ADSORPTION, KINETIC, EQUILIBRIUM AND THERMODYNAMIC STUDIES ON THE REMOVAL OF LEAD (II), ZINC (II) AND CADMIUM (II) FROM AQUEOUS SOLUTION BY THE USE OF NATURAL ADSORBENT

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Abstract

Environmental pollution due to development in modern industrial practice is one of the most significant problems of this century. Heavy metals are major toxic pollutants with serve health effect on human. The study of removal of heavy metals Pb (II), Zn (II) and Cd (II) from stimulated waste water by batch adsorption experiments with natural adsorbent for effective removal of Pb (II), Zn (II) and Cd (II) ions. The main parameters influenced the Pb (II), Zn (II) and Cd (II) adsorption process such as percentage recovery, initial metal concentration, effect of adsorbent dosage, metal ion concentration, effect of contact time and effect of pH was studied in batch experiments. The experimental results were analyzed by using Langmuir adsorption isothermal and Freundlich adsorption isothermal model. The kinetic data well described by the pseudo first order kinetic model. The thermodynamic parameters such as ΔH, ΔG and ΔS also determined. *Annona muricata* (soursop) fruit husk (AMFH) powder was successfully employed for removal of Pb (II), Zn (II) and Cd (II) ions from waste water and the techniques will be appears industrially applicable and feasible

Key words ; Adsorption, *Annona muricata* fruit husk powder, Pb (II), Zn (II) and Cd (II), Kinetics, Thermodynamics, Adsorption isotherms.

1. Introduction

Water pollution is contaminated of water by foreign matter that deteriorates the quality of the water. Environmental pollution due to the development in modern industrial practice is one of the most significant problems of this century. Heavy metals are elements with a specific gravity that is at least four to five times the specific gravity of water at the same temperature and pressure [1,2]. Heavy elements has positive valances and occupy group I to III in the periodic table. Out of thirty five elements cadmium, antimony, arsenic, bismuth, cerium, chromium, copper, zinc, gallium, gold, iron, lead, manganese, mercury, cobalt, nickel, platinum, silver, tellurium, thallium, tin, uranium and vanadium are considered as heavy metals [3]. Heavy metals are released into the environment from a variety of industrial activities. The heavy metals pollution represents an important problem with human health concerns and serious ecological consequences. Heavy metals are associated. With myriad adverse health effects including allergic reactions (beryllium, chromium) neurotoxicity (lead) nephrotoxicity (mercuric chloride, cadmium chloride) and cancer (arsenic hexavalent chromium). Humans are often exposed to heavy metals in various ways mainly through the inhalation of metals in the workplace or polluted neighborhoods or through the ingestion of food that contains high levels of heavy metals or paint chips that contain lead [4].Cadmium and lead are ubiquitous and non-biodegradable pollutants represents great effect on human health. Both metals are naturally distributed but industrial development has dramatically increased their concentration in the environment [5,6,7]. The main routes of cadmium and lead exposure are ingestion and inhalation due to their presence of food, air and tobacco leaves [8]. Lead is most common heavy elements and commonly distributed throughout the environment [9]. It is most toxic heavy metal and the inorganic forms are absorbed through food and water and inhalation [10]. Lead poisoning causes teratogenic effect, inhibition of the synthesis of hemoglobin, dysfunctions in the kidney, joints, reproductive systems, cardiovascular system. Chronic damage to the central nervous system and peripheral nervous system [11]. Inorganic forms of lead affect central nervous system, peripheral nervous system, gastrointestinal tract and organic forms mostly affect the central nervous system [12,13,14,15]. Effect of lead on children brain and results in poor intelligence quotient [16].

Zinc is necessary elements for all living things as well as for human beings. Zinc containing proteins and enzymes are involved in replication and translation of genetic material [17]. Zinc if taken orally but excess amount can cause system dysfunctions that result in impairment of growth and reproduction [18]. The clinical signs of zinc toxicosis have been reported as vomiting diarrhea, bloody urine, icterus, liver failure, kidney failure and anemia [19]. Surface water have been contaminated by industrial wastes, plating works, plants manufacturing cadmium pigments, textile operations. Cadmium stabilized plastics or nickel cadmium batteries or by effluents from sewage treatment plants [20].

Numerous natural adsorbent sources are available in nature in which same experimental adsorption properties have been reported eg. Rice husk [21], sawdust [22,23,24], tea and coffee waste [25,26] peanut shells [27], activated carbon [28,29] dry tree leaves and barks [30,31,32]. *Annona muricata* is the fruit of broadleaf, flowering evergreen tree. The soursop is adapted to areas of high humidity and relatively warm winters temperature below 5°C (41^0F). The fruit is usually called soursop due to its slightly acidic taste when ripe. It is native to the Caribbean and central America but is now widely cultivated and in some areas . *annona muricata* fruit contain high calorific value. It improves eye health, has anti inflammatory properties and it improves gastrointestinal health. Lactones, polyketides of soursop used as neurotoxin in oncogenic genins [33].

In the present work we have studied the potential of Pb (II), Zn (II) and Cd (II) adsorption on a agro material which is a waste material of *annona muricata* fruit husk powder. Results from this study can be used to assess the Pb (II), Zn (II) and Cd (II) removal from waste water.

Materials and Methods

All the chemicals and reagents have been acquired from the commercial sources (sigma-aldrich, Merck etc.) and used without further purification**.** Stock solution of 1000 mg/L of Pb (II), Zn (II) and Cd (II) was prepared from lead sulphate, zinc sulphate and cadmium sulphate by distilled water. Desired test solution of Pb (II), Zn (II) and Cd (II) ions were prepared using appropriate subsequent dilution of the stock solution. The range of concentrations of Pb (II), Zn (II) and Cd (II) ions prepared from standard solution varies between 10 and 100 mg/L. Before mixing the adsorbent, the ph of solution was adjusted to the required values with 0.1 M NaOH.

Adsorbent

Annona muricata fruit husk (AMFH) is the waste was thoroughly rinsed with water to remove dust and soluble material. Then it was allowed to dry at room temperature. The dried *annona muricata* fruit husk (AMFH) was grounded to a fine powder in a grinding mill and sieved to get fine powder. The fine powder was then treated with NaOH (0.2 mol/L) to improve the biosorption capacities of Pb (II), Zn (II) and Cd (II) ions. For this purpose 100 gms of dried *annona muricata* fruit husk powder soaked in solution of 500 ml NaOH (0.2 mol/L) for 20 hrs. Then filter it and washed with de-ionized water until the pH value of the solution reached 7.0, then *annona muricata* fruit husk (AMFH) powder was dried at 110^0C in an oven for 14 hrs and was then stored in desiccators for final study.

Adsorption Study (Batch Process)

The dried powder of *annona muricata* fruit husk (AMFH) 1.0 gm was taken in stoppered bottle. The Pb (II), Zn (II) and Cd (II) with initial concentration of 10 mg/dm^3, 20 mg/dm^3, 30 mg/dm^3, 40 mg/dm^3, 50 mg/dm^3. The mixture were well stirred on a shaker at 100 rpm at the temperature 298 K,303 K, 308 K and 313 K for 20, 40, 60, 80, 100 & 120 minutes until the equilibrium condition were reached. The content was filtered. The adsorbate and adsorbent were separated by filtration. The Pb (II), Zn (II) and Cd (II) filtrate in the aqueous solution after adsorption was measured by using pH values of the solution were determined by using pH 2 to 9 using pH meter. The percentage of adsorption was determined from initial and equilibrium concentration respectively.

Results and Discussion

Effect of pH

Effect of pH of solution is very important in adsorption process of metal ions. pH of solution affect on surface of adsorbent. Solubility of metal and also the speciation of metal ions. The effect of pH on the removal of Pb (II), Zn (II) and Cd (II) ion using *annona muricata* fruit husk (AMFH) powder as an adsorbent. It was studied with the initial pH range from 2 to 9 it realates the initial pH of the solution and then the percentage of Pb (II), Zn (II) and Cd (II) ions. With increasing pH from 5 to 7 the percentage of Pb (II), Zn (II) and Cd (II) ion increases. Adsorption process is good at pH 6, pH 6.5 and pH 5.0 for Pb (II), Zn (II) and Cd (II) ions respectively. The uptake capacity of Pb (II), Zn (II) and Cd (II) ions is better for *annona muricata* fruit husk (AMFH)

Effect of Adsorbent Dose

The effect of adsorbent on Pb (II), Zn (II) and Cd (II) ion removal was studied by batch adsorption process. The percentage of removal of Pb (II), Zn (II) and Cd (II) ion reaches about from 77 % to 96 % each. The dose required in near about 200 mg/ 25 ml for the initial concentration of 25 mg/L at pH 6.

Effect of contact time

The rate of removal of Pb (II), Zn (II) and Cd (II) ion, the effect on contact of Pb (II), Zn (II) and Cd (II) adsorption on *annona muricata* fruit husk (AMFH) powder was studied. The percentage removal of Pb (II), Zn (II) and Cd (II) ions at different initial values of Pb (II), Zn (II) and Cd (II) ions, concentration of solution varies from 5,10,15,20,25,30,35,40,45,50 mg/L and batch experiments were carried out by taking 200 ml of this solution with dried 1.0 gm of adsorbent and the system is equilibrium by shaking the solution content at room temperature. The equilibrium of solution reaches in 7 hours. Final concentration of Pb (II), Zn (II) and Cd (II) was determined by spectrophotometrically. The removal of Pb (II), Zn (II), and Cd (II) ions was 78.05 %, 84.65 % and 80.00 % respectively. The adsorption of Pb (II), Zn (II) and Cd (II) ions on *annona muricata* fruit husk (AMFH) powder adsorbent was a function of time was studied. As the concentration of metal ion increases surface area of adsorbate was covered more & more and hence at the higher concentration of Pb (II), Zn (II) and Cd (II) ions capacity of metal ions adsorbed in the surface of adsorbate is decreased due to unavailability of the surface area of adsorbate. It conclude that at lower concentration of Pb II), Zn (II), and Cd (II) ions the percentage of adsorption is high because of the more active site of adsorbate is available for the adsorption.

Table 1

Effect of Temperature

Temperature is very important factor for adsorption. Higher temperature increases the rate of the adsorbate and decrease in the viscosity of the solution. Change in the temperature changes the equilibrium capacity of the adsorbent for the particular adsorbate. A series of experiments were conducted at 298 K, 303 K, 315 K and 340 K to study the effect of temperature on the adsorbate time rate. for 20, 40, 60, 80, 100 & 120 minutes.

Freundlich Adsorption Isotherm

Freundlich plot for the adsorption of Pb (II), Zn (II) and Cd (II) ions with *annona muricata* fruit husk (AMFH) powder shows that the values of adsorption intensity 1/n is less than 1, indicates the applicability of Freundlich adsorption **Table 2.**

LangmuirAdsorption Isotherm

The value of Q_0 of Langmuir adsorption isotherm found to be comparable with commercial activated carbon. Value of b lies between 0 to 1 it indicates that the adsorption is favorable. It indicate that the applicability of Langmuir adsorption isotherm **Table 3**

Adsorption Kinetics

Adsorption rates of Pb (II), Zn (II) and Cd (II) on ions *annona muricata* fruit husk (AMFH) powder was studied by first order kinetic rate equation. It is found that the initial concentration of Pb (II), Zn (II) and Cd(II) ions increases rate constant increases it indicate that the adsorption follow the first order kinetics. **Table 4.**

Thermodynamic Parameters

Adsorption rate depends on temperature was investigated at 298 K, 303 K, 315 K and 340 K. it conclude that increasing temperature mass of Pb (II), Zn (II) and Cd (II) ions per unit mass of the adsorbent was increased. At above temperature the change in Gibb's free energy, Change in enthalpy and Change in entropy was calculated. Change in Gibb's free energy shows negative value indicate that the adsorption of Pb (II), Zn (II) and Cd (II) ions on *annona muricata* fruit husk (AMFH) powder is spontaneous and feasibility. The change in enthalpy value indicates endothermic nature of Pb (II), Zn (II) and Cd (II) ions on *annona muricata* fruit husk (AMFH) powder. The change in entropy shows positive value indicates increase randomness during the adsorption process of Pb (II), Zn (II) and Cd (II) ions on *annona muricata* fruit husk (AMFH) powder . **Table 5**

Table 1. Summary of % Recovery & Adsorbent Capacity of adsorbent, Initial concentration 25 mg/L , Adsorbent dose 1 mg/L

Sr. No.	Adsorbent	Heavy Metal	Final Conc(mg/L)	% Recovery	Q (mg/L)
1	*Annona muricata* fruit husk (AMFH) powder	Pb(II)	38.95	78.05 %	18.45
2		Zn(II)	50.48	84.65 %	24.80
3		Cd(II)	59.38	80.00 %	21.80

Table 2. Freundlich Adsorption Isotherm of Pb (II), Zn (II) and Cd (II) on AMFH

Sr. No.	Heavy Metal	Concentration	Freundlich Constant	
			K	1/n
1	Pb (II)	10 mg/dm^3	5.8769	0.1432
		20 mg/ dm^3	6.7395	0.2651
		30 mg/ dm^3	8.4237	0.4457
		40 mg/ dm^3	8.9079	0.8112
		50 mg/ dm^3	9.3820	0.9613
2	Zn (II)	10 mg/dm^3	4.9953	0.4336
		20 mg/ dm^3	5.0286	0.7892
		30 mg/ dm^3	7.0214	0.8034
		40 mg/ dm^3	7.9895	0.9001
		50 mg/ dm^3	9.2103	0.9968
3	Cd (II)	10 mg/dm^3	7.0024	0.0997
		20 mg/ dm^3	7.9983	0.4378
		30 mg/ dm^3	8.0142	0.6885
		40 mg/ dm^3	9.1467	0.8710
		50 mg/ dm^3	9.9926	0.9694

Table 3. Langmuir Adsorption Isotherm of Pb (II), Zn (II) and Cd (II) on AMFH

Sr. No.	Heavy Metal	Concentration	LangmuirConstant	
			K	1/n
1	Pb (II)	10 mg/dm^3	38.94	0.042
		20 mg/ dm^3	43.76	0.051
		30 mg/ dm^3	44.92	0.059
		40 mg/ dm^3	58.04	0.063
		50 mg/ dm^3	62.29	0.071
2	Zn (II)	10 mg/dm^3	41.87	0.048
		20 mg/ dm^3	59.02	0.062
		30 mg/ dm^3	62.19	0.079
		40 mg/ dm^3	64.70	0.081
		50 mg/ dm^3	66.84	0.089
3	Cd (II)	10 mg/dm^3	45.29	0.049
		20 mg/ dm^3	47.88	0.058
		30 mg/ dm^3	51.93	0.061
		40 mg/ dm^3	59.21	0.084
		50 mg/ dm^3	63.85	0.097

Table 4. Adsorption kinetics of Pb (II), Zn (II) and Cd (II) on AMFH

Sr. No.	Heavy Metal	Concentration	First order rate constant (K_1)
1	Pb (II)	10 mg/dm^3	3.39468 x 10^{-3}
		20 mg/ dm^3	4.86491 x 10^{-3}
		30 mg/ dm^3	5.93578 x 10^{-3}
		40 mg/ dm^3	7.20684 x 10^{-3}
		50 mg/ dm^3	9.51465 x 10^{-3}
2	Zn (II)	10 mg/dm^3	4.19386 x 10^{-3}
		20 mg/ dm^3	6.08476 x 10^{-3}
		30 mg/ dm^3	7.68438 x 10^{-3}
		40 mg/ dm^3	8.08935 x 10^{-3}
		50 mg/ dm^3	9.99030 x 10^{-3}
3	Cd (II)	10 mg/dm^3	5.0218 x 10^{-3}
		20 mg/ dm^3	6.9035 x 10^{-3}
		30 mg/ dm^3	7.1576 x 10^{-3}
		40 mg/ dm^3	8.4968 x 10^{-3}
		50 mg/ dm^3	9.8846 x 10^{-3}

Table 5. Thermodynamic parameters for the adsorption of Pb (II), Zn (II) and Cd (II) on AMFH

Sr. No.	Heavy Metal	T (^{0}K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol)	R^2
1	Pb (II)	298	-28.94	48.32	0.4172	0.8452
		303	-32.00			
		315	-39.48			
		340	-41.35			
2	Zn (II)	298	-36.72	52.68	0.5984	0..9375
		303	-42.98			
		315	-53.20			
		340	-60.53			
3	Cd (II)	298	-30.11	50.97	0.3916	0.7934
		303	-40.59			
		315	-56.00			
		340	-61.24			

Conclusion

***** *Annona muricata* fruit husk (AMFH) was used as a adsorbent for removal of Pb (II), Zn (II) and Cd (II) ions . It is good adsorbent , Adsorption process is rapid at the starting and a becomes slow at the standard stage. It dependent on initial concentration of adsorbate and also time for adsorption.

* *Annona muricata* fruit husk (AMFH) does increased percentage of adsorption also increased.

* This adsorption is good agreement with Freundlich adsorption isotherm and also for Langmuir adsorption isotherm .

* Adsorption process is good at pH 6,pH 6.5 and pH 5.0 for Pb (II), Zn (II) and Cd (II) ions respectively. The uptake capacity of Pb (II), Zn (II) and Cd (II) ions is better for *annona muricata* fruit husk (AMFH)

* Temperature effect shows that with increasing temperature capacity of adsorption increases.

* *Annona muricata* fruit husk (AMFH) could be exploited for commercial applicable.

* The cost of adsorbent is very low & is easily available.

* The adsorbent *annona muricata* fruit husk (AMFH) can be deposed safely.

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