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Application of Groundnut Shell in Natural and Carbonized forms as Adsorbent for the removal of 2,4,6-trichlorobenzoic acid from Aqueous Systems

O.O OLOLADE

¹Department of Chemical Sciences, Adekunle Ajasin University, Akungba - Akoko *Corresponding author E-mail address: *:* ogbeoluwarantimi@yahoo.co.uk

A b s t r a c t

INTRODUCTION

Herbicides belong to an important group of anthropogenic pollutants of soil and water. Despite their agricultural significance, their excessive usage has resulted in detrimental effects on human health and wildlife (Swartz *et al*.,2003; Matson *et al*., 2006), plants (Gichner *et al*.,2008), and aquatic organisms (Zhao *et al*.,1998; Lee and Chen, 2009). Acidic herbicides such as phenoxyl and chlorobenzoic are toxic for many living organisms, although none belongs to a group of very toxic pollutants. Some are mutagenic, teratogenic, and carcinogenic. Chlorobenzoic acids (CBAs) such as 2,4,6 trichlorobenzoic acid (2,4,6-TCB) represent crucial recalcitrant metabolites resulting primarily from microbial biodegradation of polychlorinated biphenyls (PCB) (Bedard, 2003; Sorensen *et al.*, 2007; Field and Sierra-Alvarez. 2008). Field and Sierra-Alvarez, 2008). Chlorobenzoic acids can accumulate in soil through their usage as herbicides, thus impairing the quality of the surrounding water.

 Several researchers have explored various adsorption techniques for the removal of organic pollutants in drinking water using adsorbent materials. In recent years, adsorption techniques using synthetic adsorbents have yielded excellent and reliable results (Gupta *et al*., 2007; Tawfik *et al*., 2012). However, some of these methods are expensive with adverse effects (Bulut *et al*., 2007). This has led to the alternative use of agricultural waste and other available low-cost adsorbent materials for the treatment and remediation of water and wastewater (Isah and Yusuf, 2012; Meenakshi and Sivakumar, 2012). Studies on GS have shown its effectiveness as an adsorbent in the removal of nickel, lead, and other organic and inorganic pollutants from aqueous solutions (Mohammad *et al*.,2006; Isah and Yusuf, 2012). In another study, Ganapaty and Mariappan (2010) reported on excellent removal of fluoride from water using
carbonized GS impregnated with zirconium impregnated with zirconium oxychloride. Similarly, the sorption efficiency study of pesticide adsorption on granulated activated carbon from GS has shown that GS-based adsorbents

favourably adsorb the pesticide (dichlorvos) (Aminu *et al*., 2010). In a related study, Uzoije *et al*. (2011) reported that activated GS is a good mop-up and lowcost alternative medium for oil-spilled surfaces. In their study, Meenakshi and Sivakumar (2012) investigated the use of activated carbons prepared from GS and Indian almond shells for the removal of Azure A dye from the aqueous solution. These adsorbents were found to be an effective alternative to commercial activated carbon. Thus, it is clear from the studies above that GS is an excellent low-cost adsorbent.

 Specifically, the current study investigated the biosorption of 2,4,6-TCB using GS in both natural and carbonized forms. To our knowledge, very few reports on CBAs exclude 2,4,6-TCB, therefore, the present work might provide some new insights on 2,4,6-TCB remediation.

MATERIALS AND METHOD

Chemicals

2,4,6-TCB was obtained from Sigma–Aldrich (Steinheim, Germany). Acetonitrile (ACN, gradient grade) was purchased from Fisher Scientific (Leicestershire, UK). All the other chemicals were of analytical grade and were obtained from Sigma– Aldrich. The 246-TCB solution was prepared by dilution of the stock standard solution (1000 mg/L) prepared in ACN.

Sorbent Collection and Preparation

 The groundnut used in this study was purchased from a local market at Ikare-Akoko in Ondo State, Nigeria. Groundnut seeds were removed by cracking and the shells which constitute about 20% by weight of each groundnut were pooled together; the shells were thoroughly washed with distilled water, and dried at 60° C in a temperature-controlled oven for 8 h. The shells were properly ground in a disk mill and subsequently sieved (0.5*µ*m mesh size). This powdered product was tagged unmodified groundnut shell (UGS). The modified groundnut shell (MGS) was produced from the UGS. This was achieved by mixing 10.0g of the UGS with 50 mL of concentrated H2SO⁴ (98% weight, 1.98 g/mL) in a 1L capacity digestion flask. A black carbonaceous residue was produced to which about 300 mL of distilled water was added and thoroughly mixed. The sample was later heated to 100°C for about 2 h under the influence of magnetic agitation. With a Buchner funnel; samples were filtered and copiously washed with distilled water until the pH of the filtrate reached 5.5. The washed MGS residue was thereafter dried at 105°C for about 2 h and put in an air-tight sample bottle inside a desiccator. The two adsorbents (UGS and MGS) were characterized for organic carbon (% OC), surface area (SA), pH, and cation exchange capacity (CEC) following the conventional method (Tao *et al*., 2006).

FTIR spectra were recorded using the ATR data collection method with a resolution of 4 cm^{-1} (Agilent Technologies) in the range of $650 - 4000$ cm⁻¹.

Adsorption kinetics

Kinetic studies were conducted in brown flasks at room temperature by shaking 0.2 g of samples (UGS and MGS) with 25 mL of 10 mg/L 2,4,6-TCB in $0.02M$ CaCl₂ solution at 200 rpm on a temperaturecontrolled shaking water bath (UNISCOPE SM 101, England). Samples were withdrawn at intervals (0, 5, 10, 15, 20, 30, 45, 60, 90, 120, 180, 300,420, and 600 min), centrifuged (5000 rpm for 15 min), and filtered using 0.22 μ m glass fiber filter. The residual concentrations of 2,4,6-TCB were determined by high-performance liquid chromatography (HPLC) as described in our recent paper (Ololade *et al*., 2014) The amount of 2,4,6-TCB adsorbed was determined by the difference between the initial and liquid-phase concentrations of 2,4,6-TCB solution. The effects of initial pH (i.e., $3, 4, 6$, and 8) at a constant $2, 4, 6$ -TCB concentration (10.0 mg/L) were investigated on each sorbent. Each experiment was carried out in duplicates.

Sorption isotherm

Adsorption isotherms were determined by the batch method for all samples. Samples (0.2g) were spiked with analytical grade 2,4,6-TCB (chemical purity $>98\%$) dissolved in 0.02M CaCl₂ background electrolyte solution and $HgCI₂$ (to prevent biological activity) in PTFE centrifuge tubes to give concentrations ranging from 20.0- 100.0 mg/L. Samples were then equilibrated for 8h based on sorption kinetics by shaking in an end-over-end shaker (70 rpm) in the dark at $25 \pm 1^{\circ}$ C. The experiment was carried out at two different pH levels (pH 3 ± 0.1 and 5 ± 0.1) for both sorbents (adjusted with 0.05M HCl and 0.05M NaOH). After equilibration, suspensions were centrifuged at 5000 *g* for 20 min. An Aliquot (5 mL) of supernatant solution was removed and filtered through a 0.22 *µ*m glass fiber filter. One control sample with only the test substance in $0.02M$ CaCl₂ solution (no GS) was subjected to precisely the same step as the test systems to check its possible adsorption on the surface of the vessels. The equilibrium concentration of 2,4,6-TCB was analyzed by HPLC as stated above. Adsorption amount (mg/g) was calculated by using the following equation:

$$
q_e = \frac{\left(C_0 - C_e\right)}{W} V\tag{1}
$$

where *W* is the weight of samples (UGS and GS) (g); *V* is the volume of the aqueous phase (L); q_e is the amount of 2,4,6-TCB adsorbed onto the unit dry mass of the samples (mg/g) , C_0 and C_e are the concentrations (mg/L) of the 2,4,6-TCB solution

before and after adsorption, respectively, that were determined. A linear response over a concentration range gave a correlation coefficient, $r^2 = 0.998$ while the coefficient of variation {(standard deviation/mean) \times 100} of the concentration ranged from 2 to 4%.

 The kinetic and equilibrium models were performed by non-linear regression of the software microcal Origin 7.0. The models were also evaluated by an error function which measures the difference between the experimental and the predicted adsorption capacities (Lima *et al*., 2007). The magnitude was determined by the following equation;

Error function

$$
= \sqrt{\sum_{i}^{p} \frac{q_{\text{imodel}} - q_{\text{isoperimental}}}{q_{\text{isoperimental}}}})^2 \cdot \left(\frac{1}{p-1}\right)
$$
\n(2)

where *q*imodel and *q*iexperiment are the value of *q* predicted by the model and those measured experimentally respectively, and *p* is the number of experiments performed.

RESULTS AND DISCUSSION

*F*error

Characterization

Table 1.0 summarizes the results of sample characterization. It is obvious from the table that, apart from SA, the %OC, exchangeable cations (CEC), and point zero charges (pH_{pze}) were higher in UGS.

Table 1 Sample characterization of natural (UGS) and carbonized (MGS)

Samples	SА	% OC CEC		PZC.
UGS	55.0	4.92	1.76	5.2
MGS	71.0	4.74	0.93	2.1

This may be attributed to the effect of treatment reagents on the modified sample. Thus, at a solution pH above pH*pzc*; 2 (MGS) and 5.2 (UGS), the total surface charge will be on the average negative. The lower the pH*pzc*, the less the repulsion and the higher the adsorption capacity. Hence, all other factors being equal, the MGS is expected to adsorb more 2,4,6- TCB than the UGS significantly. Enhanced SA in MGS by almost 16.0 m^2/g is suggestive of greater sorption by this sorbent over UGS based on previous reports (Malik *et al*., 2007).

The FTIR (Fig. 1) of both samples are quite similar except for variation in peak intensities which were generally enhanced in MGS. Both samples show
characteristic peaks from $3100-3600$ cm⁻¹ peaks from $3100-3600$ cm⁻¹ corresponding to -O–H stretching vibration of the hydroxyl group. The C-C stretching peak between

1600-1700cm-1 and the strong absorption peak between $1000-1033$ cm⁻¹ assigned to the C–O in stretching mode were both shown at higher bands in the modified sample. A characteristic sharp peak at 1267 cm⁻¹ was recorded in MGS which has been attributed to combination frequencies of (CH·OH). This peak which seems to be buried in UGS possibly protonates in MGS and consequently increases its cationic strength with a potential for higher adsorption capacity than the UGS. The FTIR data further conferred on the modified sample greater adsorbent properties than the unmodified sample.

Effects of initial pH

The role of pH in the adsorption processes of both organic and inorganic substances has been documented, and most pH effects have been related to its dependence on surface charge (pH_{zpc}). In this study, the effects of initial pH i.e. $pH₀$, on adsorption of 2,4,6-TCB was monitored using GS at a fixed solution concentration of 10 mg/L but different initial pH (3 and 5) (Fig. 2). As noted earlier, pH_{ZDC} of the samples were 2.0 (MGS) and 5.2 (UGS). Hence, the surface of MGS within the pH range studied is predominantly negatively charged while those of UGS are positively charged at $pH_0 < pH_{zpc}$ (i.e. 2, 3, and 5) due to the variable charge from pH-dependent surface hydroxyl sites (Walker and Weatherley, 1999; Seunghum and Linda, 2004).

Ordinarily, UGS is expected to adsorb more within these pH levels than the MGS based on surface charge since 2,4,6-TCB exists mostly in anionic form in the environment. However, its existence in anionic form suggests that its uptake could occur through several processes: hydrogen bonding, electrostatic interaction, complexation, or hydrophobic interaction between the TCB and the sample surfaces. Hence, the greater sorption with MGS across all pH suggests that ionic interaction could not have been the mechanism of 2,4,6-TCB removal from solution, though, adsorption may play a key role in the process. With the limited data obtained in the study, the surface area effect seems to predominate the 2,4,6-TCB adsorption process. Generally, the adsorbed amount of anionic 2,4,6-TCB decreased in response to the increasing number of negatively charged sites that are available. Very poor adsorption occurs at higher pH because the interaction becomes predominantly electrostatic. The trend reported here is in agreement with Baral *et al* (2006) who reported that an increase in pH will cause a decrease in the adsorption rate of chromium (III) ions which was adsorbed by groundnut shell.

Kinetic studies

For the kinetic modeling of the components sorption tests, pseudo-first order, pseudo-second order models, and intra-particle diffusion models are

represented respectively by Eqs. 3,4 and 5, were used.

$$
\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t
$$

Fig. 1 FTIR spectra of modified and unmodified groundnut shell (MGS and UGS).

Fig 2 Influence of initial pH on the sorption of 2,4,6- TCBA at a concentration specific level: $pH = 7.0$, $T =$ 298K, solution volume = 15 mL, $2,4,6$ -TCB = 10.0 mg/L.

$$
q_t = k_{id}t^{\frac{1}{2}} + c \tag{5}
$$

where *q*^e is the amount of soil adsorbed in equilibrium (in mg/L), q_t is the amount of soil adsorbed per unit mass of sorbent (in mg/g), *t* is the time of equilibrium, k_1 is the pseudo-first-order adsorption rate constant (per min), and k_2 is the pseudo-second-order adsorption rate constant (in $g/mg/min$, k_{id} is the intra-particle diffusion rate constants (mg/g $h^{0.5}$) and C (mg/g) is a constant that gives an idea about the thickness of the boundary layer of each sample. Generally, the higher the value of C the greater the boundary effects (Kannan and Sundaram, 2001). The kinetic plot (Fig. 3) indicates initial fast 2,4,6-TCB adsorption within the first 3 h, hence, the rate-determining step. In subsequent adsorption, slow reaction appears to be the dominant process. The rate constants, predicted equilibrium uptakes, corresponding correlation coefficients, and error functions across all pH are summarized in Table $2.$

Fig. 3 Kinetic isotherm curve for the biosorption of 2,4.6-TCB by modified (MD) and unmodified (UMD) groundnut shell. T: 298K, dosage: 0.2g.

Based on the correlation coefficient and error function, the kinetic data for both samples were best described by pseudo-second-order expression indicating both fast (k_1) and slow (k_2) uptake rates. This suggests the dominance of chemisorption at adsorption sites. The model assumes that the sorption rate is controlled by chemical sorption and the sorption capacity is proportional to the number of active sites on the sorbent (McKay and Ho, 1999; Gomez *et al*., 2007). While some literature involving the use of groundnut shell as adsorbent proves that pseudo first order shows a better fit for their adsorption process (Meenakshi and Sivakumar, 2012, Tasrina, 2012), others that involved the adsorption of organic and inorganic pollutants with GS as adsorbent are found to be in concordance with this study (Uzoije *et al*., 2011, Abdul and Aberuagba, 2005; Isah and Yusuf, 2012, Augustine *et al*., 2012).

The pseudo-second-order rate of sorption (k_2) exhibited a defined trend, decreasing with the increasing initial solution concentration of 2,4,6- TCB. This has been demonstrated to be true in several studies (Plazinski *et al*., 2009; Febrianto *et al*., 2009; Al-Ghouti *et al*., 2009; Popur *et al*., 2009). However, some studies have demonstrated the independence of k_2 on initial solute concentration (Aravindhan *et al*., 2007; Kavitha and Namasivayam, 2007; Vijaya *et al*., 2007; Sheng *et al*., 2008; Ertugay and Bayhan, 2008). Consequent to these conflicting reports, the idea of Wu *et al*. (2009) on the parameter, k_2q_e (min⁻¹) was used to define kinetic performance. This parameter is obtained by simple rearrangement of Eq. 6 to produce Eq. 7 as indicated below:

$$
\frac{dq_t}{d_t} = k_2 (q_e - q_t)
$$
\n
$$
\frac{dq_{t/q_e}}{d_t} = k_2 q_e \left[1 - \frac{q_t}{q_e} \right]_2
$$
\n(6)

Eq.7 is another form of sorption rate with a proportionality constant, k_2q_e , defined as a secondorder rate index. Estimated values in the study are included in Table 2. Again, rearranging Eq. 4 gives Eq. 8

$$
t = \frac{q_t}{k_2 q_t}
$$

(8)

$$
C_{0.5} = \frac{1}{k_2 q e} \tag{9}
$$

At the half-life of the sorption process (i.e., $t = t_{0.5}$), q_t $= 0.5q_e$. From Table 2, while the k_2q_e values obtained with both samples increased with an increase in the initial 2,4,6-TCB solution concentration, the half-life (*t*0.5) of the sorption process decreased. This suggests that the half-life of the 2,4,6-TCB sorption onto MGS and UGS was

t

attained faster at higher initial 2,4,6-TCB concentrations than at lower concentrations.

 Intra-particle diffusion model was employed to further study the adsorption process. The model indicates that the adsorption of 2,4,6-TCB on GS **Table 2:** Sorption kinetics constants during 2,4,6-TCB sorption by both UMG and MGS

occurred in three steps as typified in the Weber– Morris plot of q_t versus $t^{1/2}$ (Fig. 4). The initial fast step could be attributed to the diffusion of the 2,4,6- TCB molecules from the aqueous phase to the outer surface of the solid samples.

Results in parenthesis are data for UGS,

Fig. 4 Weber and Morris intra-particle diffusion plots for adsorption of 2,4,6-TCB on modified (MGS) and unmodified (UGS). Conditions: pH 7.0 \pm 0.1; Initial concentration, C_0 = 10 mg/l; sample dosage at 0.2g/l and temperature at 298K.

The slower second step could be attributed to the intra-particle diffusion of the 2,4,6-TCB molecules between the GS aggregates while the third stage refers to pore diffusion towards attainment of equilibrium. In the plot, the slower second step is linear but does not pass through the origin. This suggests that intra-particle diffusion is involved in the adsorption process but not the sole rate-limiting step. In addition, the multilinear nature of the plots suggests that the adsorption process is governed by more than one step (Unuabonah *et al*., 2007). The thickness of the boundary, C, across all concentrations, is several folds higher in UGS than in MGS (Table 2). In addition, the value of C decreases with increasing concentration of 2,4,6-TCB. This suggests that the molecules of UGS are more aggregated particularly at lower concentrations in aqueous solution than those of MGS. Consequently, resistance to 2,4,6-TCB mass transfer is greatly enhanced in UGS. The slope of the plots, k_{id} , where intra-particle diffusion is rate controlling differs in each case. The much higher k_{id} in MGS than the UGS further justified the resistance to 2,4,6-TCB mass transfer by UGS. The R^2 values given in (Table 2) are close to unity indicating the application of this model.

The linearity of the plots suggests that intra-particle diffusion played a significant role in the uptake of the 2,4,6-TCB.

Adsorption isotherm

Figure 5 is the plot of 2,4,6-TCB sorption isotherm of MGS and UGS at different pH levels. To interpret the experimental isotherm data, two sorption

isotherm models were employed; the Freundlich and Linear models under two different pH i.e. pH 3 and pH 5. The distribution coefficient (K_d) was determined using Eq. 10

$$
C_s = K_d C_e \tag{10}
$$

The value of K_d for both the MGS and UGS was determined from the slope of the plots of C_s vs. C_e at which the intercepts were assumed to be zero (Table 3).

Under both pH conditions, the K_d 's and R^2 are lower using UGS as adsorbent when compared to the use of MGS as the adsorbent. This suggests that the sorption of 2,4,6-TCB is favoured using MGS as the adsorbent.

The data equally showed that K_d of MGS is \approx 2.5-fold higher at pH 3 than at pH 5. Similarly, K_d of MGS is higher at lower pH. This suggests that sorption of 2,4,6- TCB is more favoured at lower pH.

 The linearized form of the Freundlich equation (Eq. 11) was employed to estimate some key parameters as shown below;

$$
\log Cs = \frac{1}{n} (log Ce) + log K_f \tag{11}
$$

where K_f is the Freundlich sorption coefficient and 1/n is the slope of the sorption isotherm. The sorption data shows that the K_f at pH 3 is 0.044 and 1.24×10^{-9} for MGS and UGS while at pH 5, K_f was 7.19×10^{-4} and 6.17×10^{-11} respectively. This shows that the MGS has a higher adsorption rate than the UGS. Higher values of K_f in MGS under both experimental conditions suggest that the binding capacity was maximized in this sorbent. However, lower values of n in MGS suggest poor affinity towards 2,4,6-TCB.

Fig. 5 Sorption isotherms of 2,4,6-TCB on treated and untreated sediments at pH= $7\pm$ 0.2 at 25°C. Background electrolyte: 0.01M CaCl2. Solid lines: modeled sorption isotherms; Data given as mean of duplicates.

Table 3 2,4,6-TCB calculated equilibrium constants using Freundlich isotherm and sorption parameters to contents of distribution coefficients, K_d , Organic carbon normalized distribution coefficient, K_{oc} .

 $K_{\rm oc}$ ($K_f/F_{\rm oc}$) is the OC-normalized sorption capacity coefficient with unit of mg/kg-OC/ (mg/L)ⁿ

N values are almost 2-fold less in UGS which suggests greater desorption of 2,4,6-TCB from MGS. The fit of data to the Freundlich isotherm model may indicate the heterogeneity of the adsorbed surface. The trend is in agreement with reports by other scholars who employed groundnut shells as adsorbents (Uzoije *et al*., 2011). The increased SA of the MGS seems to play a significant role in the sorption of 2,4,6- TCB.

CONCLUSION

This study is primarily aimed at the application of groundnut shells in both natural and carbonized forms as a relatively low-cost adsorbent for the removal of 2,4,6- TCB from aqueous systems. Experimental results as provided from this research work show that the carbonized form of groundnut shell (MGS) is more effective for the removal of 2,4,6- TCB from the aqueous system than the natural form of groundnut shell (UGS). Since the groundnut shell used in this work is abundantly and locally available, the resulting adsorbent is expected to be economically viable for the removal of 2,4,6- TCB from the aqueous solution. Results obtained were modeled using two isotherm models: Freundlich and Linear. Equilibrium isotherms were well described by the Linear isotherm. The adsorption kinetics can be well described by the pseudo-second-order model equation. Results obtained also show that a considerably lower level of concentration would favour a greater adsorption rate. Highlights of the study showed that adsorbents generated from groundnut shells compete well with those reported in the literature. The present work revealed that the adsorbent, particularly MGS, was a promising material for the removal of 2,4,6- TCB from the waste stream.

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