Adsorptive Removal of Cd²⁺ and Zn² From Aqueous System by BSG

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Abstract

The potential utilization of Brewer's Spent Grain (BSG) was investigated in the removal of Cadmium and Zinc from aqueous system. Batch sorption process assessment of the effects of process variables showed that pH, initial metal ion concentration and dosage amount affect the sorption and uptake of Cd and Zn ions by BSG. Analysis of the sorption process using different kinetic models showed that the pseudo first order kinetic models gave poor descriptions of the process for Zn was $r^2 = 0.5268$ but a good one for Cd at $r^2 = 0.9618$ while the pseudo second order kinetic model gave a good description of the process for both metal ions (r^2 >0.98). The Pseudo second order rate constant obtained for Zn (1.0812mgg⁻¹min⁻¹) is than that for Cd (0.17mgg⁻¹min⁻¹). Equilibrium isotherm analysis of the sorption process data showed that the Langmuir isotherm gave a better description of the process than the Freundlich for Cd while both Freundlich and Langmuir fitted very well for Zn sorption by BSG. The results of the studies indicate that the metal ions were favourably adsorbed onto the adsorbent with a removal efficiency of 94.46% for Zn and 77.81% for Cd.

Keywords: Brewer's Spent Grain, cadmium, zinc, sorption, Isotherm, Kinetics.

Introduction

Environmental contamination by toxic heavy metals is a serious problem due to its incremental accumulation in the food chain and continued persistence in the ecosystem (Jain et al., 2010, Sousa et al., 2010). Heavy metals are widely used in industries such as metal finishing, electroplating, mining and petroleum refining. Discharge of industrial wastewater without prior treatment adversely affects the ecosystem as a result of being nonbiodegradable (Nadeem et al., 2009). Numerous treatments and abatement techniques have been employed to remediate heavy metals in wastewater including electro-floatation, precipitation, ion-exchange, membrane and adsorption. Precipitation method although very effective however produces large volume of sludge that requires further treatment. Adsorption in comparison with other methods appeared to be preferable in terms of its efficiency and ease with which it can be applied in its application in the removal of heavy metals in wastewater (Bailey et al., 1999). Plant wastes, agricultural and industrial by-products have been utilized as cheap and unconventional adsorbents for heavy metals from aqueous solutions (Li et al., 2009). Spent grains which are the primary mixture of grain and grain husks whose major constituents are cellulose, hemicellulose and lignin that has had the majority of its sugars extracted, are the by-products of mashing process in brewery following different separation strategies, the amount of spent grain generated could be about 85% of the total by-products. Spent grain has many applications because of its high content of protein and fiber. Applications range from production of bio-plastics and bio-fuel, to agricultural uses as animal feed and compost material, to reuse as food for people. One of the promising by-products that have drawn the attention of researchers is the Brewer's Spent Grains (BSG). It has been found to be a potentially valuable resource for industrial exploitation due to its high availability and low cost (Robertson et al., 2010). The variation in percentage composition of the components was attributable to the variety of the grains used; harvest time, malting and mashing conditions and the quality and type of adjuncts used during the process (Robertson et al., 2010). Reactive functional groups such as hydroxyl, amine and carboxyl that can be activated in BSG are responsible for the binding of metal ions (Li et al., 2009).BSG has a significant potential as a bio-adsorbent for application in the remediation of metal contaminated wastewater streams. Several researchers have reported on the potential use of BSG in removal of heavy metals (Low et al., 2000, Li et al., 2009). BSG was studied by Lu and Gibb (2008) for the removal of Cu (II) ions from aqueous solutions and reported maximum adsorption capacity of 10.47 mg/g dry weight at pH 4.2. Anagnostopoulos et al., (2011) investigated the potential utilization of BSG as an adsorbent for the removal of uranium from aqueous solution. Their findings revealed that BSG exhibited maximum uranium removal at pH around 4.5 and substantial quantities of uranium were also removed even at pH values as low as 1.5, hence this ability is significant for the potential treatment of mining effluents which are usually characterized by low pH values. The present study aimed at evaluate the sorption potential as well as elucidate the mechanism of removal of BSG as a low- cost sorbent for Cd and Zn ion removal from aqua waste stream. The kinetics of Cd and Zn ion sorption on the BSG shall be analyzed using Langergren pseudo first order and pseudo second order kinetic models. The equilibrium sorption of Cd and Zn ion by BSG shall be tested with Langmuir and Freundlich isotherm models to determine the best-fit isotherm equation. The effect of some process variables like pH, sorbent dosage and initial metal ion concentration shall also be investigated.

Materials and methods

The BSG used was obtained from Cedar Feed Mill in Ondo, Ondo State, Nigeria. It was sun -dried for 3days to remove moisture and sieved using a laboratory sieved of 1000-1500 μ m. The sieved BSG was then thoroughly washed with distilled water for removal of the brewery residues and oven dried at 60°C. It was then kept in an airtight container, stored at room temperature pending its usage use as adsorbent. Cadmium nitrate Cd(NO₃)₂.4H₂O and Zinc nitrate Zn(NO₃)₂.6H₂O salts were used in the preparation of the salt stock solutions. Stock solution was prepared by dissolving the accurately weighed amounts of each salts, Pb(NO₃)₂and Zn(NO₃)₂.6H₂O in 1000ml distilled water. Working solutions of concentration ranging from 5 to 30mg/L were prepared from the stock solution by serial dilution with distilled water. All the chemicals used were of analytical reagent grade and obtained from BDH Ltd and used without further treatment. Metal ion concentrations were measured by Flame Atomic Absorption Spectrophotometer (Model 969 Solar Unicam Series), using an airacetylene flame and single element hollow cathode lamps. The instrument was calibrated with standard solution of 1 to 20 mg/L. Cadmium absorbance was measured at 228.8nm while Zinc absorbance was 213.9nm. The spectrophotometer was linked to a microprocessor using SOLAR AA software.

Sorption Studies

In order to determine the sorption isotherm, 0.1g of the adsorbents was brought in contact with 50ml of the varying concentrations of the working solutions (5-30mg/L). The mixture was agitated in a shaker (Model Uniscope SM101, Surgifriend) at ambient temperature for 4hs at a constant agitation speed of 200 rpm. At the end of the agitation, suspensions were separated by filtration and the supernatant was analyzed for residual equilibrium phase metal ions via Flame Atomic Spectrophotometer. The equilibrium sorption experimental data of the metal ions by BSG was tested with Langmuir and Freundlich isotherm models to determine the best fit isotherm equation to understand the mechanism of surface coverage.

Metals uptake by the BSG during the series of batch investigations was calculated using the mass balance equation (Oladoja et al, 2010) as stated below:

$$q_e = \underbrace{(C_o - C_e)}_{m} x V$$
(1)

Where qe_e = adsorption capacity at equilibrium, V = volume of adsorbate solution (dm³), m = mass of BSG (g) C_o = initial concentration in mg/L, C_e = concentration at equilibrium (mg/L)

The removal percentage (R %) is defined as the ratio of difference in metal concentration before and after adsorption (c_o-c_e) to the initial concentration of the adsorbate in aqueous solution (c_o) shown below (Oladoja et al, 2010):

$$\%R = \underbrace{(C_o - C_e)}_{C_o} x \ 100 \tag{2}$$

Kinetics of Sorption Studies

The time concentration profiles of the adsorption of the adsorbates were assessed to obtain the kinetic parameters by the addition of 0.4g of the adsorbent into a 200ml working solution of the 50mg/l of the adsorbates, agitated with a shaker at 200 rpm. Solution samples were withdrawn at intervals between 30mins - 4hours of contact, filtered and the supernatant was analyzed for residual metal ions. The results obtained were evaluated using the Lagergren pseudo-first order and the Chemisorption pseudo-second order (Oladoja et al, 2010) **pH Effects**

The sorption process variables were optimized by assessing the effects of pH on the sorption process by varying the pH of 20mg/l initial adsorbate solution of 50ml between pH 2-9 with 1M HCl or 1M NaOH and fixed sorbent dosage of 0.1g at ambient temperature for 120mins.

The Effect of the sorbent dose: The Effect of the sorbent dose on the sorption process was investigated at different adsorbent dosages of 0.05g-0.60g by contacting with 50ml of Adsorbate for 120mins at ambient

temperature. For all process variable optimization experiments, constant agitation speed of 200 rpm in a water bath was used.

Adsorption Isotherm Studies: Adsorption is usually described through isotherms that is, the amount of adsorbate on the adsorbent as a function of its concentration (if liquid) at constant temperature and whose parameters present the surface properties and affinity of adsorbent to solute. The evaluation of a sorbate's affinity for a particular sorbent is usually obtained from the analysis of the results obtained from the equilibrium isotherm studies. Equilibrium studies are described by sorption isotherm characterized by certain constants whose values express the surface properties and affinity for the sorbent. The results obtained in this study were tested with three isotherm equations, Langmuir and Freundlich equations .The Langmuir isotherm which hints on homogeneity describes the monolayer coverage of a sorbate on a sorbent surface at constant temperature. The linear form of the Langmuir equation is:

$Ce/q_e = 1/Kq_m + Ce/q_m$

(3)

Where Ce is the concentration of the sorbate at equilibrium (mg/L), q_e is the amount of sorbate sorbed at equilibrium per unit mass (mg/g), q_m is the monolayer sorption capacity at equilibrium (mg/g) and k is the Langmuir equilibrium constant (l/mg). The values of qmand k are obtained from the slope and intercept respectively of the plot of straight line graph of Ce/q_e against Ce.

The Freundlich isotherm is regarded as an empirical isotherm. It indicates the surface heterogeneity of the sorbent. The linearized form of Freundlich equation is given by:

 $\ln q_e = (1/n) \ln C_e + \ln K_f$

(4)

where k_fand n are Freundlich adsorption constants, related to adsorption capacity and sorption intensity respectively obtained from the plot of lnqe against lnCe which gives a straight line graph with 1/n as slope and $\log k_f$ as intercept (Oladoja et al, 2010)

Kinetics of Adsorption

The mechanism of adsorption often involves chemical or physical interaction between functional groups present on the absorbent surface and metal ions. In some cases it involves the formation of cation exchange reaction due to high cation exchange capacity of the adsorbents. The time- concentration profile characteristics of the sorption of Cd and Zn ion on BSG were tested with Lagergren pseudo- first order (Langergren, 1898) and the chemisorption pseudo-second order (Ho,1995). The linearized form of the pseudo -first order equation of Lagergren is generally expressed as follows:

 $\log (q_e-q_t) = \log(q_e) - t k_1/2.303$

Where q_e and q_t are the sorption capacity at equilibrium and time t respectively $(mg/g).k_1$ is the rate constant of pseudo – first order adsorption. A plot of $\log (q_e-q_t)$ against t gives a linear relationship from which the pseudo first order parameters can be determined from the slope and intercept of the plot(Oladoja et al, 2010). The pseudo-second order kinetics represented by the linear equation presented below was also used to test the experimental data:

$$t/q_t = i/k_2q_e + 1/q_et$$

(6)

(5)

where q_e , q_t and t have the same meaning as explained above. k_2 is the overall rate constants of pseudo-second order sorption ((g/mg)/min). The plot of t/q_t against t of equation (6) should give a linear relationship, from which qe and k2 can be determined from the slope and intercept of the plot (Oladoja et al, 2010). The initial sorption rate (h) can be obtained from the pseudo-second order linear plots, as q_i/t approaches zero: (7)

$$h = k_2 q_e^2$$

Results and Discussion

BSG Characterization: The characterization of the BSG carried out using the recommended standard methods of analysis (AOAC,1991) showed the following chemical composition (% dry weight, w/w): 16.8 cellulose, 28.4 hemicellulose, 27.8 lignin, 4.6 ashes, 15.2 proteins, 5.8 extractives, and 1.4 acetyl groups.

Equilibrium Isotherm Studies: The equilibrium relationship between the concentrations of the metal ions in the equilibrium phase and that in the BSG at a given temperature was studied to determine the maximum sorption capacity of the BSG for the metal ions. The experimental results obtained were analyzed using the Langmuir and Freundlich isotherm models to depict the mechanisms of the metal ions adsorption on BSG. The monolayer sorption saturation capacity of the metal ions qm and sorption constants K were obtained from the slope and intercept of the plot of amount of sorbed metal ions per unit mass, ge against concentration of metal

ions remaining in solution, ce shown in Fig 1-4. The different isotherm parameters from the different plots are presented in Table 1

Table 1: Langmuir and Freundlich Isotherm Parameters of the Sorption of Cd and Zn ions by BSG								
Metal	$q_m (mg/g)$	k (L/mg)	\mathbb{R}^2	Kf	1/n	n	R^2	
Cd (II) ion	20.408	0.924	0.959	9.484	0.511	1.957	0.879	
Zn (II) ion	32.258	0.408	0.977	7.852	0.390	2.564	0.974	

The value of R_L a dimensionless constant, separation factor or equilibrium parameter was calculated to characterize the isotherms (Cho et al., 2011). R_L values are usually used to indicate whether the adsorption is unfavourable ($R_L>1$), linear ($R_L=1$), favourable ($R_L<1$) (Cho et al., 2012). For the study, the value of R_L was <1, thus indicating a favourable process. The Freundlich model defines kf as the adsorption capacity constant and n as a constant indicative of the adsorption intensity. Generally, when n>1, the adsorbate is favourably adsorbed on an adsorbent and the higher the n value the stronger the adsorption intensity (Das et al., 2011). Hence, we conclude that the two metal ions were favourably adsorbed on BSG and that the adsorption capacity increases with the occurrence of new adsorption sites. The correlation coefficient R^2 of Freundlich for Cd (0.8797) is lower than that for that of Langmuir (0.9736). This suggests that the bio-sorption is assumed to be monolayer sorption with respect to Cd.



Fig1:Langmuir Isotherm for Zn





Fig 2: Freundlich Isotherm for Zn



Fig 3: Langmuir Isotherm for Cd



The data fitting to the Freundlich and Langmuir isotherm for Zn (0.9746, 0.977) respectively suggests that both isotherm show a good fit to the experimental data with well matching correlation.

Effect of initial metal ion (Cd and Zn) concentration on adsorption capacity of BSG

The results of the effect of initial ion concentration shows the relationship between concentrations and the amount of metal ion bound at fixed adsorbent dosage of 0.1 gram is shown in Fig 5a. The result obtained from the study showed that adsorption capacity increased with increasing concentration of adsorbate. For Zn there is an increase from 2.4701mg/g to 13.3026mg/g when initial concentration was increased from 5ppm to 30ppm and for Cd from 1.2775mg/g to 9.3760mg/g. This may be attributed to the fact that increase in adsorbate concentration results in increase in number of available molecules per binding sites of the adsorbent thus bringing about a higher possibility of binding of molecules to the adsorbent. Increase in initial metal concentration enhances the interaction between the metal molecules and the surface of the adsorbent. This trend is a common phenomenon in most adsorption studies (Bhattachacharyya and Sharma, 2004; Hafez 2012; Ofomaja et al.,2005). It should be noted that at the same concentration the level of uptake of the Zn ions by BSG was found to be greater than Cd ions. This could be explained in terms of difference in their ionic radii of the metals, Cd^{2+} is 0.97Å and Zn^{2+} is 0.74 Å.It could be observed from the data that the smaller the ionic size the greater the surface coverage on the biomass. This general trend may be explained by the fact that the metal ions

with smaller ionic radius diffuse faster in aqueous systems. This implies that ion with smaller ionic size would easily interact with the biomass resulting in a higher surface coverage than for ions of larger sizes. These trends have been observed by several researchers (Abia et al, 2003; Ho et al., 1995; Quek et al., 1998, Horsfall et al, 2005)



Fig 5: Effect of (a) Initial Concentration (b) pH and (c)dosage on uptake of Zn and Cd by BSG

Effect of pH of Adsorbate solution: pH effects on sorption were examined between the pH ranges of 2-6. This range was chosen because is anticipated that at highly basic pH the presence of OH- ions may lead to the formation of complexes which in turns may decrease the adsorption of metal ions by. The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization and speciation of different pollutants (Horsfall et al, 2005; Abia et al, 2003;). Adsorption is affected by changes in pH through dissociation of functional groups on the active site on the surface of the adsorbent leading to a shift in reaction kinetics and equilibrium characteristics of the adsorption process. Sorption of the metal ions could be explained on the basis interaction between the metal ions and functional groups such as hydroxyl, carboxyl amino and others on the surface of the BSG. Surface is active for the adsorption of cations at higher pH due to the deposition of OH. The removal of metal ions could therefore be the net result of the "ion exchange" and "surface complexation" phenomena occurring on the surface of the BSG. The influence of pH of metal in solution on the extent of sorption of Cd and Zn ions on BSG is shown in Fig 5b. From the plot, small amount of metal ions are adsorbed at low pH, probably due high to competition between H⁺ and the metal ions for sorption sites on the adsorbents. The increase in adsorption with increase in pH can be attributed to the fact that the positively charged metal cations are repulsed less at higher pH values as a result of increasing negative charge density on the adsorbent. Zn uptake by BSG increased from 66.39% to 94.46% as the pH increases and same holds for Cd from 56.40% to 77.81%. Optimum pH for the two metals for maximum % removal was found between pH 5-6. This conforms with past research works (Hafez 2012).

Effect of Sorbent dosage

The dosage of the adsorbent is defined as the mass of BSG (g) in the fixed volume of wastewater (ml). The results obtained when the effects of varying BSG dosage on the adsorption of the metal ions was monitored are presented in Fig 5c. The extent of sorption calculated as a percentage of the metal ions sorbed by BSG increased as the dosage of the BSG was increased. This is expected because an increase in BSG dosage will lead to an increase in the quantity of sorption sites available for sorbent –sorbate interaction. Increasing the amount of the adsorbent makes a large number of sites available leading to an increase in adsorption. % removal of Zn increased from 72% to 93% and that of Cd from 41% to 78% as the BSG dosage was increased from 0.05g to 0.60g. The increase in the removal efficiency with increasing sorbent dose was rapid at low dosage. Optimum dose was chosen for 0.4g of sorbent. Further increase in the dose led to a small change in the amount of metal removed. This is attributed to saturation of the adsorbent binding sites which is in agreement with Langmuir hypothesis of increasing competition among sorbent particles per unit volume (Converti *et al.*,1 992, Jain *et al.*, 2008, Mittal *et al* 2008). Maximum removal for Zn was 93% and Cd was 78%.

Kinetics of sorption studies

The efficiency of the adsorbent was evaluated by studying adsorption kinetics. Kinetics is an adsorption dynamics which describes the solute uptake rate and evidently control the resident time of adsorbate and possibilities of desorption .The kinetic properties of adsorbate uptake are used in selecting optimum operating conditions for the full scale batch process. The kinetic parameters provide important information for designing and modeling adsorption processes. In order to understand and elucidate the underlying mechanism of any sorption process, different kinetic models have been proposed and used to analyze data obtained from different sorption experiments. Premised on this, data obtained from the study were analyzed using different kinetic models to explicate the mechanism guiding the sorption of Zn and Cd ions by BSG. The effect of contact time on the sorption of Cd and Zn (II) ion is presented in Fig 6-7. The plot obtained when the amount of metal ions adsorbed per gram of BSG was plotted against time showed that the rate of sorption was fast at the inception of the sorption studies and became immeasurably slow when he remaining vacant sites become difficult to occupy due to repulsive forces between the solute molecules of the solid and bulk phase when the state of equilibrium was approached. The sorbate removal increased with the increase with contact time. The initial rapid uptake could be ascribed to the concentration gradient, created at the start of the adsorption process, between solute concentration in solution and that at the BSG surface. In order to understand the underlying mechanism of this sorption process, the data obtained from the sorption process were tested with Langeren Pseudo first order and Pseudo second order kinetic models. The kinetic parameters obtained from the models are presented In Table 2-3.

Kinetic model	Relationship (y =)	R^2	Constants	Values
			$k1 \text{ (min}^{-1}\text{)}$	0.0034
Pseudo First order	-3.6394 - 0.0034x	0.5268	qe,cal (mgg- ¹)	0.026
			qe,exp (mgg ⁻¹)	0.98505
			%SSE	0.42
			$k2 (mgg-^1min-^1)$	1.0812
			$h (g mg^{-1}min^{-1})$	0.3541
Pseudo Second order	2.8241 + 1.0145x	0.9999	qe (cal)(mgg ⁻¹)	0.9852
			qe (exp)(mgg- ¹	0.98505
			%SSE	0.0155

Kinetic model		Relationship (y =)	R ² Constants		Values
				$k1 \ (\min^{-1})$	0.0099
Pseudo First order		-2.2745 - 0.0099x	0.9618	qecal (mgg ⁻¹)	0.103
				qeexp (mgg ⁻¹)	0.9200
				%SSE	0.163
				$k2 (mgg-^1min-^1)$	0.17
				h (g mg-1min-1)	0.1498
Pseudo order	Second	1.0735 + 6.6742x	0.9857	qe (cal)(mgg ⁻¹)	0.9315
				qe (exp)(mgg- ¹ %SSE	0.9200 0.002

Table 3: First order, second order kinetics experimental constants of Cd ion uptake onto BSG.

q_eexp : Experimental amount adsorbed per unit gram of BSG, q_ecal- calculated amount adsorbed per

unit gram of BSG, $K_1 K_2$ -First and Second order rate constant, h- initial sorption rate, SSE-Statistical sum of error square, Correlation coefficient $-R^2$

Table 2-3 show the kinetic experimental data for Cd and Zn sorption onto BSG. Accepted kinetic model for a given adsorption is characterized by a good and high correlation coefficient, R^2 which indicate the applicability and reliability of a given model, close agreement between the calculated and experimental *qe* values (precision test) and least values for error analysis squares which is determined as Equation

SS E (%) = $\sqrt{\sum (q_e.exp. - q_ecal.)^2/N}$

(8)

Where N is the number of data points.

Comparing the two models used for the two metals, the deviations between the calculated *qe* values and the experimental *qe* values were relatively low for pseudo second order than for Langeren Pseudo first order model. Also regression coefficients for the Pseudo second order for the two metals were higher than the Pseudo first order and lastly the pseudo second ordergives a lower value for the SSE than Langeren pseudo first order. Based on these pointsit can be concluded that the Lagergren pseudo-first order kinetic model was the least to conform to the description of the sorption of the metal ions by BSG (Table 2-3).Therefore the kinetics of sorption in this research was based on the pseudo second order rate constant. Tables 2 and 3 presented the rate constants value as $k^2 = 1.0812mgg^{-1}min^{-1}$ for Zn and $0.17mgg^{-1}min^{-1}$ for Cd. These fairly high rates values are measures of speed of uptake as related to adsorption capacity and intensity and not necessarily based on concentration. Also to be noted is that k2 value of Zn is higher for Zn than Cd uptake.

Ho *et al.*, (2000) considered pseudo second order equation to be appropriate for studying metal ion sorption. The pseudo second order kinetic model considers the rate limiting step as the formation of chemisorptive bond involving sharing or exchange of electrons between the sorbate and the sorbent. In contrast to the other kinetic models, it predicts the behavior over the whole range of studies supporting a pseudo second order equation (Ho and McKay, 1998). The applicability of the pseudo second order kinetic model to experimental data is presented in Fig 10. The pseudo-second-order rate constant (k2), the initial sorption rate (h) and the equilibrium sorption capacity (qe) were obtained from the slope and intercept of Eq. (6).The values obtained showed that the model can be applied for the entire adsorption process and confirms the chemisorption of the metal ions by BSG.



Conclusion

This study showed that BSG is a promising biosorbent for the removal of Cd (II) and Zn (II) ions from aqueous system. Batch sorption study revealed that the adsorption of Cd (II) and Zn (II) was pH, dosage and initial metal ion concentration dependent. The pseudo second order kinetic model gave the best description of the sorption process. Langmuir isotherm model fitted better for the sorption of Cd by BSG while both Langmuir and Freundlich fit the experimental data of sorption of Zn by BSG. Thus, BSG has high potential for treating industrial effluents containing Cd (II) and Zn (II) ion.

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