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Adsorption of Fe^{+3} and Mn^{+2} from Ground Water onto Maize Cobs Using Batch Adsorber and Fixed Bed Column

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Abstract: The removal of iron and manganese from ground water is an important step for producing safe drinking water. A detailed investigation of the sorption of iron and manganese from ground water onto maize cobs is reported. This work deals with determination of adsorption equilibrium isotherms, kinetic, and fixed bed column studies. Results of Freundlich and Langmiur parameters revealed the favorability of maize cobs for adsorption of iron and manganese ions. Kinetic studies were carried out using from ground water samples (El-Mina Governorate, Egypt). From the kinetic studies, a model is proposed to determine the external mass transfer (Ks) which can be correlated by the following equation Ks $= A\ (\mathrm{mass})^B$. where A and B are constants. During the fixed bed column studies, the effect of process variables such as bed height, flow rate, initial concentration, and percentage breakthrough has been investigated. A simplified design method, namely, the bed depth service time (BDST) model has been applied to the experimental data and the results of this analysis are presented. The mechanism of the metal ion sorption on maize cobs was also investigated. Both the calorific values and differential thermal analysis (DTA) data proved that the loaded maize cobs can be used as solid fuel. Pretences of iron and manganese salts catalyze the thermal decomposition reaction toward more flammable gases, which increase their calorific values. The loaded maize cobs are considered a new potential source for energy conversion.

Keywords: Ground water, iron and manganese removal, maize cobs, adsorption equilibrium isotherms, kinetic studies, fired bed column studies

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INTRODUCTION

Ground waters are considered an important source of fresh water resources, particularly in populated areas, where surface water supplies are limited. Ground water has certain advantages over surface water for domestic use, as it usually contains only small amounts of different types of bacteria (unless contaminated by human activity) and it is clear and colorless unless tainted with humic material (1). Contamination of ground water can be arising from domestic and industrial waste waters which are disposed of in various ways, e.g. into the sea, into underground strata or, most commonly into surface waters, may also contaminate ground water (2).

The most common methods of removal of metals include chemical precipitation, reverse osmosis, ion-exchange resins, and adsorption. Precipitation is one of the most traditional treatment methods employed to remove heavy metals. A common hindrance to effective precipitation is the formation of soluble metal complexes with chelating agents. Maintenance of pH throughout the precipitation reaction and subsequent settling is essential, thus slowing down the time for the treatment process and making the process less flexible. Adsorption is considered a simple and cheap operation specially if a low cost adsorbent is available. Recently different low cost adsorbents have been used such as clay (3, 4) and agricultural wastes (5–10).

Three types of adsorbent contacting systems are usually encountered, which are batch, fixed bed, and fluidized bed processes (11). Batch-type processes are usually limited to the treatment of small volumes of effluent, whereas the bed-column systems have the advantage of continuous operation. Fluidized beds for effluent treatment can have high mass-transfer rates but suffer from relatively short residence times, leading to rapid breakthrough. Because fixed bed processes can provide continuous treatment with a long breakthrough time, they are widely used in wastewater treatment processes.

In this paper adsorption of manganese and iron were studied. These metals are present in ground water and prepared as synthetic solutions. The adsorbent used is low cost agricultural waste, namely, maize cobs. Three adsorption systems were used; batch system to determine equilibrium adsorption isotherms to test the favorability of adsorbent used, a kinetic batch adsorber, and the fixed bed adsorber. The last two systems were intended to analyze and identify design correlations for batch and continuous operations. Also the potential use of the loaded adsorbent as fuel was studied.

EXPERIMENTAL

The adsorbent used in this investigation was Egyptian maize cobs. Dried maize cobs were ground and sieved to obtain a particle size in the range of 225 to 300 μm were used without any pre-treatment. The chemical analysis was carried out according to TAPPI standard (12), Table 1.

Table 1. Chemical analysis of maize cobs

Component	Cellulose	Hemicellulose	Lignin	Alcohol /benzene solubility	Ash
Percentage (mass %)	50.4	26.2	16.0	4.3	3.1

Synthetic solutions of ferric chloride and manganese sulfate, both of analytical reagent grades were used during adsorption equilibrium isotherms, kinetic and fixed bed studies. Ground water samples from a well in Abokurkas-El-Minia Governorate, Egypt was also used for the kinetic studies. The samples were agitated well in a standard vessel (13) at constant temperature 22°C and constant speed 800 rpm. The chemical analysis is shown in Table 2. Iron and manganese were analyzed using atomic absorption spectrophotometry (Scan AA4, Thermo-Jorall Ash, USA).

Adsorption equilibria were established by contacting a fixed amount of adsorbent with 50 ml of metal solution (different initial concentrations ranging from 1 ppm to 50 ppm) in sealed glass bottles and the initial pH of the solution was adjusted to 5.5. The bottles were placed on a shaker at room temperature (22 ± 2°C) for three days where equilibrium has been attained. The difference between the initial concentration (C_o) and the equilibrium concentration (C_e) was used to compute the amount of metal removed per unit mass of maize q_e from the solution as follows:

$$q_e = 0.05(C_o - C_e)/M \tag{1}$$

The adsorption column was made of glass tube of 3.0-cm internal diameter and 25 cm height. The column was operated in the up-flow mode.

Table 2. Chemical analysis[a] of ground water from a well at Minia Governorate, Egypt

	pH	TDS			Hardness, $CaCO_3$		
	7.4	750			288		
	Major cation				Major anion		
Ca^{+2}	Mg^{+2}	Na^{+}	K^{+}	HCO_3^{-1}	SO_4^{-2}	Cl^{-1}	
102	60	120	14.4	231.8	87	183	
	Minor cation and anion				Trace element		
NH_4^{+}	NO_3^{-1}	NO_2^{-1}	PO_4^{-3}	Fe^{+3}	Mn^{+2}	Pb^{+2}	Zn^{+2}
0.72	9.2	9.5	0	0.88	0.96	0.05	1.37

[a] All values are in mg/l.

The ground water sample contains different types of synthetic organic chemicals mainly pesticides and herbicides.

An adsorbent-retaining sieve of 65 mesh was fixed in the lower part of the column, and then 2 mm diameter glass balls were placed at the column base (10 cm height) to provide a uniform inlet flow of solution into the column. A weighed amount of adsorbent was tapped into the column and another screen/glass balls arrangement was used at the top of the bed to prevent the disturbance of the bed. The metal salts to be contacted with the adsorbent were weighted out, added to the water tank, and mixed well. The metal salt solution was then pumped vertically upward through the column. A rotameter was calibrated to measure flow rate, which was maintained constant during each experiment. Sample ports were located at five points (5, 10, 15, 20, and 25 cm heights) enabling a series of 10 ml sample syringes to be used to withdraw samples from the center point of the bed for analysis. Samples were taken at time intervals ranging from 15 to 30 min until the metal ion concentration broke through at the top of the bed.

Thermal studies of fresh maize cobs and cobs loaded with iron and manganese, were carried out using a bomb calorimeter (G Cussions LTD, England) for calorific measurements. Differential thermal analysis (DTA) studies were carried out using a CST Stona Permo Model 202 DT analyzer, with temperature programmed at 10°C/min heating rate, from room temperature to 600°C, N_2 with a flow rate of 70 ml/min. The proximate analyses before and after adsorption were carried out according to ASTM (14).

RESULTS AND DISCUSSION

Adsorption Isotherm

The distribution of metal cations, between the adsorbent and metal solution when the system is at an equilibrium, is important to establish the adsorption capacity of the adsorbent for the metal. A plot of equilibrium metal loading (q_e) against residual concentration of metal remaining in solution after equilibrium (C_e) for Mn^{+2} and Fe^{+3} is shown in Fig.1. Adsorption isotherms were similar for the two metals (Mn^{+2} and Fe^{+3}). Maximum adsorption capacities were 2.3 and 2.5 mg metal/g maize cobs, respectively. The percentage removal of metal for initial concentrations between 1 to 40 mg/l was between 79% to 37% in case of Mn^{+2} and 80% to 39% in case of Fe^{+3}. The ability of maize cobs for adsorption of metals can be understood on the basis of chemical composition of maize cobs (Table 1). The structure of maize cob is cellulose based, and the surface of cellulose in contact with water is negatively charged (15). The metal salt will ionize to give the metal cation and will undergo attraction on approaching the anionic maize cob structure. Another species present in considerable quantities in maize cob is lignin. The lignin is mainly derived from alcohol. The hydroxyl and carboxyl groups in lignin will also exert considerable attractive forces on approaching metal cation. Data in Table 1 show that cellulose represents the main component.

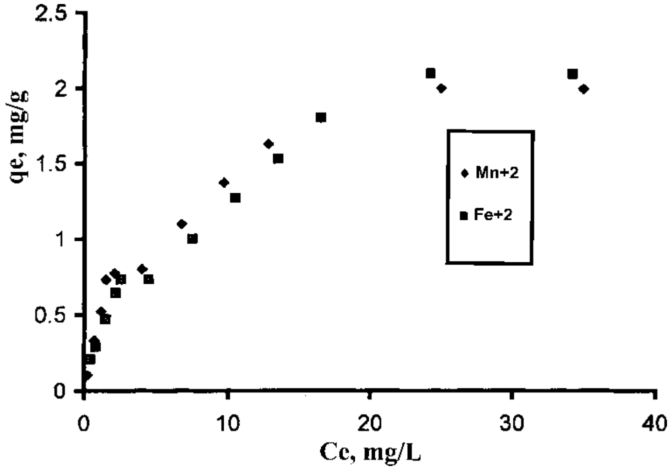

Figure 1. Adsorption isotherms of Fe^{+3} and Mn^{+2} onto maize cobs.

Analysis of adsorption isotherms for the two metals such as given in Fig. 1, is important for developing an equation that can represent the results for design purposes. Of practical use in industry is the Freundlich isotherm model. Thus, the isothermal experimental data were correlated to the Freundlich isotherm equation, i.e:

$$q_e = K_F C_e^{1/n} \tag{2}$$

A logarithmic plot linearizes the equation enabling the exponents "n" and "K_F" to be determined from equation (3):

$$\log q_e = \log K_F + \frac{1}{n} C_e \tag{3}$$

Figure 2 represents the linearized form of the Freundlich model. The constants "K_F" and "n" for the two metals in the different concentration ranges studied were calculated using the least square method (Table 3). The magnitude of the exponent "n" gives indication of the favorability and capacity of the adsorbent system. Values of $n > 1$ represent favorable adsorption (13). Values of "n" are greater than 1, which indicates, within the metal solution concentrations tested in this work, that the metals were favorably adsorbed by maize cobs.

Langmuir parameters were also calculated using the following linearized Langmuir model:

$$q_e = (K_L C_e)/(1 + a_L C_e) \tag{4}$$

Langmuir constants "K_L" and "a_L" were calculated using least square method (Table 3). The values of K_L/a_L are important since they represent

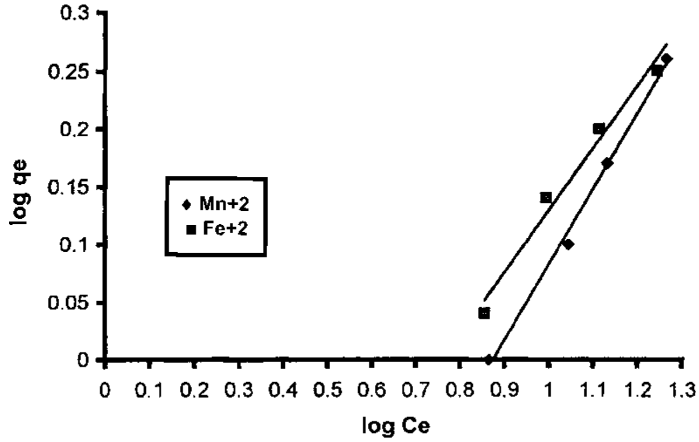

Figure 2. Freundlich isotherm of Fe^{+3} and Mn^{+2} onto maize cobs.

the maximum or monolayer adsorption capacity of maize cobs for a particular metal. The values of the separation factor or equilibrium parameter, R are also included in Table 3. They are between $0 < R < 1$ which indicates that maize cob is favorable adsorbent according to (16).

Kinetic Studies

The kinetic of adsorption in batch system was aimed to determine the rate-limiting step in the adsorption process. The mechanism of solute adsorption onto an adsorbent consists of several steps that may be chronologically described as:

1. Transfer of adsorbate from fluid phase to the particle interface across the boundary layer,
2. Intraparticle diffusion within the particle, and
3. Adsorption of solute onto the inner adsorption sites.

Table 3. Parameters of the Freundlich and Langmuir models for adsorption of Fe^{+3} and Mn^{+2} onto maize cobs

	Langmuir parameters					Freundlich parameters		
Metal ion	K_L l/g	a_L l/mg	$q_{max}{}^a$ mg/g	R^b	r^2	K_F l/g	n	r^2
Fe^{+3}	0.351	0.139	2.53	0.87	0.977	0.104	1.86	0.977
Mn^{+2}	0.473	0.207	2.29	0.82	0.999	0.132	1.53	0.959

[a] $q_{max} = K_L/a_L$.
[b] $R = 1/(1 + a_L C_o)$.

It is assumed that step (iii) is rapid, while the first and the second steps are limiting. The two resulting resistances are represented respectively by the external and intraparticle mass transfer coefficients K_S and K_p. In this analysis external mass transfer, K_s, will only be considered.

Resistance to mass transfer lies mainly in boundary layer film around the adsorbent particles. Consequently, on stirring there was a considerable shear force on the boundary layer film which made this initial resistance to mass transfer layer film fairly low, and hence the intrinsic adsorption rate was rapid until an external surface coverage of iron and manganese salts (adsorbate) had occurred on maize cobs (adsorbent).

In a well-agitated adsorber, it is considered that the concentration of adsorbate and adsorbent particles in the liquid phase is uniform. K_S can be determined from boundary conditions as shown in equation (5):

$$K_s = V/A_p[d(C_t/C_o)/dt]_{t=0} \tag{5}$$

V is the solution volume, and A_p is the total outer surface area of the particle which can be determined from the mass M and density ρ of solid used, and by assuming spherical particles of diameter d_p, that is:

$$A_p = 6M/[\rho dp(1 - \varepsilon p)] \tag{6}$$

Figures 3 and 4 showed the experimental results obtained from a series of contact studies for the adsorption of Fe^{+3} and Mn^{+2} on different masses of maize cobs. The external mass transfer coefficient depends on the driving force per unit area, and in this case, since C_o is constant, increasing the mass of maize cob increases the surface area for adsorption and hence the

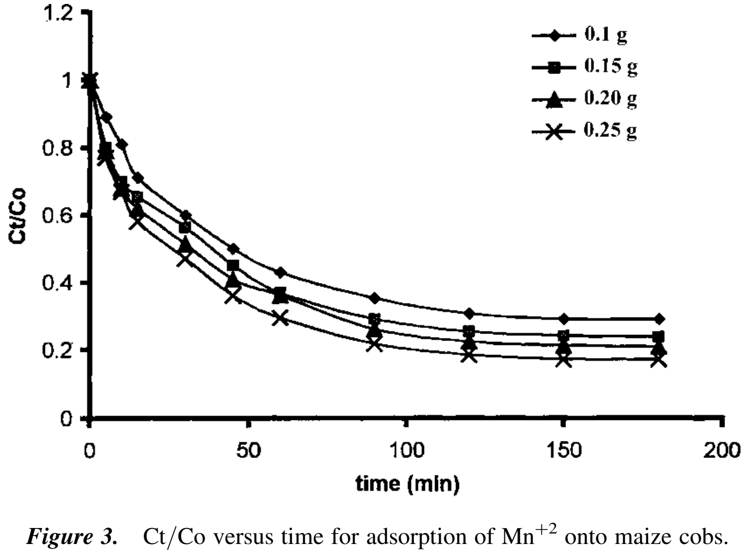

Figure 3. Ct/Co versus time for adsorption of Mn^{+2} onto maize cobs.

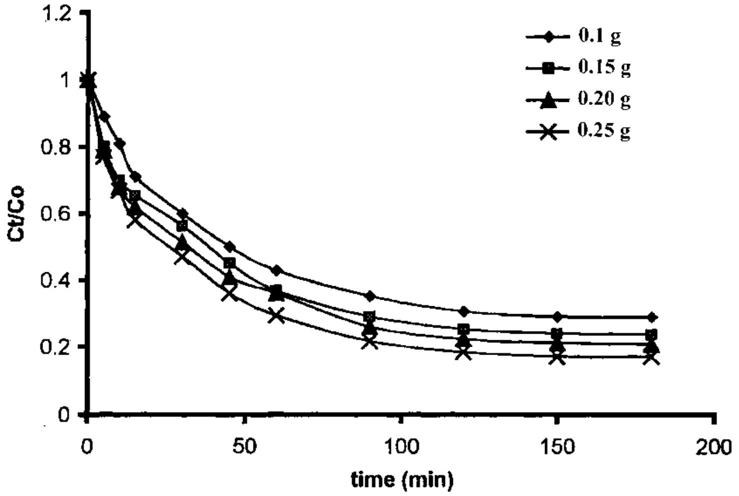

Figure 4. Ct/Co versus time for adsorption of Fe^{+3} onto maize cobs.

rate of metal removal. Because the particle size range is constant the surface area will be directly proportional to the mass of maize cob in the system. In fact, K_s decreases with increasing mass of maize cob. This effect is probably due to the fact that for small masses a small amount of external surface is presented to the metal ions and therefore there is a large driving force from the metal ions per unit surface area of maize cob. Results of kinetic data curves as C_t/C_o versus time revealed that the adsorption rate increases with increasing mass of maize cobs. Results in Table 4 are correlated by:

For adsorption of Mn^{+2}

$$K_s = 1.64\ E\text{-}3M^{0.31} \tag{7}$$

For adsorption of Fe^{+3}

$$K_s = 1.24\ E\text{-}3M^{0.32} \tag{8}$$

Table 4. Kinetic parameter K_s and D_{eff} for adsorption Fe^{+3} and Mn^{+2} onto maize cobs

Mass, g	0.1	0.15	0.2	0.25
Mn^{+2}				
K_s	0.988 E-4	0.888 E-4	0.733 E-4	0.642 E-4
D_{eff}	0.100 E-6	0.100 E-5	0.100 E-6	0.100 E-6
Fe^{+3}				
K_s	0.830 E-3	0.690 E-3	0.560 E-3	0.42 E-3
D_{eff}	0.100 E-6	0.100 E-4	0.100 E-6	0.100 E-6

It is of interest to mention that after treatment of the water from the well with 5.0 g maize cobs/liter ground water, the produced water contains 0.17 ppm Fe^{+3} and 0.20 ppm Mn^{+2} (the permissible limits for Egyptian safe drinking water standard are 0.2 ppm Fe^{+3} and 0.5 ppm Mn^{+2}).

Fixed-bed Column Studies

Adsorption in a column system, where a finite time is required to reach equilibrium, is considered in this section. To design such a system, it is necessary to know how long the adsorbent material will be able to sustain removing a specified amount of impurity from solution before replacement or regeneration is needed; this period of time is called the service time of bed. A simpler approach to fixed-bed adsorbers has been proposed (17) to correlate the service time "t", with the process variables. This model is called the bed depth service time (BDST) model and states that the service time, t, of a column is given by the following equation:

$$t = \frac{N_o}{C_o U} Z - \frac{1}{K_a C_o} \ln\left(\frac{C_o}{C_t} - 1\right) \tag{9}$$

Equation (9) has the form of a straight line:

$$t = m_x Z - C_x \tag{10}$$

where

$$m_x = N_o / C_o U \tag{11}$$

$$C_x = \frac{1}{K_a C_o} \ln\left(\frac{C_o}{C_t} - 1\right) \tag{12}$$

The experimental data were plotted as breakthrough curves in the form of dimensionless concentration, C_t/C_o against time, t (h). The breakthrough curve represents the shape of the metal concentration curve as the solution leaves the bed. Initially, all the metal ion is adsorbed in the bed and the solution leaving the bed has a metal ion concentration $C_t = 0$. However, after a certain length of time, the metal salt begins to appear in the column outlet solution. The metal ion concentration increases until its concentration in the outlet solution is equal to the metal concentration in the inlet solution, i.e. C_o. At this point, the bed is completely saturated with metal and can not adsorb any more. In practice, the flow of solution into the bed is stopped and the bed generated before this saturation point is reached. In fact, definite concentration of metal in the outlet solution is specified and is called the breakthrough concentration, C_b; and at this concentration the flow is stopped and the bed regenerated. It is standard practice to refer to and plot dimensionless concentration that is the concentration at any time, C_t, divided by the initial concentration, C_o. Thus, we have an inlet concentration

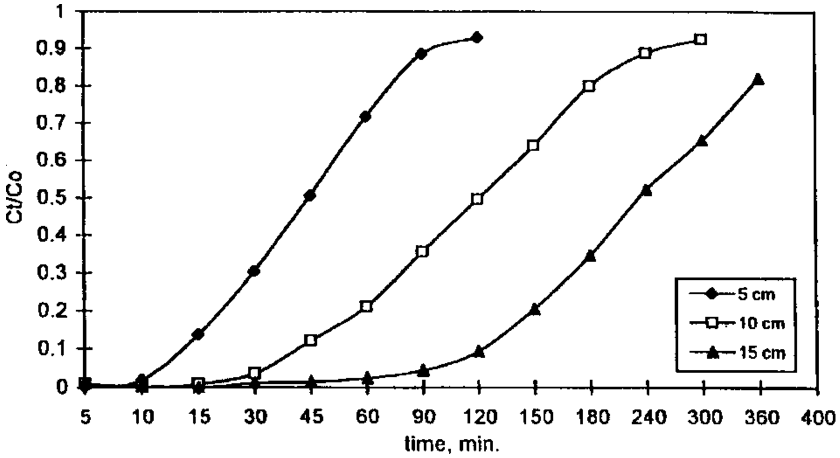

Figure 5. Breakthrough curves for Mn^{+2} onto maize cobs for different bed depths, Q = 5 ml/min, Co = 5 ppm.

$C_o/C_o = 1.0$, a breakthrough concentration C_b/C_o and outlet concentration C_t/C_o. A typical set of results is shown in Figs. 5 and 6 for the adsorption of Fe^{+3} and Mn^{+2} on maize cobs at bed depths 5, 10, and 15 cm with flow rate 5 ml/min and initial concentration 5 mg/l.

Equation (10) is the equation of straight line relating service time (t) to bed depth Z and may used directly to test BDST model. Figure 7 shows how this relationship was confirmed for the adsorption of Fe^{+3} and Mn^{+2} onto maize cobs at flow of 5 ml/min for various bed depths. The experimental data for the adsorption of metal onto maize cobs fit the BDST model well.

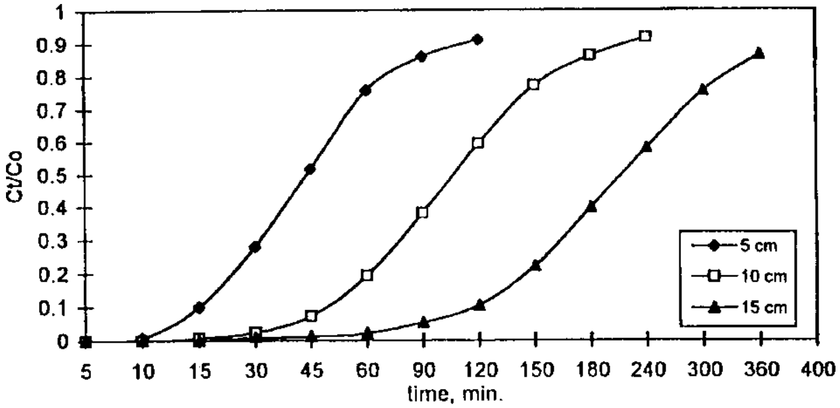

Figure 6. Breakthrough curves for Fe^{+3} onto maize cobs for different bed depths, Q = 5 ml/min, Co = 5 ppm.

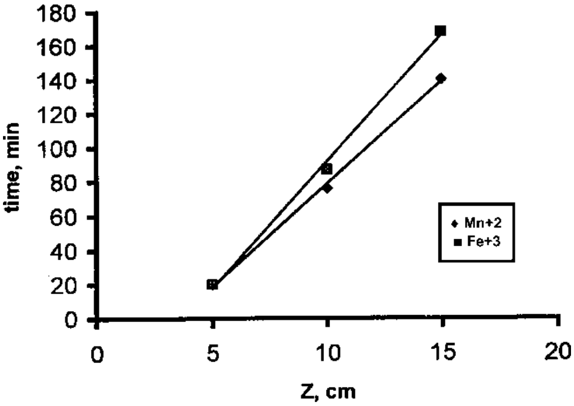

Figure 7. Effect of various bed heights for adsorption of Fe^{+3} and Mn^{+2} onto maize cobs at $Q = 5\,ml/min$, $Co = 5\,ppm$ and 20% breakthrough.

Critical bed depth Z_o (known as theoretical depth) is defined as the minimum depth for obtaining satisfactory effluent at time zero under the test operating conditions (18). Z_o can be found by setting $t = 0$ in the equation (9), the resulting equation is shown in equation (13).

$$Z_0 = \frac{U}{K_a N_0} \ln\left(\frac{C_0}{C_t} - 1\right) \tag{13}$$

The rate parameter K_a (Table 5) shows a significant increase with increasing flow rate which suggests that external film diffusion mass transfer greatly influences the adsorption for the column contact times. The intercept C_x is also shown in Table 5. On examining the data, it can be seen that C_x decreases with increasing flow rate, which is expected, since for a given bed volume, the residence time decreases with increasing flow rates which reduces the volume of effluent treated at the breakthrough. The present results are in agreement with the finding of (17) for adsorption of organic load on carbon.

Table 5. BDST equation constants for the adsorption of Fe^{+3} and Mn^{+2} onto maize cobs at 20% breakthrough

Metal ion	Flow rate (cm^3/min)	Slope m_x (min/cm)	Intercept C_x (min)	Zo (cm)	r^2	No (mg/l)	$K_a\ 10^{-1}$ (l/mg·h)
Fe^{+3}	5	14.49	52.03	3.6	0.995	51.2	319.7
Fe^{+3}	10	11.81	48.83	4.1	0.991	83.5	340.7
Mn^{+2}	5	12.15	41.74	3.4	0.997	42.9	401.1
Mn^{+2}	10	11.76	38.47	3.8	0.996	83.2	437.1

The prime objective of the fixed bed column adsorption system is to reduce the solute concentration, and the degree of reduction in solute concentration is called the percentage breakthrough value. This study represents a selected percentage e.g. 20%, 40%, and 60%, of the inlet metal concentration $C_{o.}$ Figures 8 and 9 show the effect of percentage breakthrough on service time for Fe^{+3} and Mn^{+2} onto maize cobs. The general observation is that little increase in throughput is achieved by varying the percentage breakthrough because the breakthrough curves are steep, consequently, the mass transfer zone is short.

Figure 10 shows the effect of flow rates on the BDST plots. Twenty-percent breakthrough was chosen as a medium value to characterize the performance of fixed bed adsorber. The data imply that increasing the flow rate reduces the volume of metal effluent treated at the break point.

The linear velocity (U) is proportional to the metal solution flow rate [Q (cm^3/min)] since the cross-sectional column area was constant in all experimental runs. Therefore, ratios of (U) are equal to flow rate ratios as given in the following relationship:

$$U_2/U_1 = Q_2/Q_1 \tag{14}$$

If design data are required for a change in volumetric flow rate of solution to the adsorption system, then to calculate new flow rates:

$$m'_x = m_x(Q_1/Q_2) \tag{15}$$

Figure 10 shows the BDST results obtained by calculations (dotted lines) and these are compared with the experimental data (solid lines). The theoretical Eqs. (14) and (15) are in good agreement with the experimental results at high flow rates. Data in Fig. 10 can be used to scale up laboratory tests using

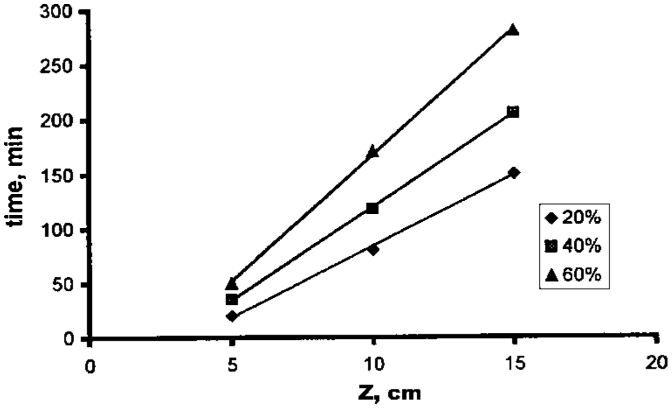

Figure 8. Effect of percentage breakthrough by BDST model for Mn^{+2} onto maize cobs, Co = 5 ppm.

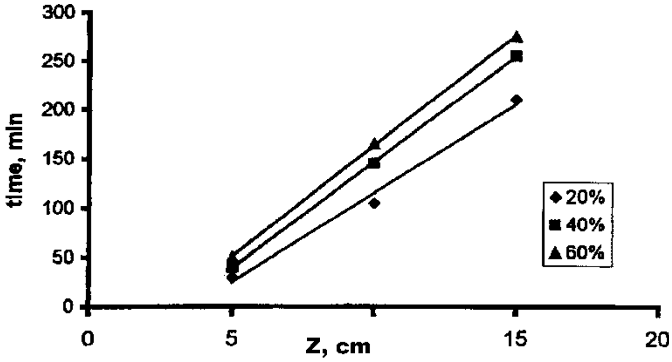

Figure 9. Effect of percentage breakthrough by BDST model for Fe^{+3} onto maize cobs, Co = 5 ppm, Q = 5 ml/min.

flow rates without running the test, this can be seen by the flow rate 15 ml/min shown as dotted line. However, it is worth noting that for very large variations in the flow rates, prediction will be less precise because in actual cases the intercepts change with changes in flow rates:

Thermal Analysis Studies

Due to the low cost of the agricultural residues, it was previously recommended (19) to use the exhausted agricultural adsorbent as solid fuel instead of

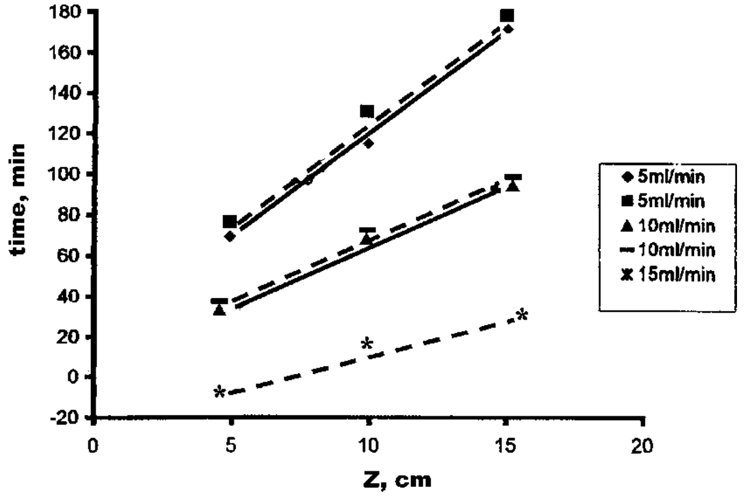

Figure 10. Percentage breakthrough line by BDST model for flow rate of Fe^{+3} onto maize cobs, Co = 5 ppm, 20% breakthrough.

Table 6. Proximate and thermal analysis of maize cobs before and after adsorption of Fe^{+3} and Mn^{+2}

	Maize cobs	Ad. of Mn+2 on (1) Maize cobs	Ad. of Fe+3 on (1) Maize cobs
Proximate analysis			
Volatile matter, %	82.61	87.31	88.61
Fixed carbon, %	14.34	10.01	9.11
Ash, %	3.05	2.68	2.28
Calorific Value, kJ/kg	18443	17807	18615
DTA analysis			
T-max; °C:			
Volatile Stage	328	332	336
Carbonize stage	440	420	432
T-range, °C:			
Volatile Stage	266–348	292–344	300–380
Carbonize stage	348–490	344–480	380–470

Ad· = Adsorption.

regenerating the residue. Thermal studies on maize cobs before and after adsorption were carried out, and the results are shown in Table 6 and Fig. 11.

DTA of maize cobs before and after adsorption is shown in Fig. 11. The results showed the presence of two exothermic peaks for the three samples. The first peak is due to evolution of combustible volatile matter and the

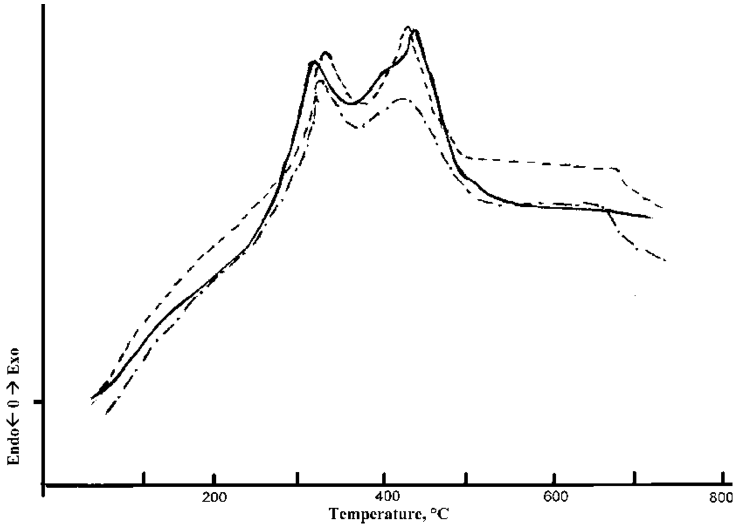

Figure 11. DTA Curves for maize cobs (—), loaded with Fe^{+3} (---) and loaded with Mn^{+2} (---).

second peak is due to formation of char (carbonaceous materials) (20–25). Results in Table 6 indicate that, the calorific values of the loaded maize cobs were improved due to the presence of the inorganic salts. Previous studies on the effect of inorganic salts on the thermal behavior of wood and agricultural residues indicated their catalytic effect on the thermal degradation with more volatiles and less char produced (20–22). The increase of calorific values of the loaded maize cobs is due to the increase of volatile matter as shown in Table 6. The volatile matter is increased at the expense of the fixed carbon. Studying characteristic feature of the DTA peaks Fig 11 support this finding. The first exothermic peaks indicate the evolution of volatile matter with increase in T_{max} as the volatile matter increased (Table 6), the second peak is due to the formation the carbonaceous matter (fixed carbon).

In other words, the addition of inorganic salts (after adsorption operation) to maize cobs may catalyze the decomposition reaction toward the formation of flammable gases more than the production of carbonaceous matter. The increase in calorific values also confirms the suggested mechanism, which relates the addition of iron and manganese salts to the production of flammable gasses. Therefore, the loaded maize cobs are considered an alternative source for energy conversion.

CONCLUSION

The experimental results showed that maize cobs could remove up to 81% of iron and up to 79% of manganese salts from ground water, after 100-min contact time.

The high adsorbance capacity of maize cobs for metal removal is a result of them being aligno-cellulosic material with a large number and array of different functional oxygen groups that have negative charge. The adsorption isotherms have been determined and the data were analyzed according to Langmuir and Freundlich models. The values of separation factor “R” and the Freundlich constant “n” indicate that the metal-maize cob system showed favorable adsorption, that is, $0 < R < 1$ and $n > 1$.

External mass transfer coefficients were calculated from kinetic studies, and data were correlated with K_s as function of mass of maize cobs. The fixed bed column studies showed that maize cobs remove the metal ions effectively. The effect of the column operating parameters, such as flow rate, bed height and initial concentration, can be predicted by the BDST model.

There is no need for regeneration of the loaded maize cobs, they can be used as fuel since the presence of metal ions improve their thermal characteristics toward formation of more flammable gases, which leads to higher calorific value.

NOMENCLATURE

A_P	Outer surface area of particle, m^2
a_L	Constant in Langmuir isotherm, l/mg
C_b	Break through point dye concentration, mg/l
C_o	Initial concentration, mg/l
C_e	Equilibrium concentration, mg/l
C_t	Dye concentration at time, t, mg/l
C_X	Intercept in equation 12
d_p	Mean particle diameter, (μm)
D_{eff}	Effective diffusivity coefficient, cm^2/s
K_a	Rate parameter of bed, l/mg · h
K_L	Langmuir parameter, l/g
K_F	Constant in Freundlich isotherm, l/g
K_p	Intraparticle diffusion-rate parameter, mg metal/g maize cob/$min^{0.5}$
K_S	External mass transfer coefficient, cm/s
m_x	Gradient in equation 10
M	Mass, g
n	Constant in Freundlich isotherm
N_o	Volumetric sorption capacity of bed, mg/l
q_e	Equilibrium metal concentration, mg/g
Q	Air flow rate, cm^3/s
r^2	Linear correlation coefficient
t	Bed operating time, min
U	Linear solution velocity, m/h
Z	Bed depth of clay column, m
$\rho_{s,}$	Density of solid, g/cm^3
εp	Particle voidage

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