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Bioremediation of Lead and Cadmium by Tea Waste

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Abstract: *Heavy metals released by a number of industrial processes are major pollutants in marine, ground, industrial and even treated waste waters. Biosorption is a process that utilizes biological materials as adsorbents and several researchers have studied this method as an alternative technique to conventional methods for heavy metal removal from wastewaters. In this study, the efficiency of tea waste has been determined in the process of heavy metal removing from single metal ion solution and mixed metal ion solutions. Metals of interest are lead and cadmium. The research is bench scale experiment type and analyses have performed by using fixed amount of adsorbent in solution with four different concentrations (5mgs/L, 10mgs/L, 15mgs/L and 30mgs/L) of each metal and also in a mixed combination. Since the pH plays a major role in adsorption, it should be maintained at 4.5 throughout the experiment. Result indicates the removal efficiency is highest for lead than for cadmium. The adsorption data fit well with the Langmiur isotherm model. Though tea waste could adsorb 80 +2% cadmium in single metal ion solution, but its adsorption of cadmium get increased to 90+2 % in mixed ion solution. This indicates that lead acts as the stimulator for cadmium. Comprehensive parameters indicate tea waste to be excellent parameters for Biosorption of lead and cadmium to treat waste waters containing low concentration of metals.*
Key Words: *Biosorption, lead, cadmium, tea waste and Langmuir isotherm.*

I. Introduction

Water pollution is a large set of adverse effects upon water bodies such as lakes, rivers, oceans and ground water caused by human activities. (Wikipedia, 2005). The search for newer technologies involving the removal of toxic metals from wastewaters has directed attention to **biosorption**, based on metal binding capacities of various biological materials. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake. (Fourest and Roux, 1992).

Recent biosorption experiments have focused attention on waste materials, which are by-products or the waste materials from large-scale industrial operations. The by-products obtained from biomaterial production are a cheap source of biosorbents. The process is effective even if the concentration is as low as 200µg/l. (Prasad and Frietas, 2000.). In this study, the efficiency of **tea waste** has been determined in the process of heavy metal removing from both single metal ion solutions and mixed metal ion solutions. Metals of interest are **lead** and **cadmium**. They were chosen based on their industrial applications and potential pollution impact on the environment.

II. Materials and methods:

Effect Of Pre –Trearment On The Biosorption Of Heavy Metals:

Metal affinity to the biomass can be manipulated by pretreating the biomass with alkalies, acids, detergents and heat, which may increase the amount of the metal sorbed (Yan and Viraraghavan, 2000). In the present study adsorbents are prepared from waste tea leaves and treated at 80 ^{0} C for 20 hours and utilized for the removal of lead and cadmium from aqueous solutions. The dried biomass was ground with a mortar and Pestle. The particles were separated by using a US standard testing sieves and stored in a sealed bottle to prevent readsorption of moisture.

Preparation Of Metal Solution:

***S*tock solution of lead:** It was prepared by dissolving 0.16g of lead nitrate in 100ml of distilled water. (Concentration of lead 1mg/ml)

***S*tock solution of cadmium:** It was prepared by dissolving 0.237g of cadmium acetate in 100ml of distilled water. (Concentration of cadmium 1mg/ml) Individually lead and cadmium standards were prepared with four different concentrations such as 5mg/L, 10mg/L, 15mg/L and 30mg/L using the respective stocks. The pH of the solution was adjusted to 4.5 by making use of digital pH meter.

Biosorption Studies:

The biosorption capacity of tea waste was determined by contacting various concentrations of 100ml of individual and mixed solution of lead and cadmium with 1 gram of tea waste in 250 ml conical flasks. The mixed solution is prepared by mixing 50ml of lead and 50ml cadmium solution of respective concentration. The Flasks were plugged with petroleum jelly and were shaken in a rotary Shaker at 120 rpm for 30 minutes and 60 minutes. It was filtered through Whatmann filter paper and the filtrate containing residual concentration of lead and cadmium were determined by atomic absorption spectrophotometer (Lead and mixed metal solution was determined by 283.8 nm and cadmium Solution was determined by 228.8 nm) in C.P. Ramaswamy Aiyar foundation, Alwarpet, Chennai.

III. Result and discussion:

The biosorption observation on the ability of tea waste to remove lead and cadmium made in this study are discussed in this section.

Effect Of Time:

Table 1 & 2 show the amount of the metal adsorbed onto biosorbents and biosorption capacity with reaction time for different metal concentration. The adsorption capacity of lead and cadmium increases rapidly in the beginning due to larger available surface area of the biosorbents. After the capacity of the adsorbent get exhausted that is at equilibrium the rate of uptake is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the biosorbents particles. (Verma et al. 2006).

Effect Of Agitation Speed:

A 30 – 40 % increase in adsorption was observed in agitated sample during 60 minutes of biosorption. This is because agitation facilitates proper contact between the metal ions in solution and the biomass binding sites and thereby promotes effective transfer of sorbate ions to the sorbent sites. This observation agrees with the previously reported biosorptive removal of Cr (V) by Rhizopus arrhizus (Niyogi et al. 1998) and Rhizopus Nigerians (Bai and Abraham, 2003).

Effect Of pH:

The experiments were not conducted above pH 6 to avoid possible hydroxide precipitation. The effect of pH on the biosorption capacity can be interpreted by the competition of the hydronium ions (H_30) and metal ions for binding sites. At low pH values, the ligands on the cell are closely associated with the hydronium ions, but when the pH is increased, the hydronium ions are gradually dissociated and positively charged metal ions are associated with the free binding sites. Other researchers (Bengudla and Benaissa, 2002; Esposito et al. 2002, Yang and Volesky, 1999) reported similar findings.

TABLE 1 The Concentration Of Residual Lead And Cadmium After Adsorption By Tea Waste:

AMOUNT OF BIOSORBENT (g/L)	TYPE OF METAL	TIME IN MINUTES	INITIAL AMOUNT OF METAL IN mg/L			
			5mgs/L	10 mgs/L	15 mgs/L	30 mgs/L
1 g	LEAD	30	0.50* mgs/L ± 0.015	0.75* mgs/L ± 0.02	0.75* mgs/L ± 0.014	0.75* mgs/L ± 0.024
		60	0.25* mgs/L ± 0.025	0.50 *mgs/L ± 0.016	0.75* mgs/L ± 0.023	0.75* mgs/L ± 0.025
	CADMIUM	30	0.50* mgs/L ± 0.023	0.94 *mgs/L ± 0.02	1.48* mgs/L ± 0.028	3.44 *mgs/L ± 0.015
.	.	60	0.48* mgs/L ± 0.02	0.94* mgs/L ± 0.028	1.39* mgs/L ± 0.022	3.12* mgs/L ± 0.02

The values are expressed as mean + SD. Statistical significance p value is *P < 0.05.

TABLE 2: The Concentration Of Residual Metals In Mixed Solution After Adsorption By Tea Waste:

AMOUNT OF BIOSORBENT (g/L)	TYPE OF METAL	TIME IN MINUTES	INITIAL AMOUNT OF METAL IN mg/L			
			5mgs/L	10 mgs/L	15 mgs/L	30 mgs/L
1 g	LEAD	60	0.42 * mgs/L $\pm$ 0.02	0.42 *mgs/L $\pm$ 0.02	0.63* mgs/L $\pm$ 0.018	0.83* mgs/L $\pm$ 0.027
	CADMIUM	60	0.19 * mgs/L $\pm$ 0.027	0.35 * mgs/L $\pm$ 0.029	0.64* mgs/L $\pm$ 0.02	1.40* mgs/L $\pm$ 0.035

The values are expressed as mean + SD. Statistical significance p value is *P < 0.05.

Biosorption Kinetics:

The lead and cadmium uptake capacity of the tea waste was evaluated using the Langmuir adsorption isotherms. The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The following equation can be used to model the adsorption isotherm,

$$q = \frac{q_{max} \times b \times c_{eq}}{1 + b \times c_{eq}}$$

Where q is milligrams of metal accumulated per gram of the biosorbent material; C_{eq} is the metal residual concentration in the solution; q max is the maximum specific uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates (Chong and Volesky, 1995).

Biosorption Equilibrium:

Adsorption isotherms are very important for the design of an adsorption based process design. In this study, the Langmuir isotherm model was used to correlate our experimental data. The equilibrium established between adsorbed component on the biosorbents and unabsorbed component in solution can be represented by adsorption isotherm. The equilibrium adsorption data for individual and mixed lead and cadmium are given in table 3. As can be seen in this table, the Langmuir isotherm indicates good monolayer coverage of metal ions on the surface of the biomass.

TABLE 3: THE AMOUNT OF METAL ACCUMULATED IN INDIVIDUAL AND MIXED METAL SOLUTION IN 60 MINUTES BY 1g OF BIOSORBENT (BASED ON LANGMUIR ISOTHERM)

Metals		**Initial concentration of metals in mgs / L**			
		5mgs / L	**10 mgs / L**	**15 mgs / L**	**30 mgs / L**
INDIVIDUAL	**Pb**	**4.51mg / L**	**9.025 mg / L**	**13.53 mg/L**	**28.51 mg/L**
	Cd	**4.09 mg/L**	**8.21 mg/L**	**12.35 mg/L**	**24.1 mg/L**
MIXED	**Pb**	**4.19 mg/L**	**9.17 mg/L**	**13.77 mg/L**	**28.37 mg/L**
	Cd	**4.62 mg/L**	**9.31 mg/L**	**13.75 mg/L**	**27.27 mg/L**

Detrmination Of Favourable Adsorption:

The essential characteristic of the Langmuir isotherms can be expressed in terms of dimensionless constant separation factor or equilibrium parameter, R_L that is defined as

$$R_L = \frac{1}{1 + b \times c_o}$$

Where b is the ratio of adsorption and desorption rates (Chong and Volesky , 1995) and C_0 is the initial concentration of metal. The R_L value indicates the type of isotherm is shown in table 4. According to Mc kay et al (1982) R_L values indicate favorable adsorption. The R_L value for individual lead and cadmium were found to be between 0.01 to 0.0008 and 0.019 to 0.003 whereas for mixed lead and cadmium were found to be between 0.016 to 0.0009. This shows the favorable adsorption of metal by tea waste.

TABLE : 4 Type Of Isotherm:

R_L	TYPE OF ISOTHERM
$R_L>1$	Unfavorable
$R_L= 1$	Linear
$0<R_L<1$	Favorable
$R_L = 0$	Irreversible

Efficiency Of Tea Waste:

The percentage of metal adsorbed by biosorbent can be calculated as follows

$$Q = \frac{Q\,max}{C_0} \times 100$$

Q is the biosorbent adsorption efficiency in percentage. Q max is the maximum uptake capacity by unit mass of the adsorbent (mg/g dry weight). C_0 is the concentration of metal ions before adsorption. (mg/L).

Effect Of Metal Ion Concentration:

Although the biosorption capacity profiles of lead and cadmium are very similar (Figure 1 & 2), the capacity of lead was substantially higher than that for cadmium. Figure 1 & 2 indicates that the adsorption of lead increases with increase in metal concentration upto 30 mg/L, whereas the adsorption of cadmium increases upto 15 mgs/L but decreases at 30 mgs/L. This enumerates that metal ion concentration rises; adsorption increases while the binding sites are not saturated.

The stimulatory role of other ions on sorption process can be well understood by comparing the metal uptake capacities of the biosorbents in the case of individual (Figure 1) and mixed (Figure 2) metal ion solution. Though tea waste could adsorb 80 + 2 % cd in single metal solution, but its adsorption of cadmium get increased to 90 + 2 % in mixed solution. This illustrates that Pb stimulates the adsorption of Cd by tea waste. This observation agrees with the previously reported biosorption removal of uranium get influenced by the presence of Zn^{2+} and Fe^{2+} by Rhizopus arrhizus (Tsezos and Volesky, 1982).

Figure1:

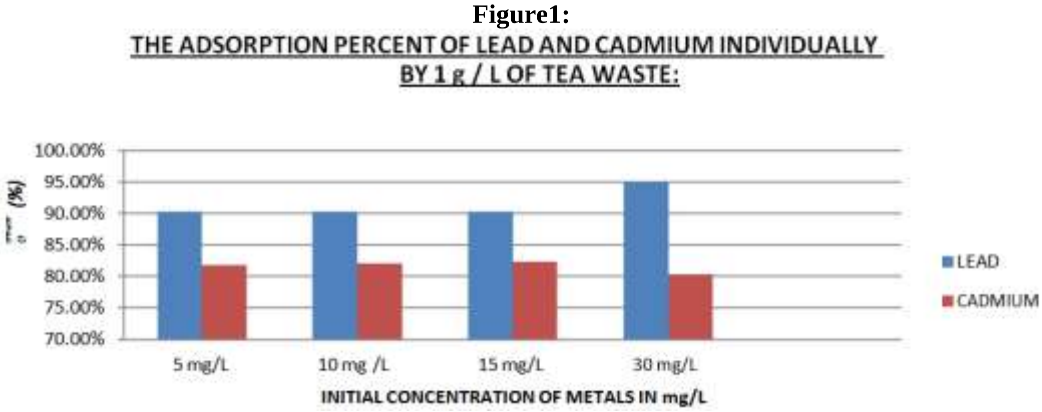
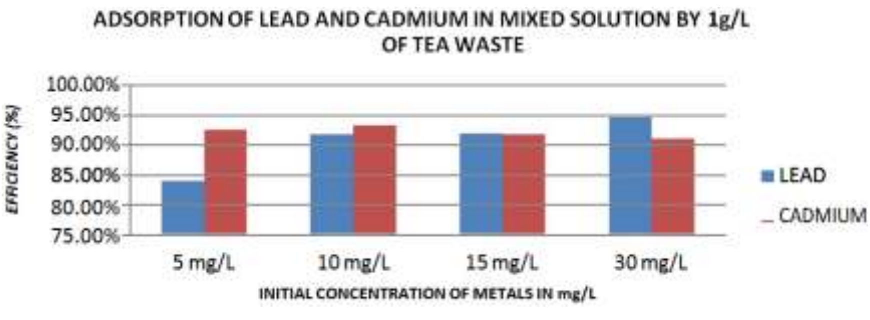


Figure2:



IV. Conclusion

The results indicate that tea waste is an excellent biosorbent for the removal of lead and cadmium ions. The pH plays a significant role in the biosorption mechanism by associating positively charged metal ions with the binding site of the biosorbent. A 30-40% increase in adsorption was observed in agitated sample during 60 minutes of biosorption. The uptake capacity of biosorbent is increased with increasing metal ion concentration for lead from 90% to 95% and for cadmium from 81.8% to 82.3%.The uptake capacity of biosorbent for cadmium is increased by the presence of lead. The adsorption of cadmium in single metal ion solution is 82.3% is increased to 93.1% in mixed metal ion solution. The data fits well to Langmuir isotherm and the monolayer maximum adsorption capacities of lead in single and mixed metal ion solutions are 28.51mg/g and 28.37 mg/g and of cadmium in single and mixed metal ion solution are 24.1 mg/g and 27.27 mg/g. Therefore, the present study clearly demonstrates the possibility of usage of low cost biosorbent, tea waste as a suitable alternative for the removal of lead and cadmium. Further studies will enhance the emerging of low cost biosorbent as the best method to remove the industrial pollutant, lead and cadmium from the industrial effluent.

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