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Sorptive Removal of Phenol from Aqueous Solution by Ammonium Chloride-Treated and Carbonized *Moringa oleifera* Seed Shells

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Abstract: ***Ammonium chloride-activated (AMSS) and carbonized (CMSS) adsorbents were prepared from Moringa oleifera seed shells, characterized and evaluated for aqueous phase removal of phenol. The effect of operational parameters such as initial phenolic solution pH and adsorbent dosage on equilibrium sorption were studied. Adsorption isotherms and kinetic experiments performed at 25 – 40^{o}C furnished some thermodynamic and kinetic parameters, respectively. Both AMSS and CMSS showed favorable attributes (pH, bulk density, attrition, iodine number/surface area, surface charge/functional groups). Phenol uptake decreased with increase in solution pH for both adsorbents. Across the temperatures, equilibrium removal efficiencies were: AMSS ($48.21 \leq RE(\%) \leq 79.3$) and CMSS ($39.88 \leq RE(\%) \leq 81.45$). Maximum adsorption capacities, Q_{max} (mg/g) were: AMSS ($6.21 \leq Q_{max} \leq 6.76$) and CMSS ($10.75 \leq Q_{max} \leq 13.16$). Free energy change ($\Delta G^o$) and enthalpy change ($\Delta H^o$) indicated that phenol uptake was feasible and exothermic for both adsorbents, but occurred via the physisorptive and chemisorptive modes for AMSS and CMSS, respectively. Adsorption kinetics obeyed the pseudo-second-order model. The adsorbents show a promise of applicability in dephenolation of aqueous effluents/wastewater.***

Keywords: Phenol, *Moringa oleifera* seed shells, Adsorption isotherms/thermodynamics, Adsorption kinetics, Wastewater remediation**.**

1. Introduction

The increase in industrial, agricultural and domestic activities has led to the discharge of large amounts of wastewater containing toxic chemicals [1]. The petroleum/petrochemical industry is listed among the many industries faced with challenges of generation of high volumes of wastewater with attendant high costs needed for effluent treatment before eventual discharge to the environment [2]. Among the broad spectrum of inorganic and organic chemicals usually present in wastewater from this industry, phenol and its derivatives (phenolics) are noteworthy because of their presence in high concentrations, toxicity and cumulative tendency in the environment [3].

Phenol is an aromatic hygroscopic crystalline solid at room temperature and pressure and when pure, solid phenol is white but is frequently colored due to contamination by impurities. Phenol is very soluble in ethyl alcohol, ether and several polar solvents, as well as in hydrocarbons such as benzene, but has a limited aqueous phase solubility (93.9 g/L) where it behaves as a weak acid with p*K*a 9.89 [4]. The phenolic compounds are used commercially as precursors of a broad spectrum of materials in the construction of automobiles and appliances, epoxy resins and adhesives, and polyamides for various applications and herbicidal preparations [5 – 7].

Phenolic compounds are usually present in industrial wastewater and can become poisonous to aquatic life, plants and humans due to bioaccumulation. In humans particularly, phenol intake of about 10 – 24 mg/L for a prolonged period can cause mouth irritation, diarrhoea, excretion of dark urine, impaired vision and other central nervous system related effects [8]. In chemically treated drinking water, phenol may combine with residual chlorine forming chlorophenol with an objectionable medicinal taste [9, 10].

Methods employed for the dephenolation of wastewater include steam stripping, solvent extraction, oxidation, ion exchange, biodegradation and adsorption methods [11 – 15]. Techniques based on adsorption phenomenon are frequently used all over the world owing to their high efficiency [16]. Due to the high cost and low regeneration capacity of conventional commercial grade adsorbents, the quest for cheaper, potent and non-toxic adsorbents from renewable resources has been in the research frontiers since the last three decades. Carbonized and non-carbonized adsorbents derived from biomass such as seed shells [17, 18], husks [19], bran [20], cobs [21], leaves [22, 23], sawdust [24], bagasse [25 – 27], coir [28], etc have shown great potential in the aqueous phase removal of phenol(ics).

Moringa oleifera, the drumstick tree, also known as horseradish tree and ben tree, is a small to medium-sized, evergreen or deciduous tree native to northern India, Pakistan and Nepal. It is cultivated and has become naturalized well beyond its native range, including throughout South Asia, and in many countries of Southeast Asia, the Arabian Peninsula, tropical Africa, Central America, the Caribbean and tropical South America [29]. The numerous nutritional and medicinal uses of this plant notwithstanding, conversion of its residues (e.g. pod husks and seed shells), which up to date remain under-utilized, to cheap and non-toxic adsorbents for wastewater treatment would afford a sustainable solid waste management and water pollution control system [30].

Consequently, the specific objectives of this study were to: (i) prepare and characterize chemically activated and carbonized adsorbents from *M. oleifera* seed shells in terms of physicochemical attributes, (ii) evaluate the effectiveness of the adsorbents to remove phenol from aqueous phase with emphasis on adsorption equilibrium, thermodynamics and kinetics.

2. Materials and Methods

2.1 Chemicals and Apparatus

Phenol (C_6H_5OH, MW = 94 g/mol) was supplied by PARK scientific Ltd UK; ammonium chloride (NH_4Cl, 99%) was of BDH patent. The apparatus used were: analytical weighing balance (Adam Equipment Co, Ltd US), muffle furnace (Carbolite, UK), mechanical shaker (Heldolp Unimax 2010, Germany), thermostatic water bath (Clifton, UK), UV-visible spectrophotometer (Jenway-6405UV, Japan), Fourier transform infrared spectrophotometer (FTIR-8400S, Shimadzu, Japan).

2.2 Preparation and Characterization of Adsorbents

M. oleifera seeds were obtained from the Central Market in Kaduna (11°10′N; 7°38′E), North-west Nigeria. The seeds were deshelled and the shells (MSS) washed with tap water followed by distilled water to remove dirt and air-dried. A portion of the air-dried shells was steeped in a saturated ammonium chloride solution overnight for chemical activation. The slurry was filtered and the residue washed repeatedly with distilled water, followed by air-drying to give the activated *M. oleifera* seed shell adsorbent (AMSS). A portion of AMSS was pyrolyzed in a muffle furnace at 350°C for 1½ h, pulverized and sieved with 2 mm to give carbonized *M. oleifera* seed shell adsorbents (CMSS).

Adsorbent pH was determined by dispersing 1.0-g triplicate samples of the adsorbent in distilled water for 4 h and measuring the pH of the resulting filtrate [31]. Bulk density was determined by the tamping procedure of Ahmedna *et al*. [32]. Attrition was determined by a procedure described by Toles *et al*., [33]. Adsorbent surface area was determined by the iodine adsorption number method during which, a 1.0-g portion of the adsorbent was slurried with an excess of standard iodine solution followed by back-titration of the unreacted iodine with standard sodium thiosulphate solution [34]. A blank titration was also performed on an aliquot of iodine solution not treated with the adsorbent. The iodine number (i.e., amount in moles of iodine adsorbed per g adsorbent) and the adsorbent surface area, (m^2/g) were calculated as reported by Wuana *et al*. [35, 36]. Titratable surface charge was determined by the Boehm titrimetric method described by Van Winkle [37]. Fourier transformed infrared (FTIR) analysis was performed according to the manufacturer's specifications.

2.3 Formation of calibration curves

A 3-mL portion of a stock (1000 mg/L) phenolic solution was put in a cuvet and placed on the UV spectrophotometer. The machine was scanned and the wavelength of maximum absorption (λ_{max} = 270 nm) was noted. Working standard phenolic solutions (20, 40, 60, 80 and 100 mg/L) were prepared by serial dilution of the stock (1000 mg/L). A plot of absorbance versus concentration furnished the calibration curve ($A = 0.0139C$; $R^2 = 0.999$) from which the concentration of phenol in real samples were calculated.

2.4 Batch Adsorption Experiments

Standard phenolic solutions (0 – 100 mg/L) were prepared by serially diluting appropriate volumes of the stock (1000 mg/L) using distilled water. The effect of solution pH on phenol adsorption was studied by treatment of 50-mL aliquots of phenolic solutions adjusted to different pH (3, 5, 7, 9 and 11) with 0.5-g of the adsorbents for 4 h at laboratory temperature (25°C). The effect of adsorbent dosage was investigated by contacting different masses (0.5, 1.0, 1.5, 2.0 and 2.5 g) of the adsorbents with 50 mL of the phenolic solution at pH 6. Adsorption isotherms were developed at different temperatures (25 – 40 °C) by dispersing separate 0.5-g portions of the adsorbents in 50-mL aliquots of each standard (0 – 100 mg/L) phenolic solution with the aid of a mechanical shaker for 4 h. adsorption kinetic experiments were performed by shaking 0.5-g portions of the adsorbents dispersed separate 50 mL aliquots of 100 mg/L phenolic solution for 10, 30, 60, 120, 180, and 240 min on a mechanical shaker at various temperatures (25 – 40°C). At the elapse of each specified time interval the slurry was filtered and the residual phenol concentration in the filtrate measured. Residual phenol concentrations in the solutions before and after adsorption were measured using a UV spectrophotometer following the manufacturer's specification.

In all batch adsorption experiments, the amount of phenol adsorbed, *Q* (mg/g) and removal efficiency, *RE* (%) were calculated using Equations (1) and (2), respectively:

$$Q(\mathrm{mg/g}) = [(C_o - C)V]/m_{\mathrm{A}} \qquad (1)$$

$$RE(\%) = 100(C_o - C)/C_o \qquad (2)$$

where C_o and C are the initial and residual phenol concentrations (mg/L), respectively, V is the aliquot of phenol solution used (L); and m_{A} is the mass of adsorbent (g) used for a particular batch treatment.

3. Results and Discussion

3.1 Adsorbents' Physicochemical Characteristics

Some physicochemical characteristics of the experimental adsorbents are recorded in Table 1. Figure 1 represents the FTIR spectra of the adsorbents. AMSS and CMSS had pH of 4.6 and 5.3, respectively. These values are within the range recorded for activated carbons from olive stones and walnut shells [38]. CMSS particularly had low ash content indicative of high carbon content. Generally, activated carbons produced from precursors with low ash content have been found to have low pH. The percentage yield of carbon was found to decrease with increase in pyrolysis time since more volatiles are released from the char resulting to a higher burn off and a corresponding lower yield.

Bulk densities (kg/m^3) for AMSS and CMSS were 294.0 and 313.0, respectively. These values are higher than the minimum requirement of (0.25 g/mL) for application in removal of pollutants from wastewater [39]. Attrition loss analysis provides us with valuable information on AMSS and CMSS for phenol removal. High attrition losses indicate that the adsorbents may be less effective and more expensive due to frequency of maintenance and purchase of additional material. However, it is important to consider the coefficient of uniformity, which indicates the range of particle sizes [40]. Both adsorbents showed acceptable attrition loss after preparation.

Table 1: Selected physicochemical characteristics of adsorbents from *M. oleifera* seed shells

Characteristic	AMSS	CMSS
pH	4.6	5.3
Bulk density (kg/m^3)	294.0	313.0
Ash content (%)	-	20.0
Attrition (%)	21.0	12.0
Iodine number (x10^{-4}mol/g)	8.3	7.8
Surface area (m^2/g)	159.9	150.3
Titratable surface charge (mmol H$^+$ eq/g)		
NaOH	1.0	0.72
$NaHCO_3$	1.3	1.2
Na_2CO_3	1.5	1.5

The iodine number indicates the extent of micropore volume distribution within the adsorbents matrices, hence the surface area. Iodine numbers (x10^{-4} mol/g)/surface areas (m^2/g) were 7.8/150.3 and 8.3/159.9 for AMSS and CMSS, respectively. The surface areas are within the range (150 – 500 m^2/g) required for wastewater treatment and removal of small molecules from aqueous solutions [41].

Titratable surface acidic groups (mmol H$^+$eq/g) were determined by the selective neutralization with a series of bases of varying strength: $NaHCO_3$, Na_2CO_3 and NaOH. $NaHCO_3$ neutralizes carboxylic groups wherein, those neutralized by Na_2CO_3 but not by $NaHCO_3$ are lactones. The weak acid groups neutralized by NaOH but not by Na_2CO_3 were postulated as phenols [27]. The order of the acidic groups on the surface of AMSS was lactones > carboxylic ≈ phenolic, while that for CMSS was lactones > carboxylic > phenolic. Aside the afore-mentioned groups, other oxygen-based acidic functional groups which may be present on the adsorbent's surface include quinine-type carbonyls, anhydrides, ethers and cyclic peroxides [31, 41].

FTIR spectra (Figure 1) served as direct means for the identification of the surface functional groups. The broad adsorption bands (1/cm) at 3415 and 3411 may be assigned to the -OH stretching vibrations of hydroxyl groups [42]. Specific olefinic vibrations may be the cause of the band at 1652 /cm for AMSS and the skeletal C vibrations in aromatic rings bands in the 1600–1400 /cm region of the spectrum. Absorption due to C–O vibrations occurs between 1300 and 850 /cm. The band at 1265 /cm may be due to esters and the strong one at 1046 /cm to C–O vibration in C–OH [25, 43]. The pyrolysis of the AMSS progressive decrease of the intensity of the latter band absorbing at 1037 /cm. Only bands attributed to aromatic C=C and C–O vibrations absorbing between 1439 and 850 /cm and a band at 767 /cm due to aromatic C–H vibrations are clearly displayed in the spectra of activated CMSS and AMSS. The spectra of the both CMSS and AMSS contains principally the bands associated to the C=C, C-O and C–H aromatic vibrations between 1437 and 767 /cm. These changes observed in the spectrum indicated the possible involvement of these functional groups on the surface of the AMSS and CMSS adsorbent in sorption process.

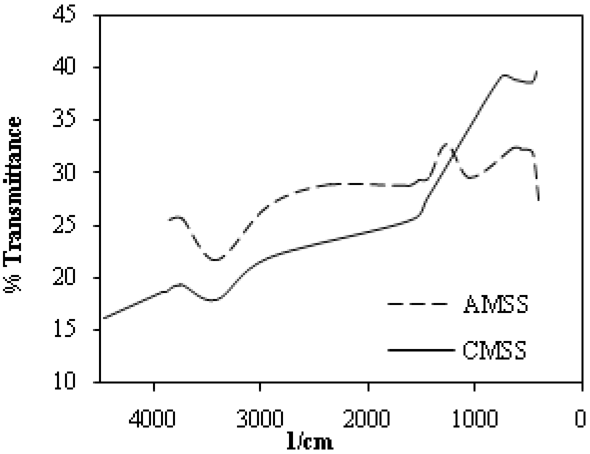

Figure 1: Fourier transform infrared spectra of ammonium chloride-activated (AMSS) and carbonized (CMSS) *M. oleifera* seed shells

3.2 Effect of Initial Solution pH on Phenol Removal

The adsorption capacity is influenced most by the pH of the solution. The pH of the solution primarily affects the surface charge of the adsorbents, degree of ionization, and speciation of phenol which may lead to change in equilibrium and kinetics phenol removal [6, 43]. The effect of initial solution pH (Figure 2) was investigated over the pH ranges of 3 – 11 at a fixed initial concentration of phenol (100 mg/L). The amount of phenol adsorbed decreased with increase in pH for both adsorbents. The highest phenol uptakes: AMSS (8.0 mg/g) and CMSS (8.8 mg/g) were recorded at pH 3; while the least: AMSS (1.6 mg/g) and CMSS (2.6 mg/g) were achieved at pH 11.

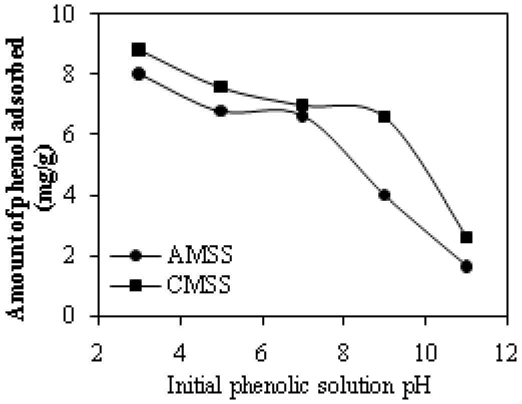

Figure 2: Effects of initial solution pH on phenol removal by ammonium chloride-activated (AMSS) and carbonized (CMSS) *M. oleifera* seed shells

Phenol ionization depends on the pH value and the ionic fraction of the phenolate ion (ϕ_{ion}). This fraction can be calculated as:

$$\phi_{\text{ion}} = 1/[1+10^{\mathrm{p}K_a-\mathrm{pH}}] \qquad (3)$$

As pH increases, ϕ_{ion} increases and, therefore, the pH-dependent nature of phenol adsorption could be explained by the fact that only the phenol molecules adsorb effectively onto surfaces of AMSS and CMSS through van der Waals interaction whereas, the phenolate anions do not, owing to their hydrophilic nature [5, 44]. AMSS and CMSS surfaces were protonated at low pH, hence strong electrostatic forces of attraction with the negatively charged phenolate. Phenol has pK_a of 10 at 25°C, hence at high pH values it behaves as an anion. Adsorption at higher pH was less due to repulsion [9, 43] and competition occurs between the OH^- ions and the phenol molecules for sorption sites [43].

3.3 Effect of Adsorbent Dosage on Phenol Removal

The adsorbent load determines the capacity of AMSS or CMSS for a given phenol concentration, which can also furnish the phenol-adsorbent equilibrium relations. Phenol uptake decreased with the increase in adsorbent loading (Figure 3) ranging from 1.7 – 9.4 mg/g for AMSS and 1.5 – 12.2 mg/g for CMSS. This trend may be explained based on the mass balance relationship in Equation (3). At increasingly higher sorbent dosages (0.5 – 2.5 g), fixed initial phenol concentration (100 mg/L) and fixed aliquot volume (50 mL), the available phenol molecules are unable to cover all the exchangeable sites on the adsorbents, leading to decreased phenol uptake at higher dosages [13, 44]. Phenol removal efficiencies expressed as a function of only the initial and final phenol concentrations, on the other hand, increased with increase in adsorbent dosage.

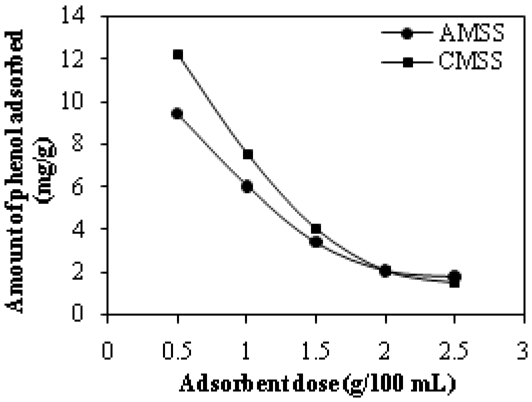

Figure 3: Effects of adsorbent dosage on phenol removal by ammonium chloride-activated (AMSS) and carbonized (CMSS) *M. oleifera* seed shells

3.4 Equilibrium Adsorption Capacities, Isotherm Profiles and Model Parameters

Figure 4 displays the isotherms for the aqueous phase adsorption of phenol on AMSS and CMSS. At the operating initial phenol concentrations [$20 \leq C_o(\text{mg/L}) \leq 100$], the range of *RE* (%) across 25 – 40°C were: AMSS ($48.21 \leq RE \leq 79.3$) and CMSS ($39.88 \leq RE \leq 81.45$). Actual sorption capacities, Q (mg/g) were $1.4 \leq Q \leq 5.2$ and $2.5 \leq Q \leq 10.7$) for AMSS and CMSS, respectively. The capabilities of the adsorbents to remove phenol varied as AMSS < CMSS, portraying CMSS as a more potent of the experimental adsorbents. The isotherm profiles are also noteworthy because they can provide information regarding the nature and intensity of sorption for a particular adsorbate-adsorbent system. The isotherms for AMSS and CMSS were somewhat L-shaped indicating that the intermolecular forces of phenol are comparatively weaker than the sorptive forces, which implies that the activation energy of adsorption is independent of surface coverage [45].

Equilibrium data for the adsorption of phenol from aqueous phase on AMSS and CMSS were fitted into the Langmuir and Freundlich isotherms represented by Equations (4) and (5), respectively:

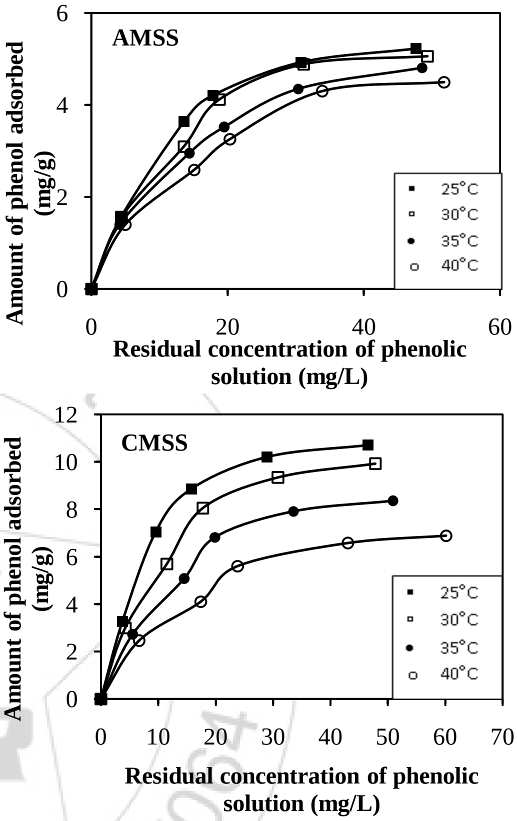

Figure 4: Isotherm profiles for adsorption of phenol on ammonium chloride-activated (AMSS) and carbonized (CMSS) *M. oleifera* seed shells

$$C/Q = C/Q_{\max} + 1/K_l Q_{\max} \tag{4}$$

$$\ln Q = 1/n_f \ln C + \ln K_f \tag{5}$$

where Q is the equilibrium amount of phenol adsorbed per unit mass of the adsorbent (mg/g), and C is the residual concentration (mg/L). Q_{max} is the maximum amount of phenol adsorbed per unit mass of adsorbent (mg/g) corresponding to complete coverage of the adsorptive sites, K_l is the Langmuir constant (L/mg) related to the energy of adsorption. K_f is Freundlich constant (mg$^{1-1/n}$L$^{1/n}$/g), related to the adsorption capacity, and n_f is a dimensionless empirical parameter related to the adsorption intensity which varies with the heterogeneity of the material [42]. A linear plot of C/Q versus C gives the inverse of the slope as Q_{max} and K_l is derived from the intercept; while a linear plot of ln$Q$ versus ln$C$ gives the inverse of the slope as n_F and intercept as K_f. The Langmuir and Freundlich isotherm parameters are recorded in Table 2.

The Langmuir model assumes that adsorption occurs at homogeneous sites and forms a monolayer. The characteristics of the Langmuir isotherm are determined by the dimensionless constant called separation factor, R_L expressed as:

$$R_l = 1/(1 + K_l C_o) \qquad (6)$$

where K_L (L/mg) and C_o (mg/L) retain their usual meaning as stated earlier in Eq. 5. R_l indicates the nature of adsorption process such that $R_l > 1$, $R_l = 1$, $0 < R_l < 1$, and $R_l = 0$ indicate that adsorption is unfavorable, linear, favorable and irreversible, respectively [47].

Table 2: Isotherm parameters for phenol adsorption on chemically activated *Moringa oleifera* seed shells (AMSS) and carbonized *Moringa oleifera* seed shells adsorbents (CMSS)

Adsorbent	Isotherm parameters	25°C	30°C	35°C	40°C
AMSS	Langmuir				
	Q_{max} (mg/g)	6.76	6.62	6.37	6.21
	K_l (x10^{-2} L/mg)	8.08	6.55	6.50	5.48
	K_l (x10^{4} L/mol)	7.60	6.16	6.13	5.15
	R_l	0.20	0.31	0.31	0.37
	R^2	0.990	0.985	0.996	0.965
	Freundlich				
	K_l (mg$^{1-1/n}$L$^{1/n}$/g)	0.83	0.79	0.71	0.62
	n_f	1.93	1.95	1.92	1.90
	R^2	0.921	0.943	0.978	0.975
CMSS	Langmuir				
	Q_{max} (mg/g)	13.16	12.99	11.36	10.75
	K_l (x10^{-2} L/mg)	0.11	7.60	6.20	5.70
	K_l (x10^{4} L/mol)	10.43	7.14	5.83	5.36
	R_l	0.18	0.26	0.32	0.35
	R^2	0.991	0.990	0.984	0.989
	Freundlich				
	K_l (mg$^{1-1/n}$L$^{1/n}$/g)	2.05	1.59	1.13	1.03
	n_f	2.12	1.97	1.91	2.05
	R^2	0.878	0.943	0.938	0.951

At the temperatures (25 – 40°C) investigated, ranges of the Langmuir parameters: Q_{max} (mg/g), K_l (×10^3 L/mol), R_l and R^2 for phenol-AMSS system were: ($6.21 \leq Q_{max} \leq 6.76$), ($5.15 \leq K_l \leq 7.6$), ($0.20 \leq R_l \leq 0.37$) and ($0.94 \leq R^2 \leq 0.990$), respectively. Correspondingly, ranges for phenol-CMSS sorption systems were: ($10.76 \leq Q_{max} \leq 13.16$), ($5.36 \leq K_l \leq 10.43$), ($0.18 \leq R_l \leq 0.35$) and ($0.984 \leq R^2 \leq 0.991$). R_l values recorded in this study are interpretive of favorable adsorption, somewhat akin to those reported for the removal of phenol from aqueous solution by yeast *Saccharomyces cerevisiae* [43], *Hemidesmus indicus* based activated carbon [13] and tendu leaf [22]. Table 3 compares the Q_{max} of some phenol-adsorbent systems in the literature with those recorded in the present study.

The Freundlich model proposes heterogeneous energetic distribution of active sites, accompanied by interaction between adsorbed molecules. At the operating temperatures (20 – 40°C), the ranges of Freundlich parameters: K_f (mg$^{1-1/n}$L$^{1/n}$/g), n_f and R^2 for phenol-AMSS systems were ($0.62 \leq K_f \leq 0.83$), ($1.99 \leq n_f \leq 1.93$) and ($0.921 \leq R^2 \leq 0.978$). Corresponding ranges for phenol-CMSS sorption systems were: ($1.03 \leq K_f \leq 2.05$), ($2.05 \leq n_f \leq 2.12$) and ($0.878 \leq R^2 \leq 0.951$). The higher values of K_f, the Freundlich constant for CMSS, showed easy uptake of phenol from aqueous solution than the AMSS [9]. Also the higher values of n_f reflects the intensity of adsorption hence signifies that the surfaces of biosorbent is heterogeneous in nature and high enough for effective separation [48].

Table 3: Adsorption capacity of some biomass-based adsorbents for phenol

Adsorbent	Q_{max} (mg/g)	Reference
Corn cobs carbon	52	[21]
Tendu leaf	8	[22]
Sugar cane bagasse-steam activated carbon	46	[27]
Sugar cane bagasse-NaOH activated carbon	101	[27]
Saccharomyces cerevisiae	27	[43]
Rice husk carbon	22	[48]
Ammonium chloride-activated *M. oleifera* seed shell	6.2 – 6.8	This study
Ammonium chloride-activated *M. oleifera* seed shell carbon	11 – 13	This study

3.5 Adsorption Thermodynamics

Basic thermodynamic parameters for phenol adsorption on AMSS and CMSS such as the Gibb's free energy change (ΔG^o), enthalpy change (ΔH^o), entropy (ΔS^o) were deduced from isothermal data. The Gibbs free energy change was calculated using Equation (7):

$$\Delta G^o = -RT \ln K_l \qquad (7)$$

where R is the universal gas constant (8.314 J/mol-K), T is the temperature (K). Meanwhile, the values of K_l, the Langmuir affinity constant, were first converted from L/mg basis to L/mol basis using Equation (8) before substitution in Equation (7).

$$K_l\,(\text{L/mol}) = K_l\,(\text{L/mg})\ \text{x}\,10^3\,(\text{mg/g})\ \text{x}\ \text{M}_r\,(\text{g/mol}) \qquad (8)$$

where M_r is the molecular weight of phenol (94.0 g/mol).

The enthalpy (ΔH^o) and entropy (ΔS^o) parameters were estimated from the Van't Hoff equation:

$$\ln K_l = \left(\Delta S^o / R\right) - \left(\Delta S^o / RT\right) \qquad (9)$$

where R and T retain their usual meanings. Actual values of ΔH^o and ΔS^o were respectively obtained from the slope and intercept of the ln K_l(L/mol) versus 1/T (K^{-1}) plots. Some basic thermodynamic parameters for aqueous phase adsorption of phenol on AMSS and CMSS are summarized in Table 4. Negative values of enthalpy change, ΔH^o (kJ/mol), -18.09 and -34.30 for phenol-AMSS and phenol-CMSS sorption systems, respectively interpret exothermicity of the sorption process [49, 50]. In the literature, ΔH^o values in the range [$-83 \leq \Delta H^o$ (kJ/mol) ≤ -830] represent chemisorption; while those in the range [$-8 \leq \Delta H^o$ (kJ/mol) ≤ -25] signify physisorption [44]. ΔH^o values obtained in this study indicate that the phenol-AMSS sorption was physisorptive, whereas that of phenol-CMSS was chemisorptive. The entropy change, ΔS^o (J/K.mol) was 13.35 and -38.75 for the phenol-AMSS and phenol-CMSS scenario, respectively, representing a spontaneous and non-reversible isothermal sorption processes. The negative ΔS^o for phenol-CMSS sorption can be explained in that, during adsorption, phenol molecules bond with the binding sites of adsorbent's surface, resulting in the loss of degree of freedom [50]. The negative values of ΔG^o (kJ/mol) for adsorption of phenol on both adsorbents ranging from [$-22.92 \leq \Delta G^o$(kJ/mol)≤ -22.14] indicate the spontaneous nature of the adsorption processes. From the literature, ΔG^o values ranges from [$-20.00 \leq \Delta G^o$(kJ/mol)≤ 0.00] represent physisorption; while those in the range [$-400.00 \leq \Delta G^o$ (kJ/mol)≤ -80.00] indicate chemisorptions [50]. The ΔG^o values recorded in this study are intermediate suggesting, an interplay of physical and chemical forces during phenol removal.

Table 4: Basic thermodynamic parameters for the adsorption of phenol on ammonium chloride-activated (AMSS) and carbonized (CMSS) *M. oleifera* seed shells

Adsorbent	*T* (K)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (J/K.mol)
AMSS	298	-22.14	-18.09	13.35
	303	-21.98		
	308	-22.98		
	313	-22.24		
CMSS	298	-22.92	-34.30	-38.75
	303	-22.34		
	308	-22.20		
	313	-22.34		

3.6 Adsorption Kinetics

The two basic kinetic parameters used for defining adsorbent and selecting appropriate conditions for the design of a wastewater treatment scheme are the adsorption capacity (derived from equilibrium considerations) and the adsorption time (defined as the time taken to remove one-half of the initial concentration of the adsorbate) [51]. In this study rate curves for aqueous phase adsorption of phenol on AMSS and CMSS are illustrated in Figure 6.

For both adsorbents, phenol uptake increased very rapidly within the first 50 min but slowed down beyond this point, gradually rendering plateaux for at higher contact times the operating temperatures, signifying that the process would not offer additional kinetic advantage when contact times longer than 4 h were employed. The uptake of phenol, somewhat diminished as temperatures were raised from 25 – 40°C, implying that phenol adsorption was less favourable at higher temperatures.

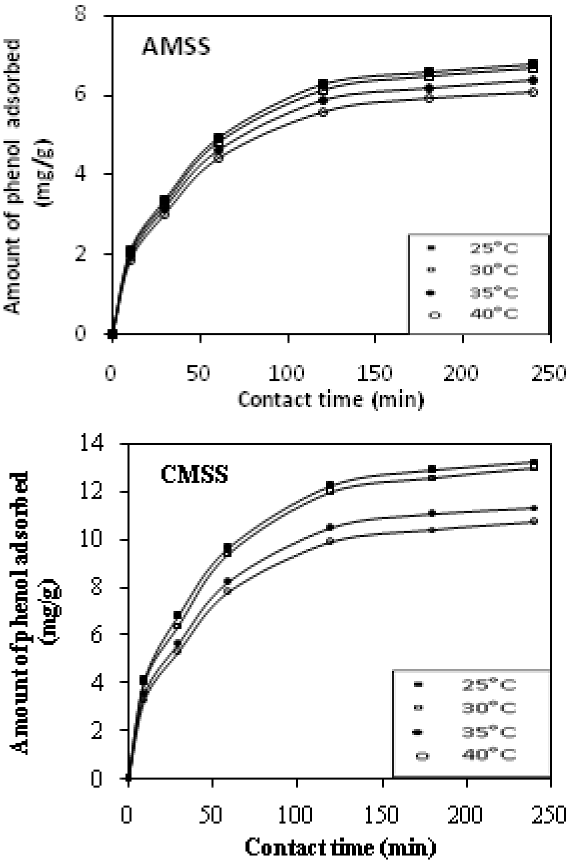

Figure 6: Rate curves for adsorption of phenol on ammonium chloride-activated (AMSS) and carbonized (CMSS) *M. oleifera* seed shells

The experimental data for the aqueous phase adsorption of phenol on AMSS and CMSS as a function of contact time were fitted into the Blanchard pseudo-second-order and the Weber-Morris intraparticle diffusion kinetic models given by Equations (10) and (11), respectively:

$$t/Q_t = 1/k_2 Q_e^{\,2} + t/Q_e \qquad (10)$$

$$Q_t = k_{id}\sqrt{t} + C \qquad (11)$$

where Q_e and Q_t are respectively, the amounts of phenol adsorbed (mg/g) at equilibrium and at a specified time, t (min); k_2 (g/mg.min) and k_{id} (mg/g√min) are the pseudo-second-order rate constant and intrapaticle rate constant, respectively [52]. Table 5 records the kinetic parameters so generated.

Considering the phenol-AMSS sorption system, the ranges of kinetic parameters recorded across the temperatures were: [$3.92 \leq k_2$ (x10^{-3} g/mg.min) ≤ 5.12] and [$3.49 \leq k_{id}$ (x 10^{-1} mg/g√min) ≤ 3.90]. Corresponding ranges for the phenol-CMSS scenario were: [$2.09 \leq k_2$ (x10^{-3} g/mg.min) ≤ 2.63] and [$6.13 \leq k_{id}$ (x10^{-1} mg/g√min) ≤ 7.51]. Based on the coefficient of determination, R^2, the pseudo-second-order model recorded the higher values relative to the intraparticle diffusion model.

Table 5: Kinetic parameters for aqueous adsorption of phenol on ammonium chloride-activated (AMSS) and carbonized (CMSS) *M. oleifera* seed shells

Adsorbent	Parameter	25°C	30°C	35°C	40°C
AMSS	*Blanchard model*				
	k_2 (x10^{-3}g/mg.min)	3.92	4.03	5.12	4.37
	R^2	0.997	0.997	0.994	0.997
	Weber-Morris model				
	K_{id} (x10^{-1}g/mg.√min)	3.90	3.83	3.67	3.49
	R^2	0.928	0.929	0.929	0.929
CMSS	*Blanchard model*				
	k_2 (x10^{-3}g/mg.min)	2.09	2.04	2.37	2.63
	R^2	0.998	0.997	0.997	0.997
	Weber-Morris model				
	K_{id} (x10^{-1}g/mg.√min)	7.51	7.45	6.49	6.13
	R^2	0.928	0.929	0.927	0.927

4. Conclusion

Ammonium chloride-activated and carbonized *M. oleifera* seed shell adsorbents prepared in this study showed favorable physicochemical characteristics and adsorptive behavior towards phenol. Equilibrium phenol uptake was well modeled by the Langmuir isotherm. Basic thermodynamic parameters indicated that phenol uptake was feasible and exothermic for both adsorbents, but occurred via the physisorptive and chemisorptive modes for AMSS and CMSS, respectively. Adsorption kinetics obeyed the Blanchard pseudo-second-order kinetic model. The adsorbents may find potential use in the dephenolation of aqueous effluents and wastewater.

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