ADSORBENT PREPARED FROM BIOMASS AS AN BIO-SORBENT FOR THE ELIMINATION OF HEAVY METAL FROM WASTEWATERS - BATCH MODE METHODS.

Dr. R. V. Ramana Murthy,
Professor, Dept. of Chemistry Mrs. AVN College, Visakhapatnam.

ABSTRACT

Date nuts dust was used to remove Pb(II) from aqueous solutions and industrial wastewaters by the adsorption. Batch mode adsorption experiments are carried out to assess kinetic and equilibrium parameters. They allow initial adsorption coefficient, adsorption rate constant and maximum adsorption capacities are to be computed. Removal of mg/g increases with increase of metal concentration and contact time. The adsorption data have analyzed and fitted to both Langmuir and Freundlich classical adsorption isotherm models. The adsorption capacity (Q_o) calculated from Langmuir isotherm was 29.53 mg Pb(II) /g *Date nuts* dust at initial pH of 2.0 at 27+2ºC for particle size 0.430 mm. increase in pH from 2-10 decreased percent removal of metal up to 7 latter onwards removal of metal is negligible coupled with regeneration study of Pb(II) by NaOH; allowed us to propose an adsorption mechanism by Ion-exchange between metal ion and H^+ ions in *Date nuts* dust surface quantitative recovery of Pb(II) is possible by NaOH.

Introduction

Lead used in battery industry, in the making of batteries, gun power industry chemical reagents, alloys preparation, lead compounds, house wear utensils, machine parts, preparation of spare parts in automobiles, leather and textile industries.

However, the number of sites, evaluated for lead is not known. Lead and its compounds are naturally present in the earth's crust and releases to the atmosphere occur from natural discharges such as windblown dust and volcanic eruptions, as well as from anthropogenic activities. It is estimated that 8.5 million kg of Lead are emitted into the atmosphere from natural sources such as windblown dust, volcanoes and vegetation each year. Five times that quantity is estimated to come from anthropogenic sources. The burning of residual and fuel oil is responsible for 62 % of anthropogenic emissions, followed by lead metal refining, municipal incineration, steel production, other lead alloy productions and coal combustion. These components releases, which totaled 3,081 metric tons, were distributed as follows: 82.2 % to land, 6.0 % to air, 2.2 % to water, and 0.8 % to underground injection.

Lead(II) is well known toxic heavy metal, which pose serious threat to the fauna and flora of receiving water bodies when discharged from industrial wastewaters. Lead(II) present in the effluents of silver refineries, electroplating, zinc base casting and storage battery industries. Kadirvelu *et al*., 2000a. As it resists corrosion even at high temperature, it can also be used in gas turbines, rocked engines and distillation plants. It is also used in coinage and costume jewelry. Skin contact with lead causes a painful disease called 'lead itch' which leads to death, reported Abbasi and Soni, 1990. In India acceptable limit of lead in drinking water is 0.01 mg/l and for discharge of industrial wastewater is 2.0 mg/ l, Kadirvelu, 1998. At higher concentrations, lead (II) causes cancer to the lungs, nose and bones. Dermatitis (lead itch) is the most frequent effect of exposure to lead. Lead carbonyl has been estimated as lethal in humans at atmospheric exposures of 30 ppm for 30 min, Namasivayam and Ranganathan, 1994. Acute poisoning of Lead(II) causes headache, dizziness, nausea, tightness of the chest, chest pain, shortness of breath, dry cough, cyanosis and extreme weakness. Parker, 1980. The toxic nature of fish, crops and algae was also reported David, 1977. Perennial toxicity associated with lead chloride exposure on female rats was also reported, Kate Smith *et al*., 1993.

The main object of present work was to evaluate the feasibility of using natural adsorbents from waste materials for the removal of Lead(II) from aqueous solutions and industrial wastewaters by using batch mode and fixed bed study. The influence of experimental conditions such as contact time, metal ion concentration, adsorbent dosage and pH effects were studied. Experimental results are analyzed to provide an adsorption mechanism. This method was applied for the removal of Pb(II) from synthetic aqueous solutions and industrial wastewaters.

Keywords: *Date nuts*, Heavy metals, pH, Wastewater treatment, Removal, Advanced techniques

Adsorbent : *Date nuts dust*

The *Date nuts* were collected from shop vendor at Visakhapatnam Andhra Pradesh, cleaned thoroughly with water and soaked in distilled water for 24 hours and again washed with double distilled water and dried under sun light. The dried *Date nuts* were pulverized and the pulverized material was screened for various particle sizes like 0.430, 0.600 and 0.800 mm.

Adsorbate: Lead solution

Analytical Reagent grade lead sulphate solution was used to prepare Pb(II) solution . A stock solution of 1000 mg /L of Pb(II) was prepared by dissolving 3.032 g of dried lead sulphate in double distilled water and made up to 1000ml.

Batch mode adsorption studies

Batch mode adsorption studies to determine the adsorption rates and maximum adsorption capacities. Batch mode adsorption studies were carried out at 27+2^{O}C using 50 ml of metal ion solution containing the desired concentration and 50 mg of adsorbent in 250 ml conical flask with lid stirring speed 220 rpm samples were separated and filtered. Pb(II) was analyzed by spectrophotometer (Stewart 1975 & APHA 2005). All the experiments were carried out at initial pH of 2.0 where the adsorption is significant but pH is more than 7.0 metal adsorption is negligible. The metal concentration on the adsorbent (q_e, mg/g) was calculated by using the following equation.

$$Qe = \frac{(Co - Ce)V}{m}$$

Where C_o, C_e are the initial and equilibrium concentrations of metal ion in solution (ml) and 'm' mass of adsorbent (mg). Adsorption isotherms were performed at 27+2^{o}C with an initial conc. of Pb(II)ranging from 10 – 40 mg/L a solution of volume 50 ml and an adsorbent weight of 50mg. The stirring time was 70 min, the effect of pH on percentage removal was studied from initial pH 2-10 using metal ion concentration 10 mg/L with 50 mg adsorbent, 0.1M HCl or 0.1M NaOH used to adjust the pH.

Batch mode desorption studies

After adsorption experiments, the metal ion loaded *Date nuts dust* was separated and slightly washed with distilled water to remove un-adsorbed metal on the *Date nuts dust* surface. They are stirred with 50ml of NaOH of various concentrations ranged from 0.002 to 0.016M for 70 min, metal ion concentrations were analyzed. All the experiments are used analytical reagent grade chemicals. All experiments were carried out in duplicate and mean values are presented maximum deviation was +5%

Results and discussion – approach of the adsorption

The effects of pH

The effects of pH on adsorption of Pb(II) ion was carried out using 50 mg of *Date nuts dust* dust in 50 ml of solution of 10 mg/L Pb(II) concentration. The pH of the solutions was adjusted to different pH values ranging from 2.0 to 10.0 and was equilibrated to 70 min. The equilibrated solutions were tested from Pb(II) concentrations spectrophotometrically (Stewart 1975 & APHA 2005). The percentage of adsorption decreased with increase in pH. The maximum of 93.73% at pH 2.0 latter decreased the percentage of adsorption up to 7.0 pH later 7-10 pH adsorption is almost constant. The adsorption of metal cations depends on the nature of metal ions, adsorbent surface and species of the metals

The high adsorption capacity of Pb(II) in the lower pH range may be due to protonation of adsorbent surface which would favour the uptake of anionic forms $HPbO_4^-$ and PbO_4^{-2}. Numerous studies consistently have demonstrated that pH is a dominant parameter in solutions, controlling adsorption and Pb(II) adsorption (Singh et al, 1992) decreases dramatically as solution pH increases. Agrwal et al, 1989 also reported similar results. Fig -1 shows the variation of percentage reduction of Pb(II) as a function of solution pH. Also suggest that lower pH 2.0 appears to be the most favorable range for adsorption of Pb(II), showing peak adsorption at 2.0. It can also observed that adsorption reduces sharply with increase in pH from 2.0 - 7.0 and thereafter no appreciable reduction is observed beyond pH 7.0 Gupta et al., (1988) have reported

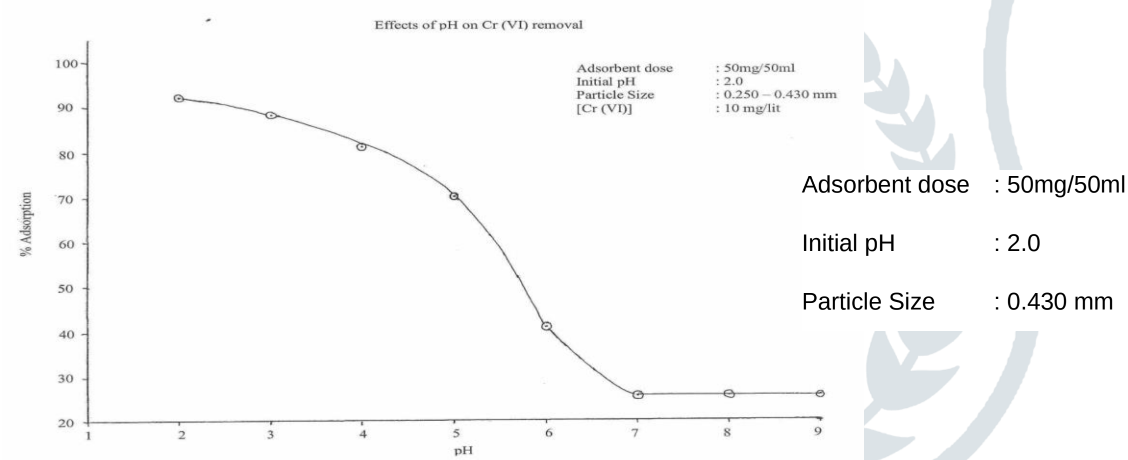

Figure - 1

Kinetic study

The kinetic study of the adsorption of Pb(II) was conducted at optimum pH where only adsorption takes place. The effect of contact time and initial metal ion concentration of Pb(II) adsorption on *Date nuts dust*. The adsorption equilibrium was reached at 9.34, 16.52, 22.32 and 26.16 mg/g for 10, 20, 30 and 40 mg/L respectively the contact time required for all the concentrations of Pb(II) removal is very short. This result is interesting because equilibrium time in one of the parameters for economical wastewater treatment plant applications. According to these results, the stirring time was 70 min for the further experiments to make sure to reach adsorption at equilibrium. The adsorption rate constants were calculated by using following equation given by Lagergern (Lagergern 1898)

$$\log(qe - q) = \log qe - \frac{Kadt}{2.303}$$

Where q and qe are the adsorption capacities at time (t) and equilibrium time, respectively. K_{ad} is adsorption rate constant. The K_{ad} values were calculated from slope of the plot, the respective linear plots of log (q_e-q) vs t. The results show that the removal of Pb(II) follows first order reaction. K_{ad} values were comparable with previous reports for adsorption Pb(II) on to various adsorbents Kalyani et al., (2004).

Table-1

Pb(II) (mg/L)	K_{ad} x 10^{-2}	Q(mg/g)
10	6.79	0.073
20	4.91	0.187
30	4.99	0.332
40	4.18	0.538

Adsorption isotherms

Adsorption isotherms of Pb(II) onto *Date nuts dust* are explained with help of two models, Langmuir and Freundlich equations to determine adsorption of Pb(II) on to *Date nuts dust* Langmuir isotherm was tested to determine maximum adsorption capacities and energy of adsorption using following equation given by Langmuir (Lodha 1997)

$$\frac{Ce}{qe} = \frac{1}{Qob} + \frac{Ce}{Qo}$$

Where Ce is equilibrium concentration (mg/L) , qe is amount adsorbed at equilibrium (mg/L) and Q_o (mg/g) and 'b' (L/mg) is Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plot of C_e/q_e vs C_e shows that adsorption of Pb(II) on *Date nuts* dust obeys Langmuir isotherm model. Q_o and 'b' were determined from the slope and intercept of the plot are found to the 31.53 mg/g and 0.085 L/mg respectively, Kadirvelu et al., (2003). The adsorption capacity of other adsorbents for Pb(II) are summarized in Table - 2 for comparison. Freundlich isotherm is also used to explain observed phenomenon with following equation

Table - 2

Adsorbent	Q_e mg/g	Reference
Rice hull	05.58	Suemitsu et al., (1986)
Natural clay	12.50	Hawash et al., (1994)
Pea mass	09.18	Lo et al., (1995)
Soya been hull	89.52	Marshal and Champage (1995)

Given by Freundlich (Freundlich 1906)

$$qe = KfCe^{1/n}$$

where C_e is equilibrium concentration (mg/L), q_e is amount adsorbed and k_f $[(mg/g)(L/mg)^{1/n}]$ and 'n' are constants incorporating all factors affecting the adsorption process, such as capacity and intensity log qe vs log Ce shows that the adsorption follows Freundlich isotherms model. K_f and 'n' values were calculated from the intercept and slope of the plot and were found to be 1.025 and 4.70 respectively Kadirvelu et al (2003).

Effects of *Date nuts dust* concentration

The removal of Pb(II) as a function of *Date nuts dust* concentration. Increasing *Date nuts dust* concentration increased the percent removal. This is due to availability of more functional surface area, functional groups.

For quantitative removal of Pb(II) from 50 ml of 10 mg/L a maximum concentration of 70 mg is required. Similar results reported in literature Kannan et al ., (2003), Prabhavati, Nagarajan et al., (2006).

Desorption studies

Desorption studies help to elucidate the adsorption mechanism and also aids the recovery of the adsorbent. Desorption of Pb(II) was tried with various NaOH concentrations. The percentage of desorption increased with increase in concentration of NaOH. A maximum of 84.0 percentage of Pb(II) was disrobed with NaOH concentration of 0.016M at agitation time of 70 min. this may be due to the fact that in alkaline pH, the surface of the adsorbate is deprotonated and hence the alkaline surface of the adsorbent leached out the negatively charged $HPbO_4^-$ and CrO_4^{-2} species. Kadirvelu et al., (2003) and Shanamugavalli et al., (2006) reported the desorption of Pb(II) from the adsorbent in the acidic medium. Desorption studies were carried out to confirm the adsorption mechanism proposed above and to recovery the metal from the adsorbent. The quantitative recovery of metal ion indicates that regeneration of adsorbent was possible, this further suggest that ion-exchange may also involved in the adsorption mechanism (Lin et al,.1992)

Removal of Pb(II) from Lead plating wastewater

The characteristics of the wastewater collected from the chromium plating industry, collected solution pH=1.64 and adjusted to pH=2 using alkaline solution, adsorption of Pb(II) was carried out at pH=2.0 Fig-3 shows the effects of adsorbent dosage on the removal of Pb(II) from the wastewater. The percentage of adsorption increased with increase in adsorbent dosage and quantitative removal was possible with a dosage of 650 mg. A maximum 90.20 percent of Pb(II) ions at agitation time was 70min, were removed from the chromium plating wastewater containing Pb(II) concentration of 26.40 mg/L, *Date nuts dust* indicating the adsorbate can be effectively used for the treatment of industrial wastewater containing Pb(II) ions Manonmani, (2002), Selvaraj et al., (1998).

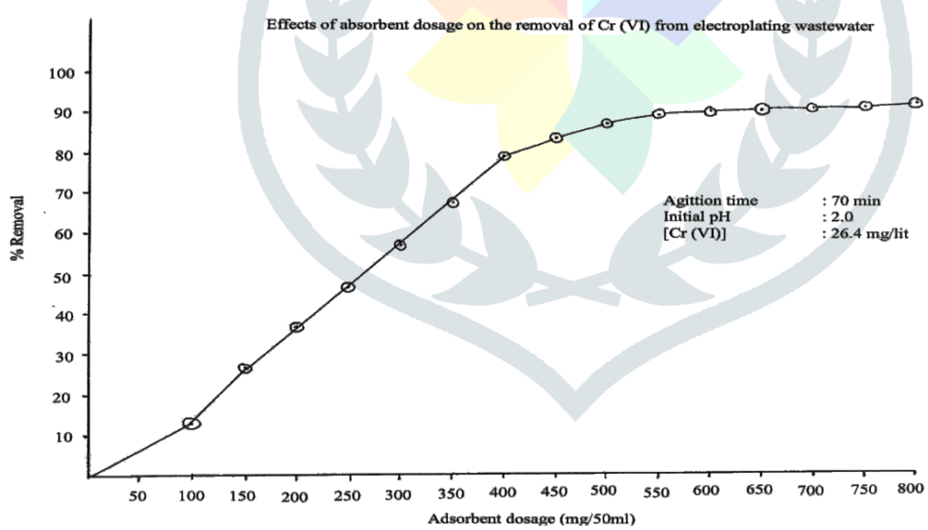

Figure – 10

Conclusion

Experimental conditions such as pH, *Date nuts dust* concentration and reaction time have been optimized to utilized *Date nuts dust* as adsorbent for the removal of Pb(II) from aqueous solution. Adsorption capacity increase with decrease of metal ion concentration and decrease with pH. The pH effect and desorption studies were studied to understand adsorption mechanism. Adsorption followed both Langmuir and Freundlich adsorption isotherms. The adsorption capacity (Q_o) was 31.53 mg Pb(II)/g of *Date nuts* dust at the initial pH of 2.0 for the particle size of 0.430 mm. The kinetic studies show that the removal of Pb(II) followed first order rate reaction given by Lagergren. Experimental results allow us to conclude an adsorption mechanism by ion – exchange between metal ion and H^+ ions on *Date nuts dust* surface. These reactions induce release of H^+ ions on the Begasse surface. The high adsorption capacity of Pb(II) in the lower pH range may be due to promotion of adsorbent surface which would favour the uptake of anionic forms $HPbO_4^-$ and PbO_4^{-2}.

References

1. *Agarwal SC, Rai SS and Mathur KC* (**1989**). Some studies on Chromium removal with coal. **J. Indian Water Works Association** 2:133.
2. APHA (**2005** 21st Edn). Standard methods for the examination of water and wastewater, **American Public Health Association**, Washington, DC.
3. *Chakravarti AK, Chowdhury SB, Chakrabarty S, Chakrabarty T and Mukherjee DC* (**1995**). Liquid membrane multiple emulsion process of Chromium(VI) separation from wastewaters. **Colloids Surf. A**: Physicochem. Eng. Aspects 103,59.
4. *Dahbi S, Azzi M and Guardia M* (**1999**). Removal of Hexavalent Chromium from wastewaters by bone charcoal. **Fresenius J. Anal. Chem**. 363, 404.
5. *Gupta GS, Prasad G and Singh VN* (**1988**). Removal of Chrome dye from water by flyash. **IAWPC, Tech. Annual** 15: 98.
6. *Kongsricharoern N, Polprasert C* (**1996**). Chromium removal by a bipolar electrochemical precipitation process. **Water Sci. Technol**. 34, 109.
7. *Kalyani S, Srinivasa Rao P and Krishnaiah A* (**2004**). Removal of Nickel(II) from aqueous solutions using marine macroalgae as the sorbing biomass. **Chemosphere** 57, pp 1225-1229.
8. *Kadirvelu K and Subbaram V* (**2003**). Activated carbon prepared from biomass as an adsorbent for the removal of Ni(II) from aqueous solution. **Indian J. Environmental Protection** 23(12): pp 1343-1350.
9. *Kannan N and Raja Kumar A* (**2003**). Suitability of various indigenously prepared activated carbons for adsorption of Mercury(II) ions. **Toxicol. Env. Chem**., 84 (1-4): pp 7-19.
10. *Lin CF, Rou W and Lo KS* (**1992**). Treatment strategy for Cr(VI)-bearing wastes. **Water Sci. Technol**. 26, 2301.
11. *Lagergren S and Svenska BK* (**1898**), **Ventempskapakad Handl**, 24.
12. *Lodha A* (**1997**). Sorption of methylene blue on to rice-husk. **Indian J. Environmental Protection**., 17(9): pp 675-679.
13. *Manonmani* (**2002**), **Ph. D Thesis**, Bharathiar University (**2002**), Coimbatore, India.
14. *Mousumisen, Manisha GD and Pradeep Roy Chowdary K* (**2005**). Biosorption of Cr(VI) by non living fusarium Sp. Isolated from soil. IIT, New-Delhi.
15. *Pagilla K and Canter LW* (**1999**). Laboratory studies on remediation of Chromium contaminated soils. **J. Environ. Eng**. 125(3), 243.
16. *Prabavathi Nagarajan and Priscilla Prabhavathi S* (**2005**). A Study of removal of Pb(II) by adsorption technique using carbonized Tamarind seed and seed coats. **Indian J. Environmental Protection** 25(5): pp 433-436.
17. *Seaman JC, Bertsch PM and Schwallie L* (**1999**). In-situ Cr(VI) reduction within coarse-textured, oxide-coated soil and aquifer system using Fe(II) solutions. **Environ. Sci. Technol**. 33, 938.
18. *Sawada A, Mori K, Tanaka S, Fukushima M and Tatsumi K* (**2004**). Removal of Cr(VI) from contaminated soil by electrokinetic remediation. **Waste Management**. 24(5), pp 483-490.

19. *Srinivasan K and Geetamani G* (**2004**). Studies on Chromium(VI) removal by activated Tamarind Nut Carbon. **Oriental Journal of Chemistry**, Vol.20(2), pp 335- 340.

20. *Stewarte* (**1975**), **Allen Black Well Scientific Publication**.

21. *Singh DB, Rupainwar DC and Prasad G* (**1992**). Studies on the removal of Cr(VI) from wastewater by feldspar. **J. Chem. Technol. Biotechnol**., 53, pp 127-131.

22. *Shanmugavalli M, Madhavakrishna S, Kadirvelu K, Sathiskumar S, Mohanraj R and Pattabhi S* (**2006**). Removal of Ni(II) from aqueous solution using silk cotton hull activated carbon. **Indian J. Environmental Protection** 26(1): pp 47-53.

23. *Selvaraj K, Chandramohan V and Pattabhi S* (**1998**). Removal of Cr(VI) from aqueous solution and chromium plating industry wastewater using photo film waste sludge. **Indian J. Environmental Protection** 18(9): pp 641-646.

24. *Tiravanti G, Petruzzelli D and passion R* (**1997**). Pretreatment of tannery wastewaters by an ion-exchange process for Cr(III) removal and recovery. **Water Sci. Technol**. 36, 197.

25. *Vasanty M, Sangeeta M and Kavita C* (**2003**). Removal of Chromium from aqueous solutions using a mixture of flyash and activated carbon, **Indian J. Environmental Protection** 23(12): pp 1321-1325.

26. *Zhou X, Korenaga T, Takahashi T, Moriwake T and Shinoda S* (**1993**). A process monitoring/controlling system for the treatment of wastewater containing Chromium(VI). **Water Res**. 27, 1049