance* (submitted for another paper) and FTIR data and the release of ammonia, we proposed the chemical reaction of the modification of lignocellulose with N-terminated siloxanes to be as presented in Eq. 2.



Fig. 2 XRD pattern of untreated and modified lignocellulose

siloxanes. The chemical modification of lignocellulose with siloxanes showed FT-IR spectral bands (Fig. 1) between 808 and 1,266 cm⁻¹, which were attributed to siloxanes because that region is their main IR absorption region. Assignment of peaks was done as reported in the literature (Brown et al. 1988; Günzler and Gremlich 2000; Homma et al. 1999; Coates 2000; Hamciuc et al. 2007). An increase of peaks intensity was observed at 1,063 and 2,964 cm⁻¹ compared with the raw material.

The presence of Si–O–Si bridge could not be easily detected by FT-IR, since the typical vibration frequencies of this group around 950 and $1,100 \text{ cm}^{-1}$ is masked by the large and intense cellulose C–O stretching band centred around $1,034 \text{ cm}^{-1}$ (Coates 2000).

The chemically modified lignocellulosic materials were soaked in water for 24 h in order to explore their stability since they are intended to be used in contact with water. No change of peak was observed in the FT-IR spectra, implying that the grafting of siloxanes onto lignocellulose resulted into a strong chemical bond between the two moieties.

XRD analysis

The X-ray diffractogram permitted to examine the major crystalline peaks on each pattern. Results (Fig. 2) showed



FT-IR of lignocellulosic materials

FT-IR spectra were examined to explore the chemical modification of lignocellulosic material after grafting of

peaks occurring at around $2\theta = 15.23^{\circ}$ and 22.23° , which represent the cellulose crystallographic plane (John and Anandjiwala 2008; Mulinari et al. 2010). The XRD showed that hot water treatment increased the crystallinity of





Fig. 3 SEM images of grass and lignocellulose modified with siloxanes



Fig. 4 TGA and DTG of lignocellulosic materials

lignocellulosic material. It was also observed that H₂SO₄ and NH130D had similar trend, as hot water, although minor.



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SEM analysis

SEM images (Fig. 3) were obtained with intention to analyse the impact of siloxanes on the morphology of the modified lignocellulose.

The SEM images did not depict an explicit change in the morphology of grass and those of lignocellulose modified with siloxanes; however, the chemically modified lignocellulose showed images more dried out and smoothly than the one of grass treated with hot water.

TGA analysis

Examining the thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) of the untreated grass and the chemically modified lignocellulose (Fig. 4), results showed weight loss around 100 °C due probably to the moisture content for all the materials. All the materials appeared to have the same thermal decomposition pattern; however, untreated grass decomposed a bit earlier than the other materials. At around 320 °C, most materials showed significant weight loss of more than 60 %. After 320 °C, the new materials formed underwent moderately decomposition compared to the residue. It was noticed that lignocellulose modified with siloxanes produced more residue (due to their Si content) than grass treated with hot water.



Fig. 5 Effect of time and adsorption of phenol red

Lignocellulosic materials containing siloxanes presented slightly different thermal decomposition features compared with other materials, probably due to the siloxane segment within the materials.

Adsorption results

Effect of contact time on phenol red adsorbed onto grass- H_2O , grass- H_2SO_4 and modified lignocellulosic material with siloxanes

Grass treated with hot water (grass-H₂O) and the resulting materials treated with sulphuric acid (grass-H₂SO₄) were investigated as adsorbents for the removal of phenol red from aqueous solution. Plots of the highest phenol red concentration (2.0 mg/l) were obtained, and results (Fig. 5) clearly indicated that adsorption at time t (Q_t) was improved five times on grass-H₂SO₄ than on grass-H₂O. Adsorption capacity of phenol red onto LNH15D, LNH40D and LNH130D was 2.312, 1.454 and 1.7462 mg/g, respectively.

This probably meant that hydrolysis of lignocellulose with H_2SO_4 freed the functional groups from intermolecular forces, therefore, improved the adsorption properties of the materials towards phenol red. In addition, it was observed that after adsorption, desorption of phenol red occurred after 60 min from grass- H_2O than from grass- H_2SO_4 . The desorption process indicated the necessity of chemical modification of lignocellulose so as to improve and sustain the adsorption process.

Adsorption of phenol red onto lignocellulose modified with siloxanes was studied (as a function of time) in order to understand its uptake rate which in turn could help to predict the adsorption mechanism. Results (Fig. 5) showed that adsorption was rapid at the beginning and then started fluctuating before reaching equilibrium (for LNH40D and LNH130D). Adsorption onto LNH15D, however, occurred normally as: sharp, moderate and equilibrium, which was reached after 120, 60 and 180 min for LNH15D, LNH40D and LNH130D, respectively. Equilibrium was maintained until the end of experiments (6 h). This was probably an indication of chemical interaction between adsorbent and adsorbate, as described earlier. The above elapsed time to reach equilibrium appeared very short compared to 50 h spent during the adsorption of the same adsorbate (phenol red) onto silica-filled ENR/PVC (Abdullah et al. 2012). The investigation of the molecular weight effect on the adsorption process depicted a slightly higher adsorption capacity of lignocellulose modified with LNH130D (highest Mw) when compared with the others. Results, however, did not show any correlation between high molecular weight and adsorption capacities of the adsorbents. Moreover, lignocellulose modified with siloxanes had an adsorption capacity in between that of grass-H₂SO₄ (highest) and grass-H₂O (lowest). As elucidated previously, these results illustrated the importance of availability of functional groups, responsible of phenol red uptake onto the lignocellulose surface.

Pseudo-first order and pseudo-second order of phenol red adsorption onto lignocellulose modified with siloxanes

Pseudo-first-order and pseudo-second-order equations were used to explain the sorption mechanism of phenol red. The pseudo-first-order equation, also known as the Lagergren equation (Annadurai and Krishnan 1996; Zawani et al. 2009; Zhu et al. 2012), describes *physisorption*. It is expressed by Eq. (3) and gives an integrated form of Eq. (4).

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = k_1(Q_\mathrm{e} - Q_\mathrm{t}) \tag{3}$$

$$\log (Q_{\rm e} - Q_{\rm t}) = \log Q_{\rm e} - \frac{k_1 t}{2.303} \tag{4}$$

The plot of log $(Q_e - Q_t)$ versus t gives a straight line and the value of k_1 can be obtained from the slope of the graph.

The pseudo-second-order model (Eq. 5) is based on the assumption of chemisorption (Ho and McKay, 1999; Srivastava et al. 2006); its linearised integrated form is given by Eq. (6):

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_2 (q_\mathrm{e} - q_\mathrm{t})^2 \tag{5}$$

$$\frac{t}{Q_{\rm t}} = \frac{1}{k_2 Q_{\rm e}^2} + \frac{1}{Q_{\rm e}} t \tag{6}$$

where k_2 is the pseudo-second-order rate constant of adsorption (g mg⁻¹ min⁻¹); t =time (min).

If the pseudo-second-order kinetics is applicable to the system, then the plot of $\frac{t}{Q_t}$ versus *t* will give a linear relationship with $\frac{t}{Q_e}$ and $\frac{t}{k_2Q_t}$ as the slope and intercept, respectively.





Fig. 6 Pseudo-first-order models



Fig. 7 Pseudo-second-order models

Figures 6 and 7 illustrate the adsorption mechanism of phenol red onto lignocellulose modified with siloxanes by means of pseudo-first-order and pseudo-second-order as linear models.

Although the correlation coefficients (R^2) of the two models were good, it appeared that the pseudo-secondorder model was the best-fitting kinetic model because of their very high R^2 values (close to unity). This suggested more plausible chemisorption rather than simple forces of association (Ho and McKay 1999). This observation is also directly related to the fact that adsorption equilibrium is maintained stable, up to 6 h without desorption. Different interactions, including (1) electrostatic forces between the positively charged ketone carrying an additional proton (in the structure of phenol red, which exists as a zwitterion) and the nitrogen of siloxane moiety of the adsorbent, (2) H-bond between -OH of phenol red and nitrogen of the adsorbent, (3) interactions due to van de Waals forces and (4) π - π electron donor-acceptor interactions between the aromatic rings of phenol red and the adsorbent could have been the driving forces underpinning adsorption. Physisorption, however, should not be ignored because of the good R^2 values of pseudo-first order. Vala and Tichagwa (2013) found that adsorption of phenol red onto clinoptilolite modified with N-terminated siloxanes involved



chemisorption and physisorption. Mittal et al. (2008) reported a pseudo-second-order kinetics for the adsorption of phenol red onto bottom ash and deoiled soya. However, Abdullah et al. (2012) and Kadhim (2012) found that adsorption of phenol red proceeded via pseudo-first order rather than pseudo-second-order mechanism, when silica-filled ENR/PVC and granite were, respectively, used as adsorbents.

Isotherms of phenol red adsorbed onto lignocellulose modified with siloxanes

The Langmuir and Freundlich isotherm models were used to describe the adsorption data. The Langmuir isotherm assumes that the surface (monolayer and homogeneous) of any adsorbent material contains a number of active sites where the adsorbate attaches itself (Vadivelan and Kumar, 2005; Satyawali and Balakrishnan, 2007; Hameed et al. 2007; Sulak et al. 2007; Mohan et al. 2007) while the Freundlich isotherm describes adsorption onto heterogeneous systems and does not assume monolayer capacity (Vadivelan and Kumar 2005; Chatterjee et al. 2007).

The Langmuir equation is:

$$Q_{\rm e} = \frac{K \cdot Q_{\rm o} \cdot C_{\rm e}}{1 + K \cdot C_{\rm e}} \tag{7}$$

The Freundlich equation is:

$$Q_{\rm e} = K C_{\rm e}^{1/n} \tag{8}$$

where Q_e is the adsorption capacity (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), Q_o is the maximum amount adsorbed (mg/g), and K and n are constants.

Linear plots of Langmuir (Eq. 8) and Freundlich (Eq. 9) permit to obtain correlation coefficients (R^2) used to compare and identify the best fitted models.

$$\frac{C_{\rm e}}{Q_{\rm e}} = \frac{1}{Q_{\rm o}K} + \frac{1}{Q_{\rm o}}C_{\rm e} \tag{8}$$

$$\log Q_{\rm e} = \frac{1}{n} \log C_{\rm e} + \log K \tag{9}$$

Langmuir and Freundlich isotherm models of phenol red adsorbed onto lignocellulose modified with siloxanes were plotted and the results are presented (Figs. 8, 9). In the linearised forms of adsorption isotherms, the most precise match was acquired with the Langmuir model. The R^2 of Langmuir model for the adsorption of phenol red on lignocellulose modified with siloxanes was higher than the R^2 values of Freundlich models. Based on the Langmuir model, it is quite logical to assume that the results depicted a homogeneous structure of adsorbents. For Abdullah et al. (2012), Langmuir and Freundlich models fitted the experimental data for the adsorption of phenol red onto



Fig. 8 Linear Langmuir isotherms of phenol *red* adsorbed onto lignocellulose modified with siloxanes



Fig. 9 Linear Freundlich isotherms of phenol *red* adsorbed onto lignocellulose modified with siloxanes

silica-filled ENR/PVC and granite were, respectively, used as adsorbents. Ghaedi et al. (2014) also reported the same feature when gold and titanium dioxide nanoparticles were loaded on activated carbon to adsorb phenol red. But, Vala and Tichagwa found that the Freundlich model was the better fitting model for adsorption of phenol red onto clinoptilolite modified with siloxanes.

The nonlinearised isotherm plot was also studied and results showed an unexpected plot of the phenol red uptake onto LNH40D (Fig. 10). This type of plot was not found in the literature, although it is close to a subtype of type VI isotherm as described by some authors (Sing et al. 1985; Rouquerol et al. 1994; Donohue and Aranovich 1998). The nonlinearised isotherms for LNH15D and LNH130D seemed to belong to the type VI isotherm; their steps indicate the complexity of the adsorption process. This nonlinearised model could also be extended to type I (for LNH15D) and type II (for LNH130D).

Conclusion

Fractionation of Kikuyu grass with H₂SO₄ was prior to the chemical modification of the lignocellulosic materials with



Fig. 10 Nonlinearised adsorption isotherm models

siloxanes. Fractionation of the material and its chemical modification with siloxanes were conducted in order to obtain adsorbents with enhanced adsorption capacity towards phenol red. The bond between the lignocellulose and siloxane moieties, investigated after Soxhlet extraction of unreacted chemicals in THF for 5 h and soaking in water for 24 h, showed to be stable. The materials prepared by grafting of N-terminated siloxanes onto lignocellulose depicted good adsorption properties when compared with grass-H₂O, making them adsorbent candidates for the removal of dyes. Adsorption appeared to follow pseudo-second-order kinetics with possible chemisorption. In the linearised form of adsorption isotherms, the most precise match was acquired with the Langmuir model.

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