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Research

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Synthesis, characterization and anionic dye sequestration capacity of cellulose nanocrystals derived from sugarcane bagasse: Experimental and regression modelling

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Abstract

This study reported the extraction of cellulose nanocrystals from sugarcane bagasse using acid hydrolysis method. Nanocrystals were characterized with scanning electron microscopy, energy dispersive X-ray, Fourier Transform Infra-Red spectroscopy and investigated for their adsorptive capacity for methyl orange (MO) sequestration. The disappearance of peaks at 1736 and 1429 cm^{-1} in addition to higher carbon content, greater crystallinity index from 1.09 to 1.21, predominantly nano range of particles (0.045 – 0.082 μm) and larger porosity are parameters that better-defined cellulose nanocrystals. A 2-fold improvement in monolayer adsorption capacity was obtained for cellulose nanocrystals (432.17 mgg^{-1}) described by Langmuir isotherm over bagasse (170.99 mgg^{-1}) described by Freundlich isotherm. Adsorption processes on both adsorbents were spontaneous, exothermic and best fitted to pseudo second order kinetics ensuing chemisorption. Polynomial regression model appropriately predicted equations that best describe the effects of different batch adsorption parameters on MO removal with better fittingness than experimentally generated data.

Keywords: Adsorption capacity, sugarcane bagasse, cellulose nanocrystals, exothermic, polynomial regression model.

Introduction

As indispensable as water is, quality water is difficult to come by particularly with the surging increase in the population-needing comfort coupled with the establishment of micro-industrial scale companies. Wastes generated at homes, companies and industries eventually find their ways into surface water thus degrading its quality (Assouline et al. 2015; Azeez et al. 2015, 2020a). This is expected to continue as the population continues to rise and more industries are created. Most pollutants that found their way into water bodies are non-easily biodegradable, recalcitrant, stable to oxidation and are as dangerous as their intermediates

and secondary metabolites (Jiang et al. 2017; Gautam et al. 2019; Beh et al. 2020). Methyl orange (MO) is a complex, highly water soluble, azo-structured anionic dye that has found usefulness in laboratories, photography and textile but its discharge in water has been reported to interrupt ecological balance along with disruption of water quality parameters (Keyhanian et al. 2016; Huang et al. 2017; Zhang et al. 2017; Adejumo et al. 2020). Hence, holistic approaches to removing highly toxic MO should be employed to meet up with water demands of the populace.

Several methods ranging from flocculation, coagulation, adsorption, biological degradation, membrane filtration, electrochemical and reverse osmosis are in use for wastewater remediation. Adsorption has been the frequently applied remediation method due to its simplicity and other encouraging attributes. However, contending with drawbacks associated with some of the above-mentioned methods as well as expensiveness of many adsorbents, different studies have reported applications of inexpensive and readily available adsorbents especially activated carbons from waste materials. These are also not without limitations as typically used adsorbents are macro-scaled and therefore large quantities would be used to achieve excellent results (Munagapati et al. 2019; Pavithra et al. 2019; Azeez et al. 2018, 2020a,b).

Meanwhile, progression in nanotechnology has made remediation a lot easier owing to the intrinsic characteristics of nanostructured materials that possess enhanced adsorptive properties as against macro-scaled materials. Moreover, their inexpensive, renewable, biodegradable, retentive and regenerative properties are too encouraging to dismiss in addition to using small quantity to achieve greater results (Suman et al. 2015; Mahfoudhi et al. 2017; Theivasanthi et al. 2018).

Nanocellulose is an environmentally compliant, decomposable, inexhaustive and non-hazardous adsorbent having a diameter dimension less than 100 nm with enhanced reactive sites together with other characteristics suitable for environmental remediation (Nechyporchuk et al. 2016; Bano and Negi, 2017). Nanocellulose has found usefulness in medicine, food and construction applications in addition to the environmental remediation of wastes due to its biocompatibility, tensile strength, abundant hydroxyl groups, large surface area and low toxicity (Dufresne, 2013; Hosseinidoust et al. 2015; Jorfi and Johan, 2015; Abitbol et al. 2016; Hakkarainen et al. 2016; Phanthong et al. 2018; Wang et al. 2019). It has been deployed for remediating dyes, volatile organic compounds, polycyclic aromatic hydrocarbons, heavy metals and pollutants of their likes (Chan et al. 2015; Jiang et al. 2017; Adejumo et al. 2020; Beh et al. 2020).

Nanocellulose is obtainable from cellulosic materials by modifying the crystallinity degree without disruption in functional group reactivities rather enhanced structural activities accompanied with improved morphological assemblage (Jiang et al. 2017; Beh et al. 2020). It is called cellulose nanofibers (CNFs) when it is extracted by mechanical processes and cellulose nanocrystals (CNC) when it is done using acid hydrolysis. Cellulose nanocrystals extracted by acid hydrolysis treatment have been extensively explored and are considered easier compared with other methods of nanocellulose syntheses (Jonoobi et al. 2015; Nechyporchuk et al. 2016; Oliveira et al. 2016; Theivasanthi et al. 2018). Nanocellulose has been prepared from widely available, abundant, cost-effective and renewable cellulosic materials such as corncob, corn straw, pineapple leaf, cassava bagasse, cotton, soy hulls, sago pith, kenaf core, rice straw, cocoa bean shell, bamboo, wood, banana leaf, newspaper, jute leaf, groundnut shell, wheat straw, sugarcane bagasse and flax fibre (Abraham et al. 2011; Neto et al. 2013; Pehlivan et al. 2013; Chan et al. 2015; Chen et al. 2011, 2015; Bano and Negi, 2017; El Achaby et al. 2018; Theivasanthi et al. 2018; Buthiyappan et al. 2019; Adejumo et al. 2020; Beh et al. 2020)

Sugarcane bagasse is a lignocellulosic fibrous residual waste from sugarcane (*Saccharum officinarum*) after sequencing its juice. It is widely available and litters carelessly in water and soil in Nigeria. It contains cellulose (45 - 55 %), hemicellulose (25 - 35 %) and lignin (18 - 24 %) and serves as a major raw material for biodiesel production (Ferreira et al. 2018). The high proportion of cellulose in sugarcane bagasse implies its predominant crystallinity and allows for modification of amorphous region. It has been used as an adsorbent for dyes, heavy metals and pesticides due to its richness in carboxyl, phenolic and hydroxyl groups essential for adsorption (Alves et al. 2016; Maya and Anjali, 2018; Buthiyappan et al. 2019). However, most studies reported the application of modified sugarcane bagasse or produced activated carbon from it. Though they were found effective as adsorbents but the additional cost of production and modification could limit these processes (Brandão et al. 2010).

Extraction of nanocellulose from sugarcane bagasse is a better alternative owing to non-disruption of inherent chirality, available functional groups, biodegradability and biocompatibility with large surface area, enhanced surface functionality and adsorptive properties (Theivasanthi et al. 2018; Adejumo et al. 2020; Beh et al. 2020).

Consequent upon novel properties of nanocellulose and its wide applications, this study was aimed at extracting nanocellulose using acid hydrolysis from sugarcane bagasse as an adsorbent for simulated dye wastewater remediation as well as predict model equations that best describe the adsorption process using polynomial regression analysis

Materials and methods

Sugarcane units were purchased at Oja-Oba market, Osogbo, Osun State, Nigeria. Sugarcane units were washed, peeled and its juice was extracted to leave residual bagasse. This was air-dried, milled to powder and oven-dried at 80 °C for 5 h to completely remove moisture. The powdered sugarcane bagasse was sieved with 425 µm mesh sieve and kept in a tight container for further use. All chemicals (NaOH, H₂SO₄, methyl orange) used are of analytical grade.

Synthesis of cellulose nanocrystals and characterization

The method of synthesis as described by Adejumo et al. (2020) was followed and is illustrated in the scheme (Figure 1). Fourier transform infrared spectroscopy (FTIR) (Model 500, Buck Scientific Inc.) was recorded in the range of 400– 4000 cm⁻¹ with a resolution of 4 cm⁻¹. Scanning electron microscopy coupled with energy dispersive X-ray was done with Jeol JSM-6400 for morphology and elemental composition.

Adsorption studies

Methyl orange preparation and batch adsorption

100 mgL⁻¹ of MO was prepared and different concentrations ranging from 10 – 50 mgL⁻¹ were used for the adsorption study. Influence of operational variables on the sequestration of MO on bagasse and cellulose nanocrystals were studied. This was achieved by varying initial solution pH from 2 to 10, initial MO concentrations from 10 to 50 mgL⁻¹, bagasse and cellulose nanocrystal dosage from 0.1 to 0.5 g, contact time from 0 to 75 min as well as temperature from 303 to 315 K. Batch adsorption was performed with 0.5 g of each adsorbent added to 50 mgL⁻¹ MO in a conical flask placed in a water bath with shaker (Uniscope water bath shaker) thermostatically regulated at 303 K for 30 min and agitated at 300 rpm for all parameters but for adsorbent dosage. Absorbance values were recorded at 480 nm with Jenway 6405 UV-Visible Spectrophotometer (Buch Scientific Inc. USA). The percentage sequestration of MO and quantity of MO adsorbed at a particular time were calculated using equations 1 and 2 respectively.

For determination of pH point of zero charges (pH_{pzc}), 0.1 g of each adsorbent was added to 0.1 M NaCl solution (200 ml) of known pH and adjusted to pH between 2 and 10 with HCl and NaOH.

Batch adsorption was investigated by

$$\% \text{ MO removal} = \frac{(C_i - C_f) \times 100}{C_i} \quad (1)$$

$$q_t = \frac{(C_i - C_t)V}{M} \quad (2)$$

q_t - amount of MO adsorbed per unit mass of adsorbent (mgg^{-1}) at time t , C_i - initial MO concentration (mgL^{-1}), C_f - final MO concentration (mgL^{-1}), C_t - concentration of MO remaining at time t , V - Volume of MO solution (L) and M - mass of adsorbent (g).

Adsorption isotherms

Four adsorption isotherms with their appropriate equations listed in equations 3 to 6b were applied to fit the equilibrium parameters between MO and adsorbents. The suitability of each model was predicted by comparing correlation coefficients (R^2); the closer it is to unity, the better it is for the description of an isotherm model.

Langmuir isotherm (Langmuir, 1918)

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max}K_L} \quad (3)$$

$$R_L = \frac{1}{1 + K_L C_o} \quad (3a)$$

Freundlich isotherm (Freundlich, 1906)

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \quad (4)$$

Tempkin isotherm (Tempkin and Pyshev, 1940)

$$q_e = B \ln A + B \ln C_e \quad (5)$$

$$B = RT/b \quad (5a)$$

Dubinin-Radushkevich (Dubinin and Radushkevich, 1947)

$$\ln q_e = \ln q_o - \beta \varepsilon^2 \quad (6)$$

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \quad (6a)$$

$$E = \sqrt{1/2\beta} \quad (6b)$$

C_e - equilibrium concentration of MO (mgL^{-1}), q_e - quantity of MO adsorbed at equilibrium (mgg^{-1}), $q_{\max}$ - maximum monolayer adsorption capacity (mgg^{-1}), K_L - Langmuir adsorption constant (Lmg^{-1}), R_L - Langmuir separation, K_f -Freundlich constants for binding energy, n - adsorption intensity, b (Jmol^{-1}) - heat of absorption and E -energy of adsorption.

Adsorption kinetics

Kinetic model studied for the fittingness of adsorption kinetics are listed in equations 7, 8 and 9. Adsorption mechanism was studied with intra-particle diffusion (eqn. 10). The suitability of each model for describing kinetic models was validated with correlation coefficient (R^2) and non-linear Chi-square test (eqn. 11).

Pseudo first order kinetics

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (7)$$

Pseudo second order kinetics

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

Elovich kinetics

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (9)$$

$$q_t = K_{diff} t^{1/2} + C \quad (10)$$

$$\chi^2 = \sum_{i=1}^n \frac{(q_{exp} - q_{cal})^2}{q_{cal}} \quad (11)$$

q_e – quantity adsorbed at equilibrium (mg g^{-1}), q_t – quantity adsorbed at time t (mg g^{-1}), K_1 – rate constant for the pseudo first order (min^{-1}), K_2 – rate constant of the pseudo second order ($\text{g mg}^{-1} \text{min}^{-1}$), K_{diff} – rate constant of intraparticle diffusion ($\text{mg g}^{-1} \text{min}^{-1/2}$), α – chemisorption rate and β – extent of surface coverage.

Adsorption thermodynamics

Parameters to describe adsorption thermodynamics were obtained from equations 12 and 13.

$$\ln K_o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (12)$$

$$\Delta G^o = \Delta H - T\Delta S \quad (13)$$

ΔS^o is change in entropy, ΔH^o is change in enthalpy and ΔG^o is change in free energy

Polynomial regression prediction of adsorption process

Data generated from adsorption isotherm, kinetics and thermodynamics were fitted to polynomial linear regression to predict optimum conditions that best describe the adsorption of MO on bagasse and cellulose nanocrystals. The polynomial regression model for prediction is based on equation 14 where a set of x interaction variables are modelled to obtain dependent y . The predictive agreement between experimentally generated and model predicted data was determined using correlation coefficient R^2 and statistical significance at 95 % confidence level. The predicted equations and validations for all experimental data are presented along with each batch adsorption parameter.

$$y = \beta_0 + \beta_1 x + \beta_2 x^2 \quad (14)$$

Where $\beta_0, \beta_1, \beta_2$ are intercepts of model

Results and discussion

Characterization of bagasse and cellulose nanocrystals

Scanning electron microscopy coupled with EDX was used to study morphological arrangement, particle size and elemental compositions of bagasse (Fig. 2a) and synthesized cellulose nanocrystals (Fig 2b). Diameters of particles of bagasse range between 2.0 and 6.4 μm with predominant particles having sizes between 3.1 and 4.2 μm (insert). Cellulose nanocrystals are nearly oval having particles in the range 0.045 to 0.193 μm predominantly between 0.045 and 0.082 μm (insert). The image of bagasse shows a more compressed morphology while the image of cellulose nanocrystal reveals a better porous morphology. These ranges and characteristics indicate nanostructure morphology of cellulose nanocrystals vital for adsorption processes (Chan et al. 2015; Yang et al. 2017a,b; Phanthong et al. 2018).

Cellulose nanocrystals contain higher weight percentage of carbon, silicon and lower weight percentage of oxygen compared to bagasse as obtained in EDX results (Fig. 2a and 2b). This implies a better adsorptive property for cellulose nanocrystals since adsorption capacity is a function of carbon content (Ojedokun and Bello, 2017; Buthiyappan et al. 2019).

To study the surface chemistry of both adsorbents, FTIR characterization spectra (Fig. 4) reveal major functional groups in bagasse (BG) and cellulose nanocrystals (NBG). Peaks at 3414 and 1053 cm^{-1} in BG indicate the presence of stretching vibrations of OH and asymmetric cellulosic bridges of C-O-C groups respectively whereas they occur at 3418 and 1047 cm^{-1} in cellulose nanocrystals. Peaks from 2897 to 2941 cm^{-1} in both adsorbents correspond to C-H of methyl and methylene. Peaks at 1736 and 1429 cm^{-1} signify the presence of uronic and acetyl C=O and C-O of esters from lignin and hemicellulose in BG but had disappeared in cellulose nanocrystals. Appearance of peak at 1121 cm^{-1} in cellulose nanocrystals attributed to SO_4^{2-} is an attestation of H_2SO_4 hydrolysis (Nechyporchuk et al., 2016). This implies a more crystalline cellulosic material in cellulose nanocrystals since hemicellulose and lignin are the amorphous regions in lignocellulose. Peaks between 1600 – 1638 cm^{-1} correspond to bending vibrations of OH associated with adsorbed water. Peaks in BG and cellulose nanocrystals spectra are representative of lignocellulose and nanocellulose reported in the literature. Moreover, the FTIR characterization indicates the retention of inherent cellulosic nature of BG in cellulose nanocrystals with complete removal of lignin and hemicellulose (Liu et al. 2016; Bano and Negi, 2017; Maya and Anjali, 2018; Ferreira et

al. 2018; Theivasanthi et al. 2018; Buthiyappan et al. 2019; Adejumo et al. 2020; Beh et al. 2020.

Further analysis of FTIR data on crystallinity index, degree of the disordered region and hydrogen bonding pattern were explored. Total crystallinity index (CI) was determined as the ratio of absorbance intensities of crystalline bands at 1373 to 2900 cm^{-1} while lateral order index (LOI) is the ratio of 1433 to 895 cm^{-1} proposed by Hurtubise and Krassig (1960) and Nelson and O' Connor (1964). The energy of hydrogen bonding (E_H) is described by equation 15. Crystallinity index and energy of hydrogen bonding are parameters to assess orderliness/crystallinity of a cellulosic material (Kumar et al. 2014; Bano and Negi, 2017; Kruer-Zerhusen et al. 2018).

$$E_H = \frac{1}{k} * \left(\frac{\nu_0 - \nu}{\nu_0} \right) \quad 15$$

Where k is $1.68\text{E}-2$, ν_0 and ν are frequencies of free hydrogen bonded OH (3600 cm^{-1}) and hydrogen bonded OH respectively.

The increase in values of CI, LOI and E_H from 1.09 to 1.21, 1.23 to 1.33 and 27.96 to 29.17 kcal imply an improvement in structural crystallinity and regularity of cellulose nanocrystals over bagasse. This aligned with results of Bano and Negi (2017) and Kruer-Zerhusen et al. (2018). The increased crystallinity index could be connected to the removal of amorphous regions of hemicellulose and lignin during NaOH treatment as obtained in FTIR and better ordered crystalline region due to formation of new hydrogen bonds (Zhang et al. 2013; Beh et al. 2020)

Effects of different parameters on batch adsorption studies

The surface charges play a prominent role in the adsorption process and as obtained for both adsorbents revealed by pH point of zero charge (pH_{pzc}), cellulose nanocrystals and bagasse were cationic below pH_{pzc} 4.1 and 8.3 respectively. At these values (pH_{pzc}), both adsorbents had zero net charge while they would be positively charged at $\text{pH} < \text{pH}_{\text{pzc}}$ and negatively charged at $\text{pH} > \text{pH}_{\text{pzc}}$. Expectedly, maximum removal of MO on these adsorbents occurred at pH 3 and 6 for cellulose nanocrystals and bagasse respectively (Fig. 4). Adsorption was maximum at these pH values due to electrostatic interaction between cationic surfaces of adsorbents (cationic at $\text{pH} < \text{pH}_{\text{pzc}}$) and anionic MO (Huang et al. 2017; Ojo et al. 2017; Moawad et al. 2020). There was an initial increase in percentage removal of MO on cellulose nanocrystals from pH 2 to 3 after which it dropped sizably till pH 10 while there was a gradual decrease in percentage removal of MO on bagasse from pH 2 to 5 followed by

an increase at pH 6 and thereafter dropped till pH 10. Prediction of effects of pH on percentage removal of MO modelled with polynomial regression follows equations 16a and 16b for bagasse and cellulose nanocrystals respectively. There was high accuracy ($R^2 = 0.928$) and statistically insignificant variations although with lower percentages between experimentally and predicted percentages of removal of MO on cellulose nanocrystals (Fig. 4). Conversely, the agreement between experimentally and predicted percentages of removal of MO on bagasse (Fig. 4) was significantly low ($R^2 = 0.015$).

$$y = 68.59 + 0.071x - 0.006x^2 \quad (R^2 = 0.015, p = 0.985) \quad 16a$$

$$y = 64.75 - 0.188x + 0.007x^2 \quad (R^2 = 0.928, p = 0.072) \quad 16b$$

Percentage uptake of MO on different dosages of cellulose nanocrystals increased from 69 – 78 % whereas a slight reduction in the percentage of adsorption on bagasse with an increase in dosage from 57.6 – 56.8 % was obtained. The increase in percentage adsorption recorded for nanocrystals may be connected to the availability of larger surface and more reactive sites for MO uptake. It is equally implying adsorption on the surface of nanocrystals. Conversely, reduction in the percentage of uptake on bagasse could be due to compactness of bagasse layers (Ojedokun and Bello, 2017; Suganya et al. 2017; Saravanan et al. 2019). Model equations of polynomial regression for predicting effects of dosage on percentage removal of MO are given as 17a and 17b for bagasse and cellulose nanocrystals respectively. The model predicted similar trends of a strong agreement without significant difference for cellulose nanocrystals and an average correlation with significant disparities for bagasse between model predicted and experimentally generated data.

$$y = 57.34 + 0.228x - 0.006x^2 \quad (R^2 = 0.57, p = 0.43) \quad 17a$$

$$y = 66.99 + 1.31x + 0.178x^2 \quad (R^2 = 0.99, p = 0.01) \quad 17b$$

Percentage sequestration of MO decreased with increase in the concentration of MO from 59.75 to 18.67 % for cellulose nanocrystals and 51.08 to 6.63 % for bagasse (Fig. 6) for lowest (10 mgL^{-1}) to the highest (50 mgL^{-1}) concentrations of MO. These reductions are related to the saturation of vacant reactive sites and pore spaces on both adsorbents (Suganya et al. 2017; Moawad et al. 2020). At low concentration, the ratio of MO molecules to adsorbent reactive sites was smaller hence higher percentage. However, as the MO concentrations increased, the ratio of MO molecules to adsorbent vacant reactive sites increased thus lower percentage. This agrees with reports of Anitha et al. (2016) and Ojo et al. (2017). The model predicted equations for initial concentrations of MO on bagasse and cellulose nanocrystals are given in equations 18a and 18b respectively. Strong correlations

with no significant differences between experimental and model data were obtained for both adsorbents. Regression model predicted an increase in the percentage of MO adsorbed with respect to initial concentrations on bagasse (Fig. 6)

$$y = 80.80 - 29.94x + 2.52x^2 \quad (R^2 = 0.89, p = 0.11) \quad 18a$$

$$y = 73.22 - 20.64x + 1.86x^2 \quad (R^2 = 0.98, p = 0.022) \quad 18b$$

The rate of adsorption with time was initially swift then became gradual until it attained equilibrium (Fig. 7) at 45 and 35 min for nanocrystals and bagasse respectively. This trend of swift uptake of MO is attributable to the initial driving force of MO to overcome the resistance of mass transfer and availability of vacant reactive sites on both adsorbents that got occupied as time progressed (Inyinbor et al. 2017; Ojedokun and Bello, 2017; Adekola et al. 2019). Regression model predicted equilibrium was attained at 20 and 15 min for bagasse and nanocrystals respectively following equations 19a and 19b. The predicted model values had significant correlations with experimental data with no significant variations.

$$y = 75.57 + 1.37x - 0.03x^2 \quad (R^2 = 0.94, p = 0.06) \quad 19a$$

$$y = 81.72 + 1.19x - 0.03x^2 \quad (R^2 = 0.98, p = 0.022) \quad 19b$$

Effects of temperature on the uptake of MO on both adsorbents were detailed between 303 – 323 K. Adsorption percentage decreased slightly insignificantly with increased temperature from 74.58 to 74.55 % and 74.51 to 74.45 % for nanocrystals and bagasse respectively. These reductions are an indication of exothermic nature of the adsorption process (Inyinbor et al. 2017; Ojedokun and Bello, 2017). Regression model predicted non-significantly varied close agreements between experimental and predicted data of effects of temperature on adsorption processing following equations 20a and 20b for bagasse and nanocrystals respectively.

$$y = 74.63 - 0.0028x - 0.0021x^2 \quad (R^2 = 0.98, p = 0.022) \quad 20a$$

$$y = 74.54 - 0.01x + 0.001x^2 \quad (R^2 = 0.99, p = 0.011) \quad 20b$$

Adsorption isotherms study

Adsorption data were fitted to Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherm to investigate the appropriateness of each isotherm for the description of adsorption process (Table 1). This was determined using correlation coefficient (R^2) closeness to unity; the closer to unity it is, the better it is for the description of the adsorption process.

The suitability of each isotherm for adsorption process on bagasse is in order (R^2); Freundlich (0.92) > Dubinin-Radushkevich (0.91) > Langmuir (0.66) > Temkin (0.64). The order of fattiness of isotherm model (R^2) for cellulose nanocrystals follows Langmuir (0.91) > Dubinin-Radushkevich (0.61) > Freundlich (0.60) > Temkin (0.56). Langmuir and Freundlich isotherms were the most appropriate to describe adsorption on cellulose nanocrystals and bagasse implying adsorption on the crystalline uniform surface of cellulose nanocrystals while it was on the heterogenous surface for bagasse. This is consonance with results of crystallinity indices calculated for both adsorbents.

Polynomial regression model predicted for both adsorbents were governed by Langmuir isotherm as obtained in correlation coefficients ($R_{NBG}^2 = 0.996$, $R_{BG}^2 = 0.94$) while improved correlation coefficients (R^2) were predicted for cellulose nanocrystals in Freundlich (0.74), Temkin (0.74) and Dubinin-Radushkevich (0.98) isotherms, decrease in R^2 values were predicted for bagasse in Freundlich ($R^2 = 0.41$), Temkin (0.57) and Dubinin-Radushkevich (0.81) isotherms.

Maximum monolayer adsorption capacity (q_{max}) calculated from Langmuir isotherm for bagasse and cellulose nanocrystals are 170.99 and 432.17 mgg^{-1} respectively. This is a 2-fold improvement in adsorption capacity of cellulose nanocrystals over bagasse. This is linked to higher carbon content and porosity in nanocrystals (Adejumo et al. 2020). Regression analysis predicted a marginal increase in q_{max} for nanocrystals (437.06 mgg^{-1}) and sizeable increase for bagasse (246.12 mgg^{-1}). Comparing q_{max} values of cellulose nanocrystals with previously reported values in other studies (Table 2), shows it is a far better adsorbent concerning performance for MO sequestration.

The parameter to determine favourability of adsorption process (R_L) was found to be 0.0153 and 0.0151 for nanocrystals as well as 0.595 and 0.533 for bagasse for experimental and predicted data respectively. This is an indication of favourable adsorption process (Azeez et al. 2018; 2020a,b).

Adsorption intensity (n) from Freundlich isotherm model is a hint to explaining favourable ($n > 1$) or cooperative ($n < 1$) adsorption process. Values of n calculated were 5.92 and 5.68 for nanocrystals and 10.21 and 16.29 for bagasse for experimental and model predicted data respectively. These values validate the favourability of sequestration of MO on both adsorbents (Inyinbor et al. 2017; Adekola et al. 2019).

Adsorption energy that helps determine nature of adsorption process calculated was 14.98 and 15.50 kJmol^{-1} for nanocrystals and 18.59 and 20.26 kJmol^{-1} for bagasse from

experimental and predicted data respectively. These values suggest chemisorption as the adsorption mode (Azeez et al. 2018; 2020a,b).

Adsorption kinetic study

Adsorption kinetic data were fitted and explained using pseudo first order, pseudo second order and Elovich kinetics. The predictiveness of each model was adjudged suitable using correlation coefficient (R^2) and non-linear Chi-square (χ^2) based on comparatively higher R^2 and lower χ^2 . The order of accuracy for prediction of adsorption kinetics follows pseudo second order ($R_{NBG}^2 - 0.999$, $R_{BG}^2 - 0.999$) > Elovich ($R_{NBG}^2 - 0.978$, $R_{BG}^2 - 0.983$) > pseudo first order ($R_{NBG}^2 - 0.969$, $R_{BG}^2 - 0.941$). Pseudo second order kinetic model was appropriately the best model to predict the kinetics of adsorption of MO on both adsorbents as shown by the correlation coefficient, non-linear Chi-square and close agreement between q_e experimental and q_e calculated (Table 3). This validates the domination of adsorption process by chemisorption as calculated from the energy of adsorption (Munagapati et al. 2019; Beh et al. 2020; Moawad et al. 2020). Regression model for predicting adsorption kinetics follows a similar trend to experimental data with improved correlation coefficients.

Mechanism of adsorption was performed using Weber and Morris intraparticle diffusion to determine the rate-determining step and the influence of mass transfer resistance on the adsorption of MO (Ojo et al. 2017). Intra-particle diffusion displays a rapid step related to the rate-controlling steps and stable step describing the rate-limiting step (Fig. 8). The rapid step explains the diffusion of MO onto the surfaces of adsorbents while the stable step designates preponderance of intra-particle diffusion in the adsorption process. Two-stage plots with deviations from origin submit that intra-particle diffusion mechanism was involved in the adsorption process but not the sole rate-determining step (Adekola et al. 2019; Azeez et al., 2020a).

Adsorption thermodynamic study

The values of ΔH° , ΔS° and ΔG° indicating energetics and spontaneity of the adsorption process of MO on bagasse and nanocrystals were evaluated from thermodynamic parameters (Table 4).

Negative values of ΔH° imply exothermic nature of adsorption process of MO on both adsorbents with reduced randomness as shown by positive ΔS° values signifying direct interaction between adsorbate and adsorbents (Suganya et al. 2017; Adejumo et al. 2020).

The values of ΔG° range from -12.57 to -13.39 kJmol⁻¹ reducing with increasing temperature. These indicate spontaneous adsorption process at all temperatures but more favourably feasible at a higher temperature (Munagapati et al. 2019). Regression model predicted approximately the same magnitude of energetics and spontaneity of the adsorption process

Conclusions

Cellulose nanocrystals using acid hydrolysis method were successfully extracted from sugarcane bagasse, characterized and investigated for their adsorptive capacity for anionic dye removal. The disappearance of uronic ester peak of hemicellulose/lignin indicated cellulose extraction while higher carbon content, greater crystallinity index, nano range of particles and larger porosity are parameters that better defined cellulose nanocrystals. A 2-fold improvement in monolayer adsorption capacity was obtained for cellulose nanocrystals over bagasse. Adsorption processes were best described by Langmuir isotherm on nanocrystals whereas Freundlich isotherm was best suited for bagasse. Adsorption processes on both adsorbents were spontaneous, exothermic and best fitted to pseudo second order kinetics ensuing chemisorption. Polynomial regression model appropriately predicted equations that best describe the effects of different batch adsorption parameters on MO removal with better fittingness than experimentally generated data

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

All data generated during this study are included in this manuscript

Competing interest

Authors declare no conflicts of interest in this study

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Authors' contribution

LA synthesized, characterized cellulose nanocrystals, did the manuscript write-up and regression modelling. AL coordinated the collection of bagasse and preparation of solutions in the laboratory. AOO and HK assisted in calculation and manuscript write-up.

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Figures

Figure 1

Scheme for the synthesis of cellulose nanocrystals from sugarcane bagasse.

Figure 2

A: SEM image and elemental composition of sugarcane bagasse. B: SEM image and elemental composition of cellulose nanocrystals.

Figure 3

FTIR spectra of cellulose nanocrystals and sugarcane bagasse.

Figure 4

Effects of pH on percentage adsorption of MO and model prediction.

Figure 5

Effects of dosage on percentage adsorption of MO and model prediction.

Figure 6

Effects of initial concentration of MO on percentage adsorption and model prediction.

Figure 7

Quantity of MO adsorbed with respect to time and model prediction.

Figure 8

Plot of intraparticle diffusion for adsorption of MO and model prediction.

Figure 9

Effects of temperatures on percentage adsorption of MO and model prediction.

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