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Detoxification of copper fungicide using EDTA-modified cellulosic material

Igwe, J. C.[1]*, Ekwuruke, A.[1], Gbaruko, B. C.[2] and Abia, A. A.[3]

[1]Department of Industrial Chemistry, Abia State University, P.M.B. 2000 Uturu, Abia State, Nigeria.
[2]Department of Chemistry, Jackson State University, Jackson, MS 39217, U.S.A.
[3]Department of Pure and Industrial Chemistry, University of Port Harcourt, River State, Nigeria.

Pesticides are poisons and can be particularly dangerous when misused or carelessly disposed. The detoxification of a copper fungicide (KOCIDE 101) using maize cob, a cellulosic material, was studied. Based on copper as the active agent (after a sorption period of 1 h), the concentration of the fungicide reduced from an initial value of 2000 to 206.25 ppm for the unmodified maize cob and to 24.31 ppm for the modified maize cob. The pseudo-first and second order rate equations were used to model the detoxification process. The intraparticle diffusivity and mechanism of the sorption was proposed. Also, equilibrium sorption isotherms were evaluated using the Freundlich, Langmuir and Dubinin-Radushkevich isotherm models. This results show that maize cob is an effective adsorbent for copper fungicide deactivation and detoxification.

Key words: Copper fungicide, maize cob, adsorption, mechanism, EDTA, detoxification.

INTRODUCTION

During the past twenty years, concern has arisen as to the presence of germicides and pesticides in the environment and the threat they pose to wild life and mankind. Certainly, germicides and pesticides have improved longevity and the quality of life, chiefly in the area of public health. The use of pesticides also constitutes an important aspect of modern agriculture. For instance, Nigeria's tropical climates favour the growth of many harmful insects, weeds and diseases, thus making this country particularly dependent on pesticides for economical crop management (Hassal, 1990).

Unfortunately, pesticides are poisons and can be particularly dangerous when misused. Fish-kills, reproductive failure in birds, and acute illness in people have all been attributed to exposure or ingestion of pesticides, usually a result of misapplication or careless disposal of unused pesticides and containers (Hassal, 1990). Pesticide losses from areas of application and contamination of non-target sites such as surface and ground water represent a monetary loss to the farmer as well as a threat to the environment. Thus, careful management of pesticides in order to avoid environmental contamination is desired by both farmers and the general public.

As toxic agents, proper treatment and disposal of used and expired germicides and pesticides are becoming an ever-increasing challenge to scientists. Deactivation, such as neutralization or detoxification of germicides and pesticides, and the safe disposal of these agents have become crucial for protection of soil, ground and surface water, to ensure a safe environment for human and animal life, for natural microbial ecosystems and for meeting the environmental protection codes (Rao and Hornsby, 1993). Deactivation of these agents is scientifically challenging for several reasons:

i.   Each agent is chemically and physically unique, thus, needs unique approach for deactivation;
ii. The end products after deactivation must be environmentally safe, and
iii. Different countries or states have different laws, thus, needs different methods, for treatment and disposal.

Copper fungicides are one of the many classes of pesticides. Their specific use in the killing and control of

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*Corresponding author email: jcigwe2001@yahoo.com.

Table 1. List of some copper fungicides.

Substance	Approximate formular	Comments
Bordeaux mixture	$CuSO_4.3Cu(OH)_2$	Made from $CuSO_4$ and lime. Used as a spray
Copper oxychloride	$CuCl_2.3Cu(OH)_2$	Made from NH_4OH and $CuCl_2$. Used as a spray and a seed dip
Basic copper carbamate cuprous oxide	$Cu(OH)_2.3CuCO_3.Cu_2O$	Use as a dust. Yellow or red copper oxide used for seed treatment and as a spray.
Copper hydroxide	$Cu(OH)_2$	Formulated as wettable powder for use as a spray.
Chestnut compound	$CuSO_4 + NH_4HCO_3$	A soluble copper fungicide used as a soil drench against damping off. Not to be used on foliage.

fungi is due to the toxicity of copper ions in solution.

A variety of copper compounds have been used for this purpose. Some, such as freshly prepared Bordeaux mixture, are gelatinous and have the advantage that the copper is thereby bound to the leaf surface. Moreover, gels dry slowly and this increases the probability of the spore being killed by the fungicides, because spores usually germinate under damp conditions. To others, such as copper oxychloride a sticking agent such as starch is added to increase adhesion after spraying (Hassal, 1990). Most copper fungicides (Table 1) are formulated either as dusts or as wettable powders (Hassal, 1990).

Copper fungicides are used to control potato blight but they are also active against a wide variety of fungi. In this respect, they can be contrasted with many organic fungicides for the later often have a narrow biological spectrum. Copper dusts are used to control the downy mildew of hop, and copper sprays are used among other things against came and leaf spots, peach leaf curl and tomato leaf mould (Hassal, 1990). In addition, a few formulations (e.g. the water – soluble chestnut compound) are applied to soil to control damping – off disease. Cuprous oxide has been employed for seed treatment and it is also used as a spray especially in the tropics. Copper derivatives of aromatic carboxylic acids (naphthenic acids) are too toxic for foliage application but are useful for the treatment of timber in barns, fences and greenhouse (Hassal, 1990).

Thus, as a result of the toxicity of copper fungicides the use of EDTA-modified maize cob for the detoxification of these fungicides was studied. Maize cob is a lignocellulosic agricultural by-product which is obtained at little or no cost. It is the inner part of the fruit after removing the grains. It has been employed in the detoxification of heavy metals and other cationic and anionic species found in waste water (Igwe and Abia, 2003; Okieimen and Okundaye, 1989; Okieimen et al., 1988).

MATERIALS AND METHODS

Materials

Maize (*Zea Mays*) cobs were obtained from a local farm in Uturu, Abia State. They were cut into small pieces, air dried and powdered in a grinder. The maize cobs meal obtained was air dried, first sieved through a 1000 μm mesh screen and then sieved through a 250 μm mesh screen. The portion of the maize cobs meal retained on the 250 μm mesh was soaked in dilute nitric acid solution (2%, v/v) overnight, rinsed with deionised water and air-dried. The cobs were divided into two parts; one part of the cobs was used for sorption studies without chemical modification and the other was modified by the introduction of EDTA. This was done by a modified method of that by Eromosele and Otitolaye (1994); as described in the modification section.

The copper fungicide used in this study is KOCIDE 101. It contains 77% of cupric hydroxide as active ingredient and 23% inert ingredients. Its metallic copper equivalent is 50% and it has a blue colour. All reagents used are analytical grade, purchased and used without further purifications.

Modification of adsorbent

A 30 g sample of the maize cob was hydrolyzed with 500 ml of 7% (v/v) aqueous sulphuric acid for 18 h at 65°C. The mixture was filtered, the maize cob washed with deionised water several times and then dried at 50°C. Now, 17 g of the hydrolyzed product was refluxed in a mixture of 300 ml pyridine and 56.7 g of EDTA for 3 h at 70°C. The mixture was cooled, followed by addition of 300 ml of deionised, water and then filtered. The filtered product (EDTA-modified) was washed copiously with deionised water and dried at 50°C for 12 h.

Batch sorption experiments

Studies on sorption of copper (II) ions from aqueous solution of KOCIDE 101, a $Cu(OH)_2$ fungicide, by modified and unmodified maize cob were conducted by the introduction of a 2 g sample of the maize cob into 100 ml of the copper (II) ion fungicide solution of known concentration. Effect of initial concentration was investigated by varying concentration as 2000, 1800, 1600 and 1400 ppm. At the end of 60 min (depending on the initial sorption dynamics test), the cobs were removed from the mixture by rapid filtration and Cu(II) ion concentration in the filtrate was determine by flame atomic absorption spectrometer (FAAS) model 200 A. The amount of Cu(II) ions adsorbed was gotten by difference.

The kinetics of sorption of the copper fungicide was investigated using a fixed initial concentration (2000 ppm) and time variation of 10, 20, 30 and 40 min. At the end of each time the filtrate was analyzed as stated above. All the tests were carried out at a constant temperature of 30°C and pH of 7.5. All experiments were carried out in triplicates and results presented are average values of each experiment.
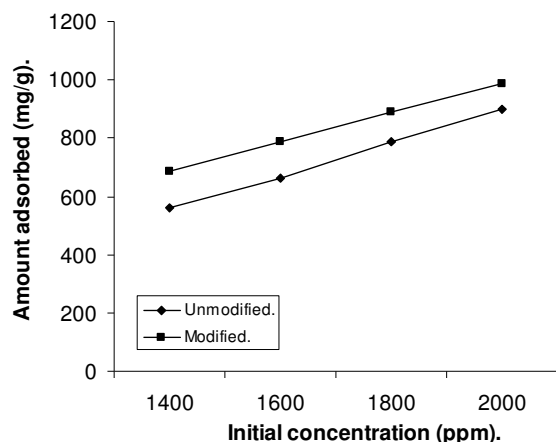
Figure 1. Amount adsorbed (mg/g) against initial concentration (ppm) for copper fungicide detoxification using modified and unmodified maize cob.
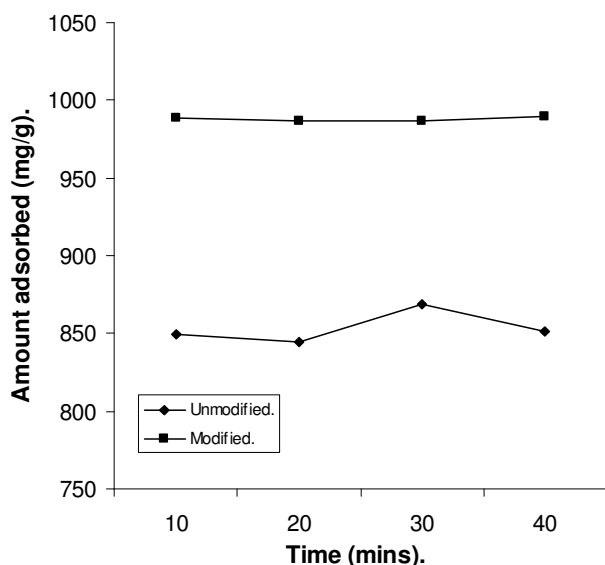

Figure 2. Amount adsorbed (mg/g) against time (min) for copper fungicide detoxification using modified and unmodified maize cob.

RESULTS AND DISCUSSION

The results for the amount of the copper fungicide adsorbed as the initial concentration changes is shown on Figure 1 for modified and unmodified maize cob. The results show that the amount of Cu(II) ions bound by the maize cobs was dependent on the initial Cu(II) concentration. It can be seen that the amount of Cu(II) ion removed from the solution increased with an increase in the initial concentration of Cu(II) ion solution, which ranged from 1400 to 2000 ppm. For the 2000 ppm initial concentration, the equilibrium concentration of Cu(II) sorbed was

559.55 mg/g of sorbent representing about a 2-fold increase over the equilibrium value at 1400 ppm. Figure 2 shows the amount adsorbed against time for the modified and unmodified maize cob. From this figure, we find that the amount adsorbed as time increases for the modified maize cob was higher compared to that of the unmodified maize cob. We can also observe that the graphs are flat showing that the amount of Cu(II) ions adsorbed did not appreciably increase with time after the initial sorption increase.

The mechanism of sorption here appears complex and may involve co-ordinate chelation between copper (II) ions and carbonyl oxygen on the substrate; formation of ionic bonds between metal ions and acidic groups on substrate and chemical combination between copper (II) ions and substrate (Eromosele et al., 1996). However, when substrate is chemically modified with EDTA sorption is considerably enhanced. This can be explained from a viewpoint that in addition to the initial form of sorption by the cobs, the EDTA incorporated into it also complexes with much more Cu(II) ions to form the stable EDTA-Cu(II) chelate, hence, there was much reduction in the initial concentration of Cu(II) ions. For instance, the initial concentration of Cu(II) ion was 2000 ppm before sorption but reduced to as low as 24.31 ppm after sorption for 1 h. Similar results were obtained using various other initial concentrations of the copper fungicide after sorption for 1 h.

Actually, the mode of fungitoxic action of copper is uncertain, although it was initially reported to be fungistatic rather than fungicidal, that is, stops growth rather than kills. Factors that influence the amount of copper taken up by fungal spores may throw some light on the mode of action of copper ions or at least on their availability at the site of action. It has been reported (Rao and Hornsby, 1993) that the amount of copper adsorbed becomes less as the hydrogen ion concentration of the external medium increases. Also reagents that form stable complexes with copper may reduce both the uptake and the toxic effect of copper. Thus EDTA reverses the inhibition of germination of *Alternaria* spores pretreated with copper. Various sulphydryl compounds, including glutathione and cysteine, have a similar effect (Hassal, 1990). Thus, chelates come in to play a part in two related but different contexts, namely (a) the solubilization of copper from an insoluble fungal residue and (b) the removal from poisoned but still variable fungal spores of copper that is already attached to some component of their walls. A picture thus seems to be emerging, not of the importance of a chelate complex per say, but of the relative stabilities of different complexes, present at each stage along the line from the components of fungal exudates to the toxic complex at the ultimate site of action within the spore.

Again, it is still not clear whether copper exerts its ultimate toxic effect in the cuprous or the cupric form. Investigations, show that copper adsorbed onto algal cells are replaced by univalent silver ions almost quantitatively on
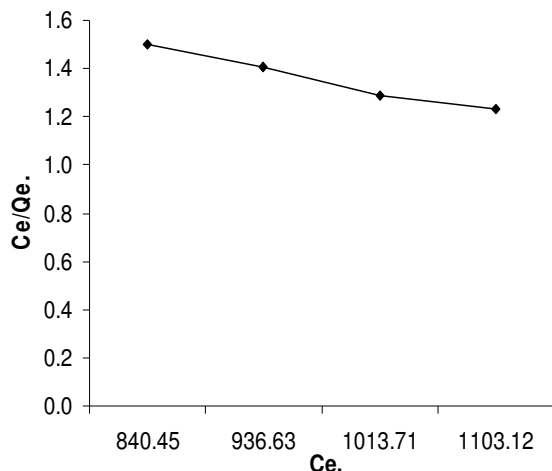
Figure 3. Langmuir isotherm plot for copper fungicide detoxification using unmodified maize cob.
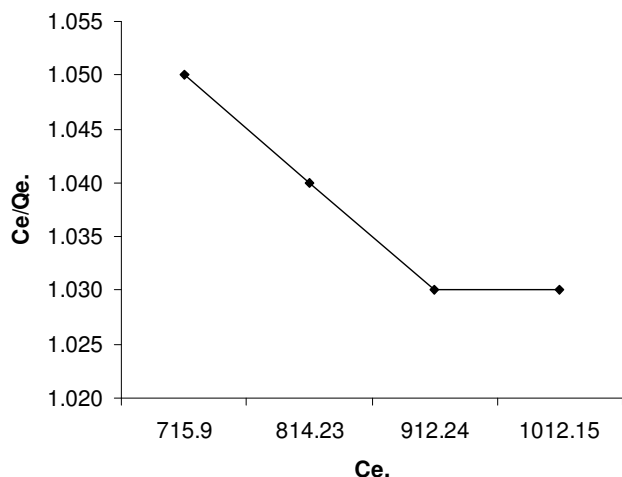

Figure 4. Langmuir isotherm plot for copper fungicide detoxification using modified maize cob.

an equivalent-for-equivalent basis. If the copper was assumed to be divalent, this demonstrates that in algae the vast majority of copper ions adsorbed form cupric complexes but it does not exclude the possibility that a small but important percentage could form cuprous complexes at a relatively few vital sites.

Sorption isotherm studies

Several sorption isotherms have been developed for the analysis and modeling of the adsorption of materials using various adsorbents. The parameters of these sorption isotherm models express the surface properties and affinity of the sorbent at a fixed temperature and pH. Three models were used to fit the experimental data. These are the Langmuir model, the Freundlich model and the Dubinin-Radushkevich model.

The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface and expressed by (Gang and Weixing, 1998);

$$Ce/qe = 1/Xmk_L + Ce/Xm \qquad (1)$$

Where Xm (mg g^{-1}) is the maximum sorption upon complete saturation of the biomass surface and K_L (dm^3 g^{-1}) is a constant related to the adsorption/desorption energy. The langmuir plot of specific sorption (Ce/qe) against equilibrium concentration (Ce) is shown on Figure 3 for unmodified maize cob and Figure 4 for modified maize cob. The slopes and intercepts of these plots were used to calculate Xm and K_L, which are presented in Table 2.

The Langmuir model assumes the surface of the sorbent to be homogeneous and the sorption energies to be equivalent for each sorption site. Solute immobilization occurs without mutual interactions between the molecules sorbed on the surface (Guibal et al., 1998). Also, the favourability of adsorption of the copper fungicide onto the modified and unmodified maize cob was tested using the essential features of the Langmuir isotherm, expressed in terms of a dimensionless constant called separation factor, S_F, proposed by Mckay and Poots (1980). The separation factor S_F is defined by the following relationship;

$$S_F = 1/(1 + K_L C_O) \qquad (2)$$

Where K_L = constant from Langmuir equation and Co = initial metal ion concentration (ppm). The parameter indicates the shape of the isotherm as follows;

$S_F > 1$	Unfavourable isotherm
$S_F = 1$	Linear isotherm
$S_F = 0$	Irreversible isotherm
$0 < S_F < 1$	Favourable isotherm.

The values calculated for S_F is shown on Table 2. Although the R^2 values are high (and good), for the Longmuir isotherm, the Xmax and K_L are negative indicating unfavourable isotherm. This is also confirmed by the value of S_F being greater than one for both unmodified and modified maize cob.

The Freundlich model was chosen to estimate the adsorption intensity of the sorbent towards the biomass and it is given by equation (3) (Gang and Weixing, 1998):

$$qe = K_F Ce^{1/n} \qquad (3)$$

Where qe = the adsorption density (mg/g) and Ce = concentration of metal ion in solution at equilibrium (mg/L). K_F and n are the Freundlich constants determined from the slope and intercept of the linearised equation (i.e. equation 4) by plotting ln qe against ln Ce.

$$\ln qe = \ln K_F + 1/n \ln Ce \qquad (4)$$

Table 2. Values of Langmuir, Freundlich and Dubinin-Radushkevich sorption isotherm constants and their correlation coefficients for copper fungicide sorption on unmodified and modified maize cob.

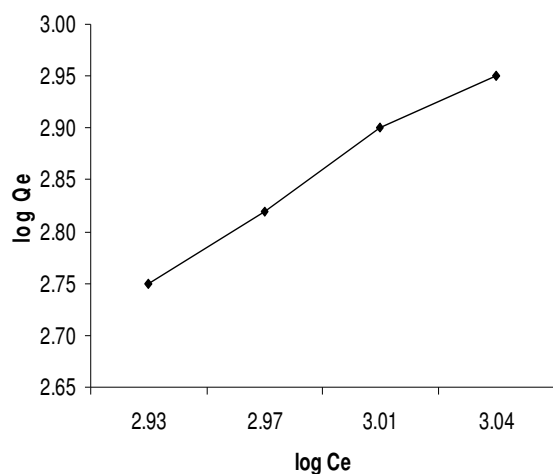| Sorption isotherm	Constant	Unmodified	Modified
Langmuir	Xmax	- 933 . 707	- 14113.529
	K_L	- 4.462 x 10^{-4}	- 6.449 x 10^{-5}
	S_F	9.29	1.15
	R^2	0.9694	0.9819
Freundlich	K_F	438.53	1.584
	$1/n$	1.84	1.06
	R^2	0.9998	0.9998
Dubinin-Rudushkevich	q_D	4125.74	2403.55
	B_D	0.3361	0.1798
	E(KJ/mol)	1.22	1.67
	R^2	0.9839	0.9779

Figure 5. Freundlich isotherm plot for copper fungicide detoxification using unmodified maize cob.
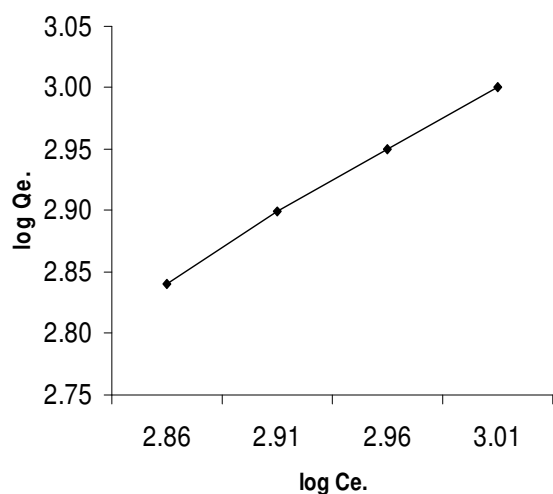

Figure 6. Freudlich isoterm plot for copper fungicide detoxification using modified maize cob.

The plots are shown on Figure 5 for the unmodified maize cob and Figure 6, for the modified maize cob. K_F and n determine the curvature and steepness of the isotherm (Akgerman and Zardkoohi, 1996). The values of n also indicate the affinity of the sorbent towards the biomass. The values of n and K_F as well as their R^2 values are shown also on Table 2.

Examination of the plots suggests that the Freundlich isotherm is a better model than the Langmuir isotherm model for the sorption process. The K_F value of unmodified maize cob (438.53) is greater than that of the modified maize cob (1.584). Also, the $1/n$ value for unmodified (1.84) is greater than that for modified (1.06). These suggest that the modified maize cob had a greater sorption capacity than the unmodified maize cob.

The Dubinin-Radushkevich model was used to estimate the characteristic porosity of the adsorbent and the apparent energy of adsorption. The model is given by the equation below (Horsfall et al., 2004);

$$qe = q_D \exp \left(-B_D[RT \ln(1 + 1/Ce)]^2\right) \qquad (5)$$

Where B_D is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the adsorbent from infinite distance in the solution and q_D is the Dubinin – Radushkevich isotherm constant related to the degree of sorbate sorption by the sorbent surface (Horsfall et al., 2004). The linear form of the equation is given as;

$$\ln qe = \ln q_D – 2B_D RT \ln (1 + 1/Ce) \qquad (6)$$

A plot of ln qe against RTln(1 + 1/Ce) is shown on Figure 7 for the unmodified maize cob and Figure 8 for the modified maize cob. The modified cob gave higher values than the unmodified cob. B_D and q_D were gotten from the slope and intercept of the plots. The apparent energy (E) of adsorption from Dubinin-Radushkevich isotherm model was computed using the relation (Horsfall et al., 2004);
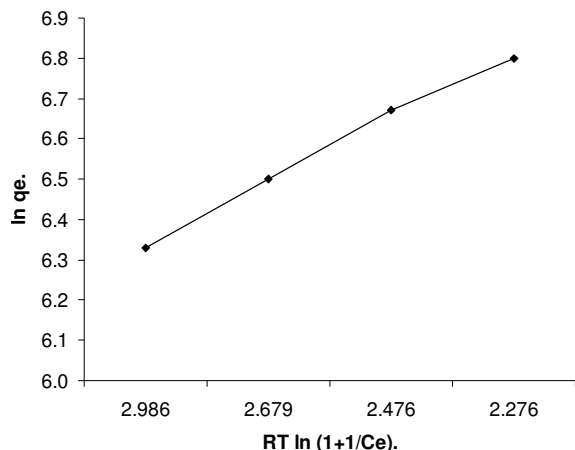
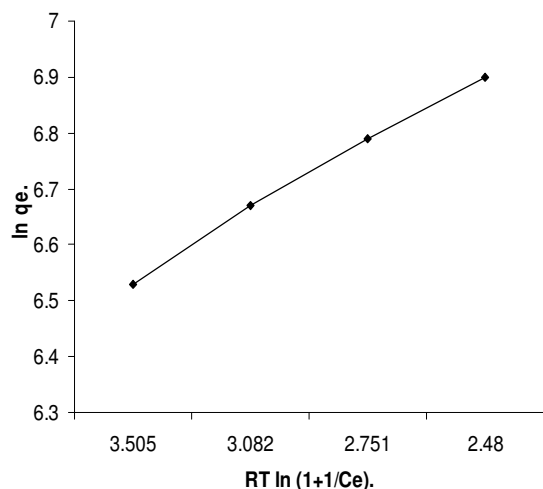**Figure 7.** Dubinin-Rudushkevich isotherm for copper fungicide detoxification using unmodified maize cob.

Figure 8. Dubinnin-Radushkevich isotherm for copper fungicide detoxification using modified maize cob.

$$E = 1/\sqrt{2}B_D \qquad (7)$$

The values of the constants and the R^2 values are shown on Table 2.

The Dubinnin-Radushkevich model is more general than those of the Langmuir and Freundlich (Nestle and Kimmich, 1996). It does not assume an energetically homogenous surface and propose a non homogeneous distribution of sorption sites. In particular, the Dubinin-Radushkevich model assumes that ionic species bind first with the most energetically favourable sites and that multilayer adsorption then occurs. From the results, we can see that the R^2 values are high (0.9839 for unmodified and 0.9779 for modified cob), indicating a good fits. Physiosorption processes usually have adsorption energies less than 40 KJ mol^{-1} and the energies of 1.22 and 1.67 KJ mol^{-1}, indicates physical sorption processes for the adsorption of the copper fungicide on modified and
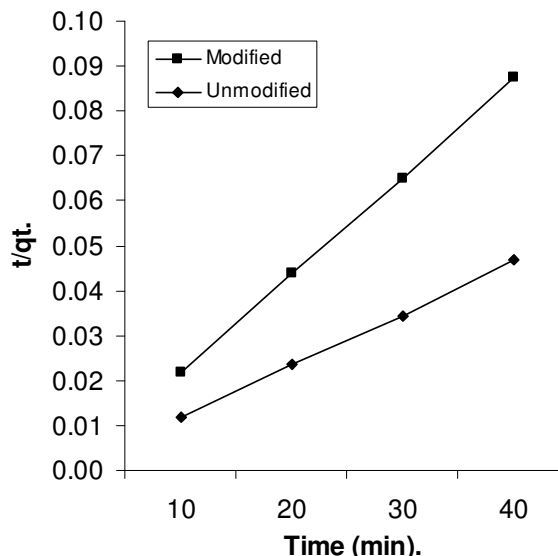

Figure 9. Pseudo-second order rate plot for copper fungicide detoxification using modified and unmodified maize cob.

unmodified maize cob, respectively. Also, Ho et al. (1995) has earlier reported that the typical range of bonding energy for ion-exchange mechanisms is 8-16 KJ mol^{-1}. The very low values in this study (Table 2) indicate ion-exchange mechanism.

Sorption kinetics

The effect of contact times on the copper fungicide detoxification is presented in Figure 2. In an attempt to understand the sorption process more clearly in a batch adsorption process, the linear form of the kinetic rate expression model for a pseudo-second order reaction developed by Ho et al. (1995) was applied to the experimental data. The equation is expressed as

$$t/qt = 1/ho + 1/qe\,(t) \qquad (8)$$

Where qt is the amount of copper fungicide on biomass surface (mg/g) at any time t, qe is the amount of copper fungicide sorbed at equilibrium (mg/g), ho is the initial sorption capacity (mg/min).

The initial sorption rate, ho, as $t \rightarrow 0$ is defined as

$$h = k_2 qe^2 \qquad (9)$$

Where k_2 is the pseudo-second order rate constant (g/mg-min).

The initial sorption rate ho, the equilibrium sorption capacity and the pseudo-second order rate constant k_2, were determined experimentally from the slope and intercept of a plot of t/qt against time (min) shown in Figure 9. The data showed that the sorption process was

Table 3. Pseudo-second order kinetic constants for copper fungicide detoxification using unmodified and modified maize cob.

Adsorbent type	K_2 (g/mg-min)	qe (mg/g)	ho (mg/min)	R^2
Unmodified	6.74×10^{-3}	861.33	5000	0.9998
Modified	2.475×10^{-6}	20000	990.10	0.9998

rapid and that the modified maize cob also has higher values than the unmodified maize cob. The k_2, qe, ho and R^2 values were calculated from the plots and are given in Table 3. We can observe from the table that the unmodi-fied cob had a higher initial rate than the modified. Also the values of the R^2 shows that the pseudo-second order model gave a very good fit to the experimental data. Similar results have also been reported (Demirbas et al., 2004; Gang and Weixing, 1998; Ho et al., 2000; Igwe et al., 2005a).

Intraparticle diffusivity

The adsorptive removal of the copper fungicide is only feasible when there is contact between the maize cob and the Cu(II) ions. Therefore, diffusion precedes adsorp-tion. A number of factors have been known to affect diffusion before adsorption (Findon et al., 1993; Igwe and Abia, 2005). These includes (i) diffusion of the solute from the solution to the film surrounding the particle (ii) diffusion from the film to the particle surface (external diffusion) (iii) diffusion from the surface to the internal sites (surface diffusion or pore diffusion), and (iv) uptake which can involve several mechanisms: physico-chemical sorption, ion-exchange, precipitation or complexation. The first one is bulk diffusion, the second is external mass transfer resistance and the third is intraparticle mass transfer resistance. When intraparticle mass trans-fer resistance becomes the rate limiting step, the mecha-nism of sorption is particle diffusion controlled.

The intraparticle diffusivity was estimated using equa-tions (10) as developed using the linear driving force con-cept by Chanda et al. as reported in our previous work (Igwe and Abia, 2005);

$$\ln (1-\propto) = -kpt \qquad (10)$$

Where $\propto$ (alpha) is the fractional attainment to equilibrium (FATE) given by equation (11), Kp is the rate constant for intraparticle diffusivity.

$$\propto = [M]_t^{n+} / [M]_\infty^{n+} \qquad (11)$$

Where M represents the copper metal and n+ is the char-ge on the ion. This means that alpha is the concentration of the metal ion at any time, t divided by the concen-tration at equilibrium. Using linear regression analysis to model equation (10), the following regression equations were calculated;

$$y = -0.0251 + 1.095 \times 10^{-3}x \qquad (12)$$
$$y = 6.67 \times 10^{-4} + 9.0 \times 10^{-5}x \qquad (13)$$

for unmodified (12) and modified maize cobs (13), res-pectively. The R^2 values are 0.2573 and 0.9823 for un-modified and modified cobs, respectively. Although high R^2 value was obtained for modified cob, their Kp values are negative hence the mechanism of sorption is said to be predominantly film diffusion controlled and the exter-nal mass transfer resistance is the rate limiting step. Thus, the sorption process cannot be described as parti-cle diffusion controlled but film diffusion controlled.

Conclusion

The detoxification of KOCIDE 101, a copper fungicide us-ing EDTA-modified and unmodified maize cob, a cellu-losic material, was studied on the basis of equilibrium sorption isotherm and pseudo-second order rate kinetics. Using the R^2 values, the Freundlich isotherm gave the best fit followed by the Dubinin-Rudushkevich isotherm, and lastly, the Langmuir, isotherm. The experimental data also followed the pseudo-second order rate equation. It is also important to note that the success of this method depends primarily on the cellulosic materials such as maize cob which are capable of adsorbing heavy metal ions from their solution (Ofomaja et al., 2005; Horsfall and Spiff, 2004; Abia et al., 2003) and reagents that form stable complexes with copper may reduce the toxic effect of copper and other metals (Igwe et al., 2005b; Okieimen and Orhorhoro, 1986; Roberts and Rowlands, 1973). Thus EDTA was used for the chemical modification of the maize cob. Also, generally, the method of detoxification employed for pesticide deactivation depends on whether application is to a contaminated area or to some pesticide left over and the chemical composition of the particular pesticide For instance, activated charcoal has been effectively used to deactivated or "tie up" pesticides and other organic contaminants in cases of accidental pesticide spill (Miller and McCarty, 1999). Once the pesticide has been adsorbed onto activated charcoal, it is biologically inactive and cannot cause injury to plant or grasses. It is also beneficial where an herbicide needs to be inactivated for seeding or springing of turf grasses.

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