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Two Parameter Isotherm Models of Colour Pigments Removal from Cottonseed Oil onto Biopolymer Prepared from Oyster Shell Waste

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Abstract

The effectiveness of chitosan prepared from oyster shell powder and its application in removing colour pigments and other impurities from cottonseed oil was carried out in this study. The bleaching was carried out at various adsorbent dosages (1.0 to 3.0 g). The bleaching adsorbents, (oyster shell powder, OSP and chitosan prepared from oyster shell powder COSP) were characterized using X-Ray Fluorescence (XRF) for the elemental composition, X- Ray Diffraction (XRD) for mineral composition and crystallinity, Scanning Electron Microscopy (SEM) for the surface morphology, and Fourier Transform Infrared (FT-IR) was used to investigate the presence of functional groups in the samples. The results showed that there was alteration in the concentration (wt %) and distribution of different compositional elements. The XRD analysis revealed the amorphous and crystalline characters in OSP while it suggested pure crystalline character in COSP and entirely composed of aragonite (2θ value of 29.2). The differences observed in surface morphology of the samples revealed some changes that occurred during the preparation of COSP and the absence and shifting of absorption bands in COSP indicated changes in the structure of the samples. The bleaching process was tested with four different isotherms (Langmuir, Freundlich, Temkin and Dubinin – Radushkevich (D-R). The adsorption process followed Freundlich isotherm (R2 is 0.891 in COSP and 0.929 in ROSP). The free mean energy of the process revealed that the adsorption occurred via chemisorption in both OSP and COSP (9.132 and 18.9 EkJ/mol respectively). The result also revealed that OSP improved the colour of cottonseed oil (% bleaching efficiencies at 1.0 and 1.5 g were 81.20 and 76.18 respectively) better than COSP (% bleaching efficiencies at 1.0 and 1.5 g were 66.7 and 70.63 respectively).

Keywords: Oyster shell; Chitosan; Isotherms; Bleaching; Cottonseed oil

Introduction

Chitosan is a semi crystalline polymer in the solid state [1]. Chitosan has been proved to be biologically renewable, biodegradable, biocompatible, non-antigenic, non-toxic (used in food industry) [2] and biofuntional [3]. Chitosan (Figure 1) is a natural polysaccharide that is synthesized from the partial deacetylation of chitin, a natural polymer made up of randomly distributed β-(1-4 linked D glucosamine and N- Acetyl-D-glucosamine that is found in the hard outer shells of crustaceans such as crabs, oyster, periwinkles and shrimps [4,5].

Chitin (Figure 2) in its natural state occurs as ordered crystalline micro fibrils which form structural components in the exoskeleton of arthropods or in the cell walls of fungi and yeast [6]. Chitosan has a fiber – like structure and of high molecular weight and similar to cellulose in structure but slightly different due to the amine (-NH2) group attached to carbon 2 position of chitosan instead of the hydroxyl (OH) group found in the cellulose. Unlike the plant fibre, chitosan possesses a positive ionic charge which is responsible for its ability to chemically bind with negative charged fats, lipids, cholesterol, metal ion, proteins and macromolecules [7]. Chitosan is well known to be an excellent adsorbent because it contains hydroxyl (-OH) and amino (-NH2) groups that serve as metal binding sites [8]. The ability of chitosan to chemically form bond with negatively charged fats, lipids, and cholesterol and metal ions has made it effective and efficient for the bleaching of edible oils such as palm kernel oil. Chitosan is soluble in most mineral and organic acids due to the protonation of its amino groups though relatively stable in sulphuric acid solutions but insoluble at higher pH levels. Chitosan has been investigated to have other biological properties such as antimicrobial [9] and antioxidant activities [10] and has many applications in area of biomedical and other industries [11]. Chitosan can be modified by chemical or physical processes in order to enhance the reactivity of the polymer or improve the sorption kinetics depending on the area of application. The chemical modification improve its adsorption properties and to change the solubility properties of chitosan in water or acidic medium. This may include substitution reactions, chain elongation (cross-linking, graft copolymerization and polymer networks), and depolymerization (chemical, physical, and enzymatic) [12]. Chitosan forms salt with inorganic and organic acids like glutamic acid, lactic acid, hydrochloric acid and acetic acid [13]. Vegetable oils and fats are essential components of human diets. Nearly all oils produced in the world are of vegetable source [14]. The crude vegetable oils are mixture of different free fatty acids, mono- di- and triglycerides, phosphatides, glycolipids, pigments, sterols and tocopherols, flavonoids, tannins, and trace amounts of metals may also be present [15]. Nutritionally, vegetable oils are excellent sources of energy and important vehicles of liposoluble vitamins in the human body [16].

Cottonseed oil is obtained from the seeds of cotton plant and known as a by-product with about (12 %) of the gross value of the total product. Due to unique fatty acid profile, cottonseed oil is different among other vegetable oils as it holds a comparatively high level of unsaturation and considered as a healthy vegetable oil [17]. Its fatty acid composition is distinctive of the oleic/linoleic group of vegetable oils, as these two fatty acids make up 73 % of the total fatty acids (oleic acid and linoleic acid 17 % and 56 %, respectively) along with palmitic acid approximately (23%) [18].

Bleaching is a critical step in the physical and chemical refining process of edible oils and selecting the optimal condition for the bleaching process depends on the quality and type of crude oil. Bleaching is not just declourization of edible vegetable oils but involve selective removal of pigments and impurities by the physical and chemical interaction of an adsorbent with an oil to improve its quality including the removal of trace metals such as Cu, Fe. The bleaching process is applied after degumming and neutralization in the chemical refining and it is more appropriately referred to as adsorption treatment [14].

As a result of the increasing world population, there is a growing demand for edible oil. The refining process is inevitably becoming the most essential step adopted by oil processors for producing edible oil with improving taste, appearance and increase the shelf life for fulfilling the high demand. Physical refining is extensively used in the vegetable oil industry [19].

Oyster shell contributes adversely to the environmental management in the coastal regions, especially places where fishery appears to be a highly profitable business and oyster as dominant products of shellfish farm. Such industry has a potential of serious problems about disposal of oyster shell waste and hence constitute a nuisance to the environment [20]. The presence of clay minerals, particularly SiO_2 and Al_2O, contributes to the high adsorptive property of oyster shell [21]. The aim and objective of this study were to characterized and investigate the potential application of chitosan prepared from oyster shell powder for the removal of colour pigments and other impurities from cottonseed oil.

Materials and Method

Sample collection and materials

Oyster shells were obtained from Borokiri in Port-Harcourt (River state) from the river side. The cotton seed oil was purchased in Gausau, Zamfara state, Nigeria. All reagents used were of the analytical grade.

Methods

Preparation of oyster shell: The shells were properly washed with hot water to remove the flesh reminants and surface dirts and then air dried for five days. The shells were crushed and ground to powder form using a roller mill machine. The powdered sample was sieved into different particle sizes using sieve of (300, 250, 200, 150, 100 µm).The particle size of 100 µm was stored and used for the study and labeled as raw oyster shell powder (OSP).

Demineralization of oyster shell powder: The sample (250 g) was weighed and then transferred into a 1000 mL beaker. 1M HCl (300 mL) solution was added and stirred thoroughly. The mixture was then heated in a water-bath at 100 ℃ for 60 min. The resulting hot mixture was filtered and washed with distilled water until a neutral pH was attained.

Deprotenization of oyster shell powder: The dried demineralized sample (200 g) was weighed into a beaker and 400 mL of 1 M NaOH (solid/liquid ratio 1:2 w/v) was added. The mixture was heated using a thermostatically controlled hot plate with stirrer at 80 ℃ for 1 hr. The resultant mixture was filtered, washed with distilled water until a neutral pH was attained. Ethanol (100 mL) was added to the resulting solid sample and allowed to stand for 24 hr to remove colour pigments. The resulting chitin was filtered and dried in an oven at 80 ℃ for 1 hr.

Deacetylation of oyster shell powder: The resulting chitin from the deproteinization stage was deacetylized by adding 60 %

NaOH solution to the sample and stirred thoroughly. The mixture was washed until a neutral pH was attained and dried at 100 ℃ for 45 min. The drying was continued at 150 ℃ for another 20 min till the residue was properly dried. The resulting powder which was the chitosan was labeled as COSP (chitosan oyster shell powder).

Characterization OSP and COSP

The OSP and COSP were characterized using XRF, FT-IR and SEM. X-Ray diffraction (XRD), the x ray diffraction method was used to determine the mineral compositions of the sample. X Ray Fluorescence was used to determine the chemical compositions of COSP while Fourier Transform Infrared spectrometry (FT-IR) was used to investigate the presence of functional groups in the sample and Scanning Electron Microscopy (SEM) was used to observe the surface morphology of the sample.

Bleaching Process

Degumming: This is the preliminary stage during bleaching of oils and the main objective of degumming is to remove the unwanted gums which can interfere with the stability of the oil in a larger scale production. Degumming was carried out by adding food grade acid, 0.1 % phosphoric acid (85 %) to the hot oil (30 g) in a beaker heated at 60 ºC and stirred thoroughly.

Bleaching of Cotton Seed Oil (CSO): The bleaching of cottonseed oil was carried out in a batch method. The degummed (CSO) (30) was weighed into a beaker and COSP (1 g) was added, heated at 80 ℃ for 30 min. The mixture was filtered with a whatman No 1 filter paper as quickly as possible to prevent undesirable oxidation. This same procedure was carried out using 1.5, 2.0, 2.5 and 3.0 g and same was repeated for OSP.

Analysis of bleaching performance: The absorbance of cottonseed oil using both the COSP and OSP was carried out using the UV-visible Spectrophotometer model 752. The bleaching efficiency of adsorbent was evaluated by monitoring the absorbance at 420 nm and expressed in terms of absorbance of light passing through the medium (CSO bleached with COSP and OSP). The percentage colour reductions of the bleached oil was calculated using equation 1

$$\text{Bleaching Efficiency \%} = \frac{\mathrm{Ao-At}}{\mathrm{A0}} \times 100 \text{ ---------- } (1)$$

Where, A_0 = Absorbance of unbleached cottonseed oil (initial absorbance)

A_t = Absorbance of bleached cotton seed oil at time t

Data analysis

Adsorption isotherm studies: The adsorption isotherm is important from both a theoretical and a practical point of view because the application of adsorption isotherm provide information describing the interaction between the adsorbate and the adsorbent of any system [22]. There are several equations for analyzing experimental adsorption equation data. In the present study, Langmuir, Freundlich, tempkin and D-R isotherms were used to test the adsorption of colour pigments and other impurities from CSO onto COSP and OSP.

Langmuir isotherms: The Langmuir isotherm has been employed to explain the adsorption of oil pigment and other minor oil solutes during oil processing though, developed by Langmuir in 1916 to describe gas adsorption. The model assumes that the adsorbate is bound to a fixed number of energetically equal, specific sites, each adsorbing one molecule with no interaction occurring between molecules on adjacent sites. The Langmuir isotherm has been applied to pigment adsorption from vegetable oil in the form of equation 2

$$\frac{\mathrm{Xe}}{\mathrm{x/m}} = \frac{1}{\mathrm{q_m K_L}} + \frac{\mathrm{X_e}}{\mathrm{q_m}}. \text{ --------- } (2)$$

Where x = amount of solute adsorbed, X_e is the amount of unadsorbed solute (the equilibrium concentration of adsorbate in solution mg/ L), m is the amount in grams of adsorbent used,(x/m is the adsorption capacity at the equilibrium solute concentration) 'q_m' maximum adsorption capacity (mg/g), and K_L is a constant of the intensity of the adsorption.

Freundlich isotherms: Freundlich in 1926 developed an empirical equation that correlates the capacity of the adsorbent with the residual solute concentration using equation 3 [23].

$$x/m = kc^{n} \text{ or } kc^{1/n.} \text{ ------------ } (3)$$

Where x = amount of solute adsorbed (mg), m = amount of adsorbent (g), c = amount of residual solute (concentration) (mg/L) at equilibrium. The Freundlich model is used to estimate the adsorption affinity of the sorbents towards the adsorbate [24]. K is a constant indicating adsorption capacity, and n is a constant of the energy of adsorption. Empirical data are evaluated for Freundlich behaviour by using the equation in its logarithmic form, as equation of a straight line [25].

$$\log \frac{\mathrm{x}}{\mathrm{m}} = \log \mathrm{k} + \mathrm{n} \log \mathrm{X_e} \quad \text{------------- } (4)$$

Temkin isotherm model: Tempkin isotherm is the early model describing the adsorption of hydrogen onto platinum electrodes within the acidic solutions [26]. The isotherm contains a factor that explicitly taking into consideration the amount of adsorbent-adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage which is attributed to adsorbate-adsorbate repulsions. It also assumes that adsorption is due to uniform distribution of binding energy contrary to Freundlich model. The amount of adsorbate is given as follows:

$$\mathrm{q_e} = \left(\frac{\mathrm{RT}}{\mathrm{b}}\right) \mathrm{aC_e} \quad \text{---------- } (5)$$

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$$q_e = B\ln A + B\ln C_e \quad \text{---------- (6)}$$

$$B = \frac{RT}{b} \quad \text{------------ (7)}$$

q_e (mg/g) and C_e(mg/g) are the amount of adsorbed pigments per unit weight of adsorbent and unadsorbed pigment at equilibrium respectively. A and B are the Temkin constants. The Temkin isotherm parameters were obtained by plotting qe against lnCe. It would be worth noting that the constant B is related to heat of adsorption.

Dubinin- Radushkevich isotherm model: Dubinin – Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [27,28]. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well.

$$q_e = (q_s)\exp(-K_{ad}\varepsilon^2) \quad \text{------- (8)}$$

$$\ln q_e = \ln(q_s) - (K_{ad}\,\varepsilon^2) \quad \text{------- (9)}$$

q_e = amount of adsorbate in the adsorbent at equilibrium(mg/g); q_s = theoretical isotherm saturation capacity(mg/g); K_{ad} = Dubinin-Radushkevich isotherm constant (mol^2/kJ^2); ε = Dubinin – Radushkevich isotherm constant. The approach was usually applied to distinguish the physical and chemical adsorption of metal ions with its mean free energy (E kJ/mol) for removing a molecule from its location in the sorption space to the infinity which can be computed by the relationship [29,30].

$$E = \left(\frac{1}{\sqrt{2B_{DR}}}\right) \quad \text{------ (10)}$$

B_{DR} is the isotherm constant

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \quad \text{---------- (11)}$$

Where R=8.314 J/molK; T = absolute temperature; C_e= adsorbate equilibrium concentration (mg/L). One of the unique features of the Dubinin – Radushkevich (D-R) isotherm model lies on the fact that it is temperature – dependent, which when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed lnqe against ε^2 the square of potential energy. All suitable data will lie on the same curve, named as the characteristic curve [31]. The constant such as q_s and K_{ad} are determined from the appropriate plot using equation 8.

The mean free energy E (kJ/mol) which is defined as the free energy change when one mole of ion is transferred to the surface of the solid. Mean free energy was calculated using the equation 12

$$E\ (kJ/mol) = (2k)^{-1/2} \quad \text{----------- (12)}$$

The value of E (kJ/mol) is used to estimate the kind of adsorption. If the value of E (kJ/mol) is in the range of 8-16 kJ/mol, the adsorption type is explained by ion-exchange, if E (kJ/mol) is less than 8 (E<8) the adsorption type is due to physisorption as a result of weak Van der Waal forces of attraction and if E greater than 8 (E>8) the adsorption type is chemical adsorption.

Results and Discussion

Characterization of COSP and OSP

Scanning Electron Microscopy (SEM): The Figure 1(a) showed the surface topography of OSP and (b) COSP as revealed by scanning electron microscopy. The result showed that most of the impurities and molecules have been leached as it was revealed on the surface of COSP and large cavities were observed between the irregular shapes solid which also appeared smooth as observed on the surface morphology.

Figure 1: *Scanning Electron Microscopy (SEM) morphology of OSP.*

Fourier Transform Infrared (FT-IR) analysis: The FT-IR spectrophotometer (Shimadzu 8400s, Japan) is an important analytical technique to identify the functional groups in compounds. (Figure 2) shows the FTIR spectrum of OSP while the absorption bands were presented in (Table 1). The peak at 3280.1, 1144.3 and 1628.8 cm^{-1} were due to the presence of hydroxyl group (OH) intermolecularly H-bonded.

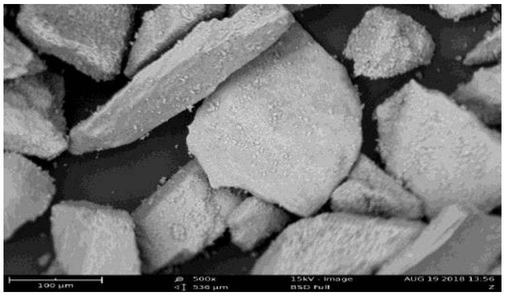

Figure 2: *Scanning Electron Microscopy (SEM) morphology of COSP.*

Table 1: *Absorption bands of OSP.*

Absorption band (cm^{-1})	Funtional groups
3280.1	OH intermolecularly (H-bonded)
3011.7	NH stretching
2922.2	CH_2 asymmetric
2076.1	CH_2 asymmetric
1744.4	C=O stretching vibrations

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1628.8	OH (water of crystallization)
1543.1	NH AmideII)
1461.1	CO_3^{-2} in $CaCO_3$
1379.1	NH (amide) group bonded to aliphatic compound
1237.5	C-O (carboxylic)
1144.3	OH group
1028.7	Stretching vibration Si-O-Si open chain

The absorption band at 3011.7 cm^{-1} resulted as a result of the presence of NH stretching while the peaks at 2922.2 and 2076.1 cm^{-1} showed the presence of CH_2 asymmetric (aliphatic). The peak that appeared at 1744.4 cm^{-1} was due to carbonyl group C=O stretching vibrations. The absorption band at 1543.1 cm^{-1} was as a result of the presence of NH group of amide II while the peak at 1461.1 cm^{-1} resulted from carbonate ions from calcium carbonate. The band at 1379.1 cm^{-1} showed the presence of NH (amide) group bonded to aliphatic compound and the absorption peak at 1028.7 cm^{-1} was due to the stretching vibrations of Si- O-Si open chain.

(Figure 3) shows the FTIR spectrum of COSP while the absorption bands were presented in (Table 2). Pawlak and Mucha (2003) mentioned that the FT-IR analysis of chitosan was based on the identification of bands and its vibrations [32]. The broad and strong intensity absorption band at 3239.1 cm^{-1} indicated the presence of a hydroxyl group (O-H). The absorption peak at1558.0 cm^{-1} was a characteristic absorption band due to NH_2 Bending (deformation of amide group).

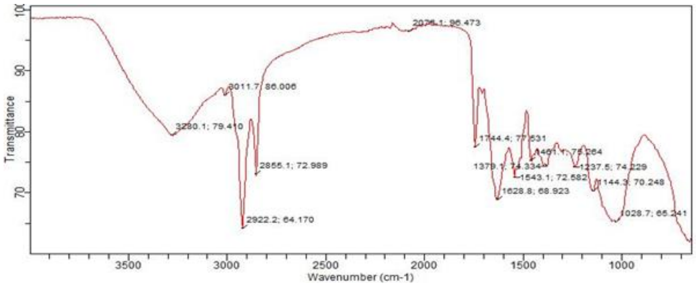

Figure 3: *FT-IR spectrum of OSP.*

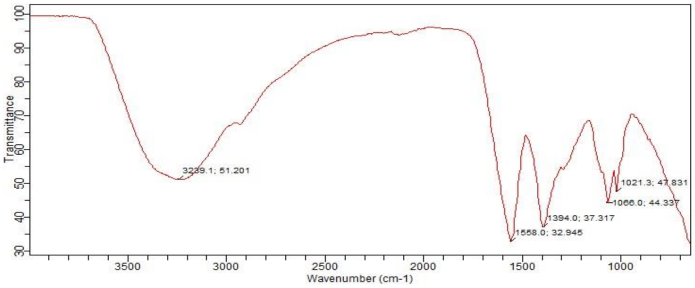

Figure 4: *FT-IR spectrum of COSP.*

The absorption band at 1394.0 cm^{-1} suggested the presence of amide III while the absorption peak at 1066.0 cm^{-1} revealed the presence of – C-O-C-due to glycoside linkage (Pawlak and Mucha 2003) and the presence of absorption band at 1021.3 cm^{-1} indicated the presence of NH_2 (amino) group. The broad peak at 3239.1 cm^{-1} and the absence of bands 1744.4, 1628.8, 1461.1 cm^{-1} showed clearly the difference between the OSP and COSP (Figure 4).

Table 2: *Absorption bands of COSP.*

Absorption bands (cm^{-1})	Functional groups
3239.1	O-H stretching
1558	NH_2 bending (deformation of amide group)
1394	Amide III group
1066	-C-O-C- glycoside linkage
1021.3	NH_2 (amino group)

Table 3: *X-Ray Fluorescence (XRF) of OSP and COSP.*

Elements	Concentration (wt. %)	
	OSP	COSP
Na_2O	0.000	0.000
MgO	1.129	1.164
Al_2O_3	1.377	1.505
SiO_2	4.350	4.424
P_2O_5	0.078	0.062
SO_3	0.319	0.146
Cl	0.135	0.090
K_2O	0.194	0.134
CaO	91.169	89.403
TiO_2	0.121	0.075
Cr_2O_3	0.004	0.000
Mn_2O_3	0.017	0.013
Fe_2O_3	0.675	0.562
ZnO	0.000	0.000
SrO	0.432	0.402

X-ray diffraction result

The x-ray diffraction is a synthesis instrument used for the identification of crystalline phases of inorganic compound. The spectra obtained from the XRD as shown in (Figure 5(a) and (b)) showed the characteristics mixture of crystalline and amorphous solid particles in OSP while COSP exhibited a very single strong crystalline character and this was revealed at 2 θ values of 29.2, the peak is a characteristic of $CaCO_3$ (aragonite). It is an indication that the major crystalline phase of COSP is aragonite ($CaCO_3$). It clearly showed the crystalline nature and phase composition of COSP.

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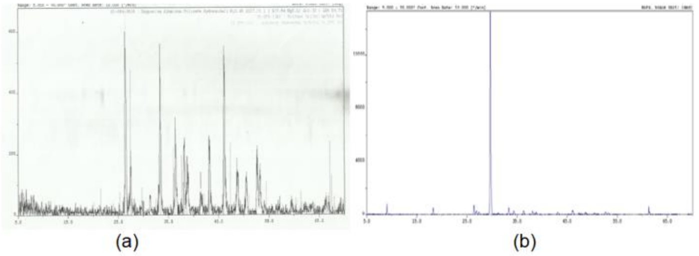

Figure 5: *X-Ray Diffraction spectra of (a) OSP and (b) COSP.*

X-Ray Fluorescence (XRF)

The XRF result for the synthesized chitosan from oyster shell powder and the raw oyster shell powder were presented in the (Table 3). It was observed that the decrease in the concentration (wt. %) of COSP showed that most of the minerals were leached during the process. The result showed that the synthesized COSP has little or no trace of other element or impurities capable of affecting its potential in bleaching vegetable oil.

Table 4: *Adsorption isotherm constants for the bleaching of cottonseed oil with COSP and OSP.*

	COSP		OSP	
Langmuir	$q_{max(mg/g)}$	0.242	$q_{max(mg/g)}$	-0.791
	K_L(L/mg)	-2.582	K_L(L/mg)	-6.044
	R_L	0.071	R_L	0.024
	R^2	0.923	R^2	0.876
Freundlich	K_f(mg/g)	128.1	K_f(mg/g)	0.024
	1/n	4.936	1/n	2.114
	R^2	0.891	R^2	0.929
Temkin	B(mg/g	2.833	B(mg/g	-6.223
	A (L/min)	1.126	A (L/min)	-4.098
	R^2	0.326	R^2	0.964
D-R	q_m(mg/g)	-3.654	q_m(mg/g)	0.241
	β(mol^2kJ^{-2})	-0.001	β(mol^2kJ^{-2})	-0.006
	E(kJ/mol)	18.9	E(kJ/mol)	9.132
	R^2	0.658	R^2	0.936

Effect of Dosage

(Figure 6) shows the bleaching efficiency of chitosan prepared from oyster shell powder (COSP) and oyster powder (OSP). The result revealed that the adsorbent showed effect on the colour index of cottonseed oil. It was observed that the bleaching efficiency shows optimum value at adsorbent dosage of 1.0 g in both COSP and OSP and no further improvement was observed on the colour of cottonseed oil as the percentage bleaching efficiency began to decrease with increase in the quantity of adsorbent dosages, this is as a result of the saturation of the available exchangeable sites of the adsorbent dosage that inhibit further pigments and impurities adsorption onto its surface and adsorption equilibrium has been reached between the adsorbent-oil mixtures. Zhang reported that decreased after certain point may be as a result of the decrease in total adsorption surface area available to the adsorbent resulting from overlapping or aggregation of adsorption sites [33]. The result revealed that OSP removed much colour pigments from cottonseed oil and improved on its colour than COSP based on the percentage bleaching efficiencies.

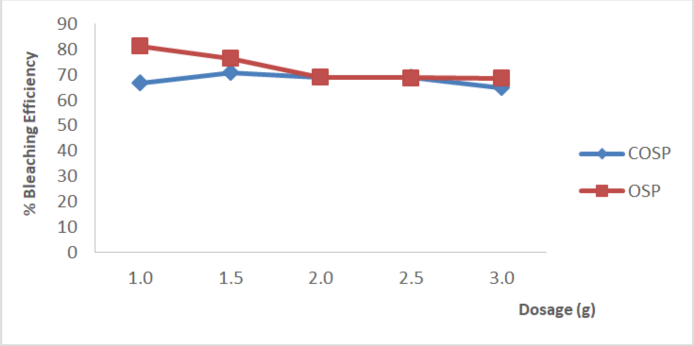

Figure 6: *Chart of % bleaching efficiency of both COSP and OSP at various adsorbent dosage.*

Adsorption isothermal studies

The adsorption potential of OSP and COSP was tested using four isotherm models (Langmuir, Freundlich, temkin and Dubinin-Radushkevich) in order to understand the variation in the performance of the bleaching of CSO using OSP and COSP. Isotherm constants are used as indicators to assess the efficiency of bleaching adsorbents. The equilibrium isotherms parameters were summarized in (Table 4). The values of constants of the isotherms were calculated from the slopes and intercepts of the plots as shown in (Figure 7).

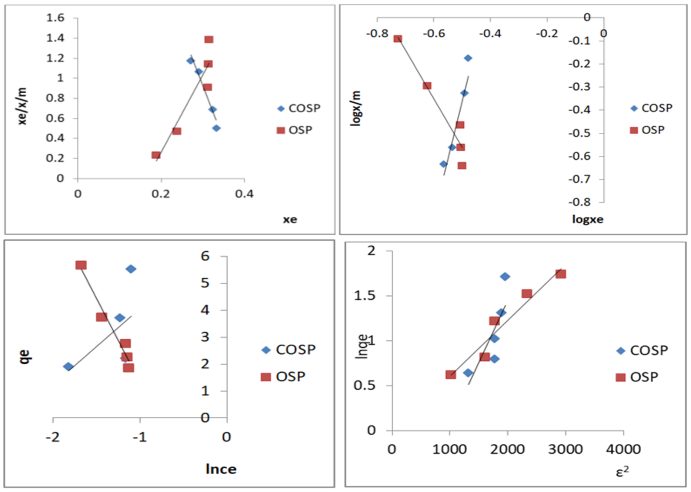

Figure 7: *Isotherm plots of (a) Langmuir, (b) Freundlich, (c) Temkin and (d) D-R.*

The result showed that Freundlich isotherm was most suitable to explain the adsorption process in COSP and OSP. It was also observed that, with respect to COSP, the Langmuir isotherm has the highest correlation coefficient value (0.923) but was adjudged not adequate to explain the process as a result of its negative value of K_L (-2.582 L/mg) while in OSP, the negative value of the maximum binding energy obtained in Temkin isotherm made it not fit to explain the adsorption process. However, the values of Langmuir dimensioless parameter (R_L) were less than 1($R_L<1$) in both COSP and OSP an indication of favourable adsorption. Freundlich parameter 1/n values for COSP and OSP were between 1 and 10 showing a favourable adsorption process however, COSP has higher adsorption strength with 1/n value of 4.936 as compared with ROSP 2.114. The mean free energy obtained for COSP and OSP were higher than 8 kJ /mol and this suggested that the adsorption process would proceed via chemisorption in both COSP and OSP.

Conclusion

The raw oyster shell powder (OSP) showed stronger affinity for colour pigments and other impurities in cottonseed oil better than the chitosan prepared from oyster shell powder (COSP). An obvious revelation that OSP is an excellent adsorbent for pigments removal from cottonseed oil. The adsorption process followed Freundlich isotherm in both COSP and OSP. The free mean energies of both COSP and OSP were greater than 16 kJ/mol which showed that the adsorption occurred via chemical adsorption. Therefore, since OSP is cheap, it could serve as an alternative to the more expensive conventional bleaching agents such as bentonite, activated charcoal etc. and more so OSP is readily available.

References

1. Rinaudo M. Chitin and chitosan properties and applications. Progress in Polymer Science. 2006; 7: 603-632.
2. Pokhrel S, Nath Yadsv P, Adhikari R. Applications of Chitin and Chitosan in Iindustry and Medical Science: A Review. Nepal J Sci Technol. 2015; 16: 99-104.
3. Malafaya PB, Silva G, Reis RL. Natural-origin polymers as carriers and scaffolds for biomolecules and cell delivery in tissue engineering applications. Advanced Drug Delivery Rev. 2007; 59: 207-233.
4. Cheung RC, Bun Ng T, HO Wong J, Yee Chan W. Chitosan: an uptake on potential biomedical and pharmaceutical applications. Mar Drugs. 2015; 13: 5156-5186.
5. Tolaimate A, Desbrieres J, Rhazi M, Alagui A, Vincendon M, Vottero P. On the influence of deacetylation process on the physicochemical characteristics of chitosan from squid chitin. Polymer. 2000; 41: 2463-2469.
6. Younes I, Rinaudo M. Chitin and Chitosan Preparation from Marine Sources. Structure, Properties and Applications. Mar Drugs. 2015; 13: 1133-1174.
7. Li Q, Dunn ET, Grandmaison EW, Goosen MFA. Application and properties of chitosan. J Bioact Compat Pol. 1992; 7: 370-397.
8. Abdolmaleki AY, Zilouei H, Khorasani SN. Characterization of Electroplating Parameters of Chitosan/Poly (vinyl alchohol) Nanofibers to Remove Phenol via Response Surface Methodology. Poflym Scfi. 2018; 4: 1-9
9. Martins AF, Facchi SP, Follmann HD, Pereia AG, Rubira AF, Muniz EC. Antimicrobial activity of chitosan derivatives containing N-quaternized moieties in its backbone: a review. Int J Mol Sci. 2014; 15: 20800-20832.
10. Ngo DA, Kim SK. Antioxidant effects of chitin, chitosan, and their derivatives. In Advances in Food and Nutrition Research. Kim, S.K, Ed., Academic Press: Waotham, MA, USA. 2014; 73: 15-31.
11. Chauhan H, Dave G, Patel R, Shah M, Bishnol A, Ral S. Synthesis and antimicrobial properties of chitosan: A Case Study. EC Microbiology. 2017; 9: 193-200.
12. Prashanth KV, Tharanathan RN. Chitin/Chitosan: modifications and their unlimited applications potential- an overview. Trends Food Sci Technol. 2007; 18: 117-131.
13. Gavhane YN, Gaurav AS, Yadav AV. Chitosan and its application: A review of literature. Int J Res Pharma Biomed. 2013; 4: 312-331.
14. Guliyev NG, Ibrahimov HJ, Alekperov JA, Amirov FA, Ibrahimova ZM. Investigation of activated carbon obtained from the liquid products of pryrolysis in sunflower oil bleaching process. Int J Industrial Chem. 2018; 9: 277-284.
15. Mengistie T, Alemu A, Mekonnen A. Comparison of physicochemical properties of edible vegetable oils commercially available in Bahir Dar, Ethiopia. Chemistry International. 2018; 4: 130-135.
16. Djikeng TF, Womeni HM, Kingne F, Karuna MSL, Rao BVSK, Prasad RBN. Effect of sunlight on the physicochemical properties of refined bleached and deodorized palm olein. Food Res. 2019; 3: 49-56.
17. Shah SN, Mahesar SA, Abro KA, Sherazi ST, Nizamani SM. FTIR characterization and physicochemical evaluation of cottonseed oil. Pak J Anal Environ Chem. 2017; 18: 46-53.
18. Gunstone FD. The Chemistry of Oils and Fats: Sources, Composition, Properties and Uses, Blackwell Publishing Ltd, 9600 Garsington Road, Oxford OX4 2DQ, UK. 2008.
19. Sim BI, Muhamad H, Lai OM, Abas F, Yeoh CB, Nehdi IA, et al. New insights on degumming and bleaching process parameters on the formation of 3-monochloropropane-1, 2-diol esters and glycidyl esters in refined, bleached, deodorized palm oil. J Oleo Sci. 2018; 67: 397-406.
20. Gil-Lim Y, Byung-Tak K, Baeck-Oon K, Sang-Hun H. Chemical and mechanical characteristics of crushed oyster shell. Waste Management. 2013; 23: 825-834.
21. Salawudeen TO, Dada EO, Alagbe SO. Performance evaluation of acid treated clays for palm oil bleaching. J Eng Applied Sci. 2007; 2: 1677-1680.
22. Langmuir I. The Adsorption of gases on plane surfaces of glass, mica, and platinum. JAM Chem Soc. 1916; 40: 1361-1403.
23. Freundlich H. Colloid and capillary chemistry, Metheum, London. 1926.

24. Jimoh OT, Muriana M, Izuelumba B. Sorption of Lead (II) and Copper (II) ions from aqueous solution by acid modified and unmodified melina arboreal (Verbenaceae) leaves. J Emerg Trends Eng Appl Sci. 2011; 2: 734-740.
25. Achife EC, Ibemesi JA. Applicability of the Freundlich and Langmuir adsorption isotherms in the bleaching of rubber and melon seed oils. J Am Oil Chemists' Society. 1989; 66: 247-252.
26. Temkin MI. Kinetics of ammonia synthesis on promoted iron catalysts. Acta Physiochim. Urss. 1940; 12: 217-222.
27. Dabrowski A. Adsorption- from theory to practice. Adv Colloid Interface Sci. 2001; 93: 135-224.
28. Gunay A, Arslankaya E, Tosun I. Lead removal from aqueous solution by natural and pretreated clinoptilolite adsorption equilibrium and kinectics. J Hazard Matter. 2007; 146: 362-371.
29. Dubinin MM. The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surfaces. Chem Rev. 1960; 60: 235-266.
30. Hobson JP. Physical adsorption isotherms extending from ultrahigh vacuum to vapor pressure. J Phys Chem. 1969; 73: 2720-2727.
31. Foo KY, Hameed BH. Insight into the modeling of adsorption Isotherm systems. Rev Chem Eng J. 2010; 156: 2-10.
32. Pawlak A, Mucha M. Thermogravimetric and FTIR studies of chitosan blends. Thermochimica Acta. 2003; 396: 153-166.
33. Zhang J, Li Y, Zhang C, Jing Y. Adsorption of malachite green from aqueous solution onto carbon prepared from Arundo donax root. J Hazard Matter. 2008; 150: 774-782.

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