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ORIGINAL ARTICLE

Comparative Evaluation of Cadmium Ion Uptake byWastes Generated from *Zea mays*

Chidi Edbert Duru

Surface Chemistry and Environmental Technology (SCENT) Research Unit, Department of Chemistry, Imo State University, Owerri, PMB 2000, Imo State, Nigeria

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KEYWORDS

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ABSTRACT: The removal of cadmium ions from aqueous solution by *Zea mays* husk (HK), stalk (SK), cob (CB) and seed chaff (SC) which are wastes generated after harvesting or processing this cereal were studied and compared. Batch adsorption studies were utilized to decide the impact of different parameters on the process. Cadmium ion uptake by the adsorbents increased with increase in pH from 3 – 6, with HK and CB showing a steady increase as pH changed. The removal efficiency of all the adsorbents increased with adsorbent dose. However, after 0.4 g load of adsorbent, the removal efficiency of SC became independent of adsorbent load. The maximum adsorption capacity of HK, SK and CB was attained in 12 minutes while SC reached this point in 9 minutes. The adsorption equilibrium data for all the adsorbents fitted well in the Freundlich isotherm model. The adsorption intensities of all the adsorbents from this model were greater than 1, and indicated that metal ion adsorption by these adsorbents were favourable physical processes. The rate of cadmium ion adsorption onto the adsorbents was better explained by the pseudo second-order kinetic model. The calculated equilibrium adsorption capacity of HK (16.36 mg/g) and SK (13.51 mg/g) showed that they had potentials for commercial application in the remediation of cadmium ion polluted water.

INTRODUCTION

Global industrialization has brought about improvement in the standard of living, but at the same time resulted in the production of environmental pollutants at unsustainable levels. These pollutants which are both organic and inorganic in form are difficult to dispose and most times persistent in the environment with adverse impact on health [1, 2]. The introduction of toxic heavy metals like chromium, lead, arsenic, nickel, mercury and cadmium into water bodies and soil by industrial production activities has jeopardized the survival of flora and fauna in these parts of the ecosystem [3 - 6]. Due to their toxic effects, soil and water bodies have been made unproductive and completely abandoned.

Cadmium is a heavy metal found in the earth's crust along with other heavy metals like zinc, lead, nickel and copper. It is used by many industries in the colouring of glass, production of alloys, production of pigments, plating of steel, production of batteries and stabilizing plastics. Waste materials containing cadmium stream from these industries and end up in soil polluting both soil and surface water within the giving area [7]. These wastes come in contact with humans either byinhalation or ingestion. Health effects of the accumulation of cadmium in human organs includes infertility, bone fracture, diarrhea and stomach pains, psychological disorders, damage to the central nervous system, reproductive failure, etc [8].

*Corresponding author: chidiedbertduru@gmail.com (Ch. E. Duru)
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The use of cheap and ecofriendly remediation methods in the treatment of heavy metal polluted water has attracted a lot of research attention in the past and recent times [9-11]. Various biomass wastes in their natural or modified forms have been utilized for heavy metal removal from water [11-13]. *Zea mays* is a cereal grown in many parts of the world with many tons of biomass waste produced from it after harvest [14]. This crop was at one time an annual crop but has been engineered to become a biannual plant. Itswasteshave shown a lot of potentials in the adsorption of different heavy metals from aqueous solutions [15- 17].The kinetics of cadmium ion removal from aqueous solutions by adsorption onto powdered corn cobs was studied by Ismail et al. [18]. The adsorption capacity of this biomass from the pseudo-second order kinetic model at 25 ^{o}C was obtained as 18.15 mg/g. The uptake of zinc, cadmium and manganese ions by adsorption onto maize stalks was studied by Jagung [19]. He found the adsorption capacity for this biomass to be 18.05 mg/g. Reports on the adsorption of cadmium ions from aqueous solution by *Z. mays*husk and seed chaff in their natural forms are either not available in literature or dearth.

In many rural communities in Africa and other continents, water pollution by toxic heavy metals has remained a great challenge and treatment facilitiesare dearth. The adsorption of these metals using plant biomass remains the only available, promisingand affordable means of obtaining treated water for domestic purposes in these areas. This paper evaluated and compared the adsorptive potentials of *Z. mays*husk, stalk, cob and seed chaff in the uptake of cadmium ions from aqueous solution, to determine the most viable part to be applied in treating water polluted by this metal.

MATERIALS AND METHODS

Adsorbent Collection and Preparation

Z. mays seeds (genus Oba super II) were obtained from the National Agriculture Food Council, Umudike, Abia State Nigeria and planted. At maturity, the husk (HK), stalk (SK) and cob (CB) were collected, completely washed with faucet water and afterward rewashed with deionized water. The seeds were crushed using an electric blender. The paste was poured into a nylon sieve, washed repeatedlyto remove all the starch from the kernel and the seed chaff (SC) residue was collected. These products were sun dried for five days and then oven dried at 100 ^{o}C for 3 hours. An electric grinder was used to pulverize the biomass materials and the power of each sieved to particle size of 30 mesh using standard sieves[20]. The powdered *Z. mays* parts were then stored in a dessicator (Figure 1).

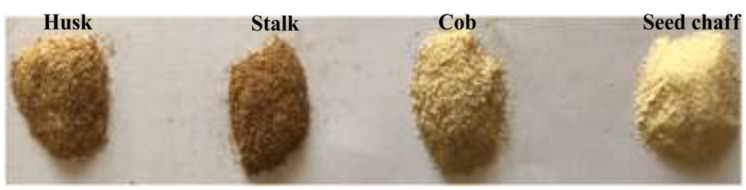

Figure 1. Powdered *Z. mays* parts used in this study

Preparation of Metal Solutions

Chemicals of analytical reagent grade were utilized all through the study and were prepared with deionized water. Stock solution of the metal was prepared in distilled water using suitable amounts of cadmium (II) nitrate, $Cd(NO_3)_2.4H_2O$ (M.W: 308.48 g/mol; Assay: 98 %, Sigma-Aldrich). Working standards were prepared by progressively diluting the stock solution with distilled water.

Experimental Procedure

Adsorption studies

Batch adsorption process was used throughout and was done in a thermostatic water bath shaker set at 30 ^{o}C. 0.5 g of each adsorbent was transferred into a250 mL Erlenmeyer flasks with 100 mL solution of metal ions of desired concentration. The samples were agitated on a shaker water bath for 15 minutes and the liquid phase was taken out and filtered using 0.45 μm membrane filters (Millipore

Corporation, USA). The final concentration of metal ions in the filtrates for each adsorbent were analyzed using a fast sequential flame atomic absorption spectrometer (FAAS), model 240FS AA (Agilent Technologies, USA). The percentage removal of cadmium ions from aqueous solution (% r) at a given time *t*, was calculated from Eqt. 1 and the concentration of metal ionadsorbed at equilibrium per unit mass of each adsorbent was calculated using Eqt. 2.

$$\% \, r = \frac{(C_o - C_t)}{C_o} \tag{1}$$

$$q_e = \frac{(C_o - C_e).V}{m} \tag{2}$$

WhereC_o is the initial concentration of metal (mg/L), C_t is the concentration of the metal at time *t*, C_e is the equilibrium concentration of the adsorbate (mg/L) in solution,q_e is the quantity of metal adsorbed at equilibrium by the adsorbent (mg/g), *V* is the volume of the solution (L) and *m* is the mass of adsorbent (g).

Effect of pH

The impact of pH on the adsorption of cadmium by the adsorbents was determined in 100 mL of test solutions containing 100 mg/L of cadmium ions at different pH (3-6). Adjustment of pH to the desired values was done using 1 M HCl or 1 M NaOH before the addition of each adsorbent. pH measurements were done using a Checker plus pH tester by HANNA. 0.5 g of each adsorbent was added to the test solution at a given pH and the mixture agitated for 15 min. The concentrations of cadmium ions in the solutions after this period were measured.

Effect of Adsorbent Dose

The effect of dose of adsorbent on the adsorption of cadmium ions by each adsorbent was studied using different biomass concentrations (0.2, 0.4, 0.6 and 0.8 g) in 100 mL of 100 mg/L of metal ions at pH 6. Each adsorbent of a given weight was mixed with the metal solution and the mixture agitated for 15 min. after which theconcentration of cadmium ions in the solutions was determined.

Effect of Contact Time

The effect of contact time on the adsorption of cadmium ions by the adsorbents was determined at 3 minutes intervals for 15 minutes, using 100 mg/L of cadmium ion solution at pH 6. Adsorbent of weight 0.5 g was transferred into100 mL of the metal solution in each reactor and agitated. The reactors were withdrawn at the specified time intervals and the concentration of metal ions at a given time determined.

Effect of Initial Metal Ion Concentration

The adsorption of cadmium ions at different initial concentrations (100, 50, 25 and 12.5 mg/L)in solutions of pH 6 were studied. Adsorbent of weight 0.5 g was added into100 mL solution of metal ion at a given concentration and agitated for 15 min. After this time, an aliquot was collected from each flask, filtered and the metal ion concentration determined.

Modeling of Adsorption Data

The data from the study were used to model the adsorption isotherm and kinetic parameters. The adsorption isotherms were evaluated using the Langmuir (Eqt. 3), Freundlich (Eqt. 4) and Elovich(Eqt. 5) models[21, 22].

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{3}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

$$\ln \frac{q_e}{C_e} = \ln K_E q_m - \frac{q_e}{q_m} \tag{5}$$

Where C_e (mg/L) is equilibrium concentration of metal ions, q_m (mg/g) is maximum adsorption capacity of the adsorbent, K (L/mg) is Langmuir constant, q_e (mg/g) is adsorption capacity at equilibrium, C_o (mg/L) is initial concentration of metal ions, K_F ($mg^{1-\frac{1}{n}} L^{\frac{1}{n}} g^{-1}$) is relative adsorption capacity of the adsorbent, n is adsorption intensity and K_E (L/mg) is Elovich equilibrium constant.

The pseudo-first order (Eqt. 6) and pseudo-second order (Eqt. 7) rate equations were used to model the adsorption kinetics of cadmium ions onto the adsorbents [23, 24, 25].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

Where t (min) is the contact time, k_1 (min^{-1}) is the pseudo-first order rate constant, q_t (mg/g) is adsorption capacity at time t, q_e (mg/g) is adsorption capacity at equilibrium and k_2 (g/mg.min) is the pseudo-second order rate constant.

RESULTS AND DISCUSSION

Effect of pH

The impact of pH on the adsorption of cadmium ions onto HK, SK, CB and SC was determined at pH 3 – 6 because precipitation of cadmium ions from the solution started at pH ≥7. The dependence of the adsorption capacities of the biomass materials on solution pH is shown in Figure 2.

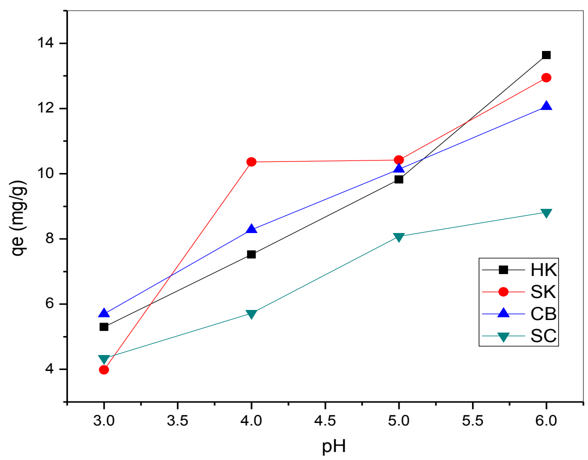

Figure 2. Effect of pH on cadmium ion uptake by *Z. mays* wastes

The equilibrium adsorption capacities of all the biomass materials increased with increase in pH. A consistent increase in adsorption capacity with increase in pH was observed for HK and CB. Adsorption capacity of SK increased as pH changed from 3 – 4,was almost constant between 4 –5 and continued to increase after this point. Though the adsorption capacity of SC increased as the pH increased,its capacity to take up cadmium ions under this condition was the least. The surface potentials of the biomass materials were positively charged at lower pH values as a result of their protonation by the high concentration of H^+ and H_3O^+ ions in the solution [26]. These charges reduced the attraction of the metal ions in the solution by the adsorbent surfaces. However, increase in pH created more negatively charged surfaces on the adsorbents, which facilitated metal ion uptake. The removal efficiency of HK, SK and CB increased with increase in dose of adsorbent. Metal removal efficiency for SC increased between 0.2 – 0.4 g, and remained almost constant up to 0.8 g of adsorbent. This observation could be as a result of the overlap of adsorption sites due to overcrowding of adsorbent particles, making them inaccessible by the metal ions [27].

Effect of adsorbent dose

The effect of different doses of adsorbent on the removal of cadmium ions from aqueous solution is shown in Figure 3.

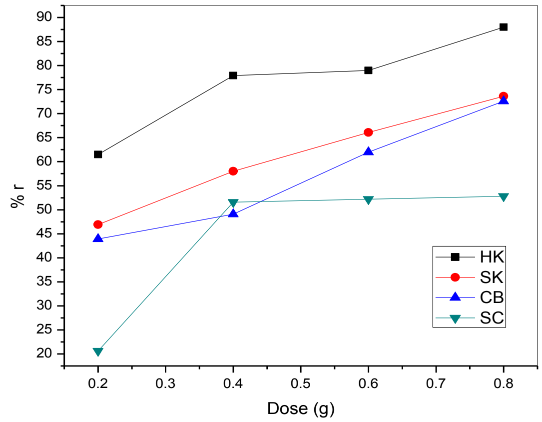

Figure 3. Effect of adsorbent dose on cadmium ion uptake by *Z. mays* wastes.

Effect of Contact Time

The dependence of removal efficiency of the different adsorbents on contact time was used to determined the time at which maximum adsorption of cadmium ions was reached on the adsorbent surfaces (Figure 4).

Maximum adsorption capacity of HK, SK and CB was reached in about 12 minutes, while it took SC about 9 minutes to attain this point. This observation is an indication that SC had less number of available adsorption sites for cadmium ions relative to the other adsorbents studied.

Effect of Initial Metal Ion Concentration

Figure 5 shows the impact of initial cadmium ion concentration on the equilibrium adsorption capacity of the biomass materials.

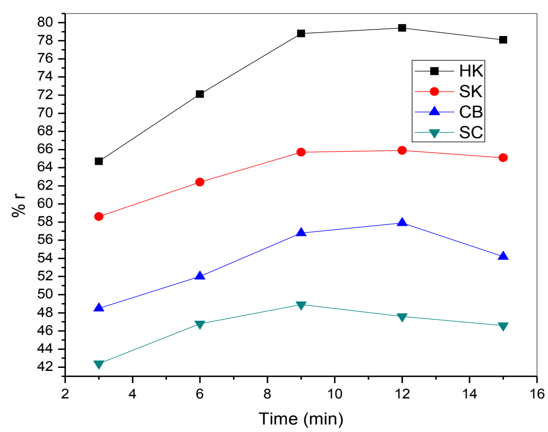

Figure 4. Effect of contact time on cadmium ions uptake by *Z. mays* wastes

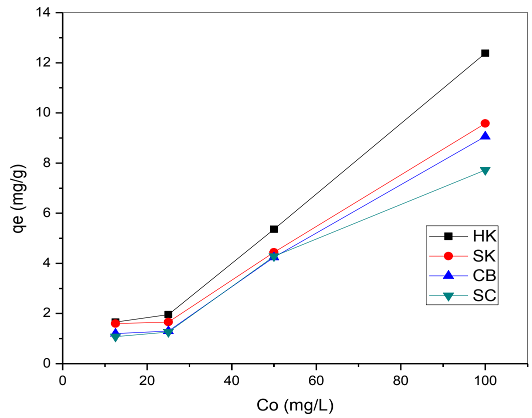

Figure 5. Effect of initial metal ion concentration on uptake of cadmium ions by*Z. mays* wastes

The equilibrium adsorption capacity of all the adsorbents showed a steady increase in metal ion adsorption after 25 mg/L of cadmium ions.The adsorption capacity of HK increased sharply and rapidly with increase in metal ion concentration. A slight decline in the linearity of adsorption of metal ions by SC after 50 mg/L was observed. This suggested that the effect of cadmium ion concentration on the adsorption capacity of this adsorbent became less significant as the initial metal ion concentration increased.

Modeling of Adsorption Data

Isotherm Studies

The equilibrium adsorption datafrom the study were tested on the Langmuir, Freundlich and Elovichisotherm models. The mathematical parameters from thesemodels are summarized in Table 1.

The linear regression correlation coefficient (R^2) for all the adsorbents showed that their adsorption data were best fitted in the Freundlich model. The Freundlich constant $K_F$which is an approximate indication of the adsorption capacity and 1/n which is a function of the adsorption force [28] are shown in Table 2.

Table 1. Mathematical parameters from the isotherm models

Adsorbent	*Langmuir*			*Freundlich*			*Elovich*		
	R^2	**Intercept**	**Slope**	**R^2**	**Intercept**	**Slope**	**R^2**	**Intercept**	**Slope**
HK	–0.4829	4.779	–0.018	0.9266	–0.379	0.832	–0.4263	–1.524	0.023
SK	–0.4778	6.935	–0.015	0.8729	–0.676	0.636	–0.2601	–1.269	–0.046
CB	–0.4250	9.336	–0.045	0.8752	–1.089	0.972	–0.1659	–0.924	–0.112
SC	–0.4684	9.718	–0.024	0.7826	–1.844	0.769	–0.7690	–1.522	–0.060

Table 2. Freundlich isotherm constants

Adsorbent	$K_F(mg^{1-\frac{1}{n}}L^{\frac{1}{n}}g^{-1})$	***n***
HK	0.68	1.20
SK	0.51	1.57
CB	0.34	1.02
SC	0.16	1.30

The value of n gives an indication of the extent of non-linearity between solution concentration and adsorption as follows: if n = 1, the adsorption is linear; if n > 1, the adsorption is a favourable physical process and if n < 1, the adsorption is by a chemical process [29]. The value of n for all the adsorbents was greater than 1 and showed that cadmium ion adsorption onto the adsorbents was a favourable physical process. This implied that uptake of metal ions occurred by multilayer adsorption on the heterogeneous surface of the biomass with an infinite increase in the quantity of ions adsorbed as initial metal ion concentration increased [30]. Since the uptake of cadmium ions onto the adsorbents was by physisorption which requires minimal energy to occur, desorption of the metals ions from the adsorbent surfaces would be an energy efficient process. This makes them promising recyclable materials for large scale industrial use in the treatment of cadmium ion polluted water.The K_F values suggested that SK and HK had the highest adsorption capacity of the adsorbents studied.

Kinetic Studies

Data obtained from the rate studies were tested on the pseudo-first order and pseudo-second order kinetic models. Mathematical parameters for the plots of In ($q_e - q_t$) vs t and t/qt vs t for pseudo-first order and pseudo-second order equations respectively are shown in Table 3.

The pseudo-second order model gave a better fitting for the data (Figure 6). The kinetic parameters for the pseudo-second order rate model are summarized in Table 4. The experimental adsorption capacity ($q_{e(exp)}$) of the adsorbents were very similar to those obtained from the models ($q_{e(cal)}$).

The adsorption capacities of the adsorbents increased in the order HK > SK > CB > SC. The adsorption of cadmium ions from aqueous solutions by different plant biomass have been reported previously by other researchers (Table 5).

Table 3. Mathematical parameters from the kinetic models.

Adsorbent	Pseudo first-order			Pseudo second-order		
	R^2	Intercept	Slope	R^2	Intercept	Slope
HK	0.9415	2.48	–0.406	0.9970	0.032	0.061
SK	0.9034	1.48	–0.332	0.9987	0.033	0.074
CB	0.9252	1.85	–0.351	0.9925	0.039	0.087
SC	0.1694	0.51	–0.195	0.9966	0.014	0.105

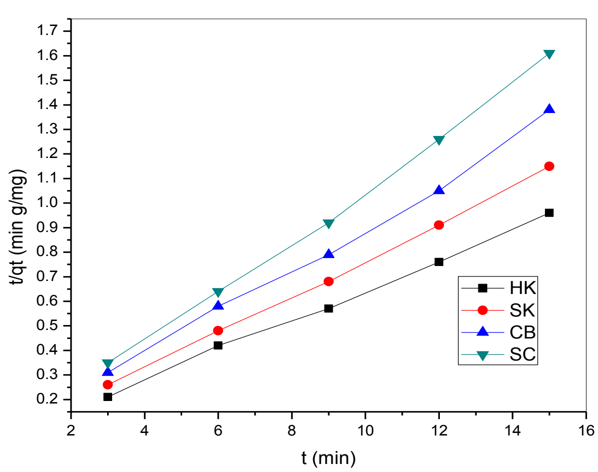

Figure 6. Pseudo-second order kinetic plot for the adsorbents.

Table 4. Pseudo-second order rate constants for the adsorbents.

Adsorbent	Parameter		
	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	k_2 (g/mg.min)
HK	15.98	16.39	0.116
SK	13.28	13.51	0.175
CB	11.56	11.49	0.194
SC	9.87	9.52	0.776

Table 5. Literature reports on plant biomass adsorbents for cadmium ion uptake from aqueous solution.

Biomass	q_e (mg/g)	Reference
Mango leaves	4.08	[31]
Maize stalk	18.05	[19]
Corn cob	18.15	[18]
Cassava tuber bark waste	26.3	[32]
Coffee husk	6.90	[33]
Cocoa shell	4.94	[34]
Tea wastes	11.30	[35]
Peanut hulls	5.96	[36]
Rice husk	8.58	[37]
HK	16.39	This study
SK	13.51	This study
CB	11.49	This study
SC	9.52	This study

Comparison of their results and the present study showed that *Z. mays* husk and stalk are promising biosorbent materials for the treatment of cadmium ion pollution in aqueous systems.The relative rate at which cadmium ions occupied the surfaces of the adsorbents per minute as indicated by the rate constant k_2 was in the order 6.7, 1.7, 1.5 and 1. This suggested that the cadmium ion adsorption sites for cadmium ions on SC were fewer and this was responsible for the low adsorption capacity observed for this biomass.

CONCLUSIONS

The cadmium ion adsorption potentials of *Z. mays* husk, stalk, cob and seed chaff obtained from the same species of the plant was investigated and compared. The uptake of cadmium ions by the adsorbents increased with increase in pH, adsorbent dose, contact time and initial metal ion concentration. The experimental data for all the adsorbents fitted well in the Freundlich isotherm model, which indicated that cadmium ion uptake occurred by multilayer adsorption on a heterogeneous surface. The pseudo-second order model explained the rate of cadmium ion adsorption by all the adsorbents. The equilibrium adsorption capacities of the adsorbents obtained from this model were similar to those obtained from the adsorption experiments and showed that the husk and stalk were promising adsorbents for large scale treatment of cadmium ion polluted water.

CONFLICT OF INTERESTS

The author states that there is no conflict of interest.

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