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Removal of Toxic Metal ion Lead from Industrial Effluents using Bioadsorbent

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Abstract: *Over seventy percent of the earth's surface is covered with water and is vital for all known forms of life. Most of this water (about 97.5%) is in the oceans and seas and is too salty to drink or grow crops. Of the remaining 2.5%; 1.73% is frozen in the icecaps of Antarctica and Greenland leaving only about 0.77% available for our fresh water supply. Of the total water on the earth, only 0.0008% is available and renewable in rivers and lakes for human and agricultural use [1]*

Keywords: *water*

I. INTRODUCTION

1.1 Background

Over seventy percent of the earth's surface is covered with water and is vital for all known forms of life. Most of this water (about 97.5%) is in the oceans and seas and is too salty to drink or grow crops. Of the remaining 2.5%; 1.73% is frozen in the icecaps of Antarctica and Greenland leaving only about 0.77% available for our fresh water supply. Of the total water on the earth, only 0.0008% is available and renewable in rivers and lakes for human and agricultural use [1]. It is the water that falls as rain or snow or that has been accumulated and stored as groundwater that we depend on for our "clean" water resource. For 1.5 to 2.5 billion people in the world, clean water is a critical issue. It is estimated that by the year 2025, there will be an additional 2.5 billion people on the earth who will live in regions especially (Asia) Ranipet already lacking sufficient clean water.

Basic Reference Guide to the Sources and Symptoms of the Common Toxic Metals:

Sources

Arsenic - pesticides, beer, table salt, tap water, paints, pigments, cosmetics, glass and mirror manufacture, fungicides, insecticides, treated wood and contaminated food.

Cadmium - cigarettes, (tobacco and marijuana), processed and refined foods, large fish, shellfish, tap water, auto exhaust, plated containers, electroplating, motor oil, galvanized pipes, air pollution from incineration and occupational exposure.

Copper - tap water, pesticides, swimming in pools, intra-uterine devices, vegetarian diets, dental amalgams, nutritional supplements - especially prenatal vitamins, birth control pills, weak adrenal glands and occupational exposure.

Lead - tap water, cigarette smoke, hair dyes, paints, inks, pencils, glazes, pesticide residues and occupational exposure in battery manufacture and other industries.

Mercury - dental amalgams, large fish, shellfish, medications, air pollution, manufacture of paper, chlorine, adhesives, fabric softeners and waxes.

Chromium - steel alloys, bricks in furnaces, dyes and pigments, plating, leather tanning, and wood preserving.

Nickel - hydrogenated oils (margarine, commercial peanut butter and shortening), shellfish, air pollution, cigarette smoke, plating and occupational exposure.

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II. EXPERIMENTAL SECTION

2.1 Preparation of the Adsorbent

Neem Leaves (Azadirachata Indica) and Jute (Corchorus Capsularis) Sticks were collected from Ranipet District Tamilnadu then washed thrice with tap water to remove dust and water soluble impurities and are dried until the leaves and sticks become crisp. The dried leaves and sticks are powdered. Then the neem leaf powder (NLP) and jute sticks powder (JSP) are sieved to achieve uniform size. The resulting NLP and JSP fractions are preserved in glass bottles for use as an adsorbent. Nut Shell (Arachis hypogaea) was collected and prepared nut shell powder (NSP). The bio-adsorbents were chosen keeping in view low cost, easily available, safety to health and ease of application.

2.2 Preparation of Calibration Curve

100 ml standard solutions of different concentration such as 0.5 ppm, 1 ppm, 2 ppm , 4 ppm, were use for calibration curve. For each concentration, four replicate measurements were performed and average values were used for calibration curve. The calibration curve was straight line and it follows the Beer- Lambert law.

2.3 Determination of Heavy Metals (Pb) from Wastewater Samples

The water samples were digested as follows. The samples ($100cm^3$) were transferred into a beaker and 5ml concentrated HNO_3 was added. The beaker with the content was placed on a hot plate and evaporated down to about 20ml. The beakers were cooled and another 5ml of concentrated HNO_3 was added. The beakers were covered with watch glass and returned to the hot plate. The heating was continued, and then small portion of HNO_3 was added until the solutions appear light coloured and clear. The beaker wall and watch glass were washed with distilled water and the samples were filtered to remove some insoluble materials that could clog the atomizer. The volume of the samples was adjusted to 100 cm3 with distilled water. A blank sample was digested so as to allow a blank correction to be made. This was done by transferring 100ml of distilled water into a beaker and digested as described above.

2.4 Batch Equilibration Method

The adsorption experiments were carried out in a batch process at 25°C temperature. The known weight of adsorbent material was added to 100 mL of metal ion solutions with an initial concentration from 4.0 mg/L- 10.0mg/L. The contents were shaken thoroughly using a mechanical shaker .The solution was then filtered at preset

III. RESULTS AND DISCUSSION

3. 1 Adsorption of Metal ions from Prepared Standard Solution

3.2 Adsorption of Metal ions from Industrial Effluent

3.1.1 Lead

3. 1. 1. 1 Effect of Contact Time and Initial Metal ion Concentration

The experimental results of adsorptions at various Pb(II) ion concentrations of 4.0, 6.0, 8.0 and 10.0 mg/L at different contact time were shown in Figures 1, 2 and 3, of NLP, NSP, and JSP, respectively. The equilibrium data reveal that, percent adsorption decreased with an increase in initial Pb(II) ion concentration, but the actual amount of Pb(II) ion adsorbed per unit mass of NLP, NSP and JSP increased with increase in Pb(II) ion concentration. It means that the adsorption is highly dependent on initial concentration of Pb(II) ions. It is because of the fact that at lower concentration, the ratio of the initial number of Pb(II) ion to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of Pb(II) ions is dependent upon initial concentration . It took five hours to reach equilibrium for all concentrations. Figures 2 and 3 reveal that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the Pb(II) ions on the NLP, NSP and JSP surface.

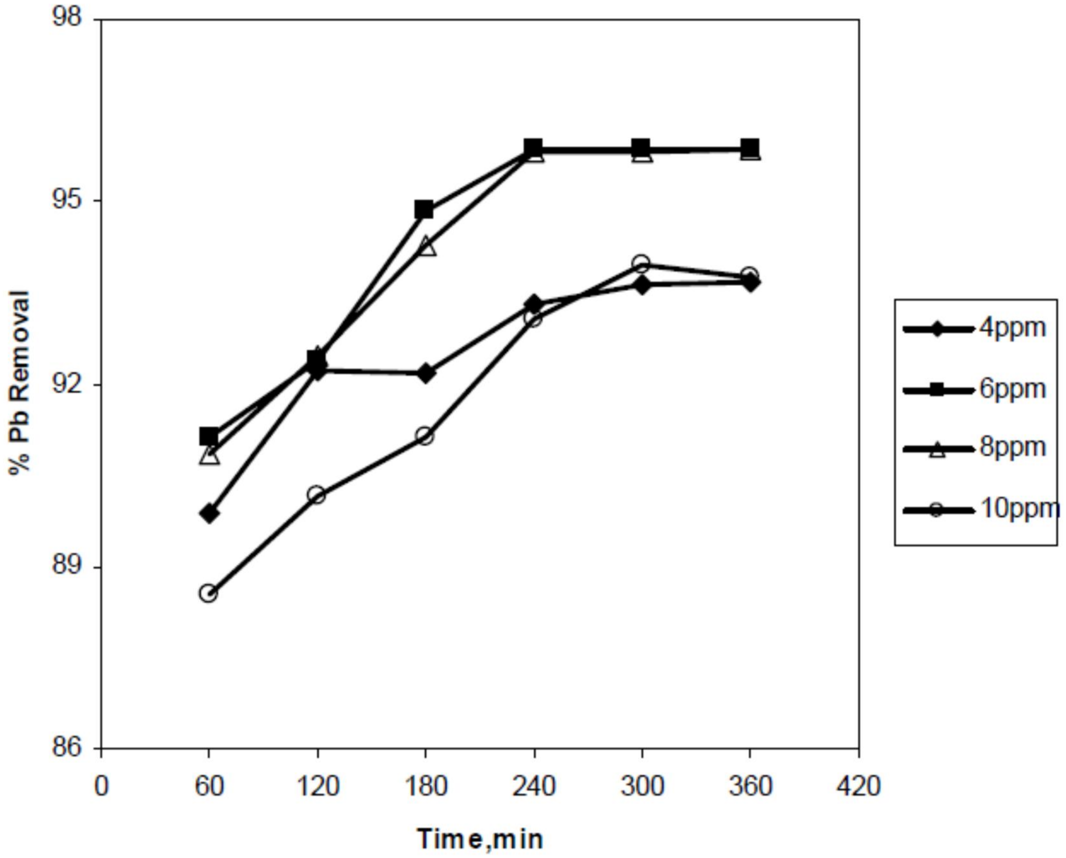

Figure 1: % of Pb(II) Removal vs Contact time with NLP

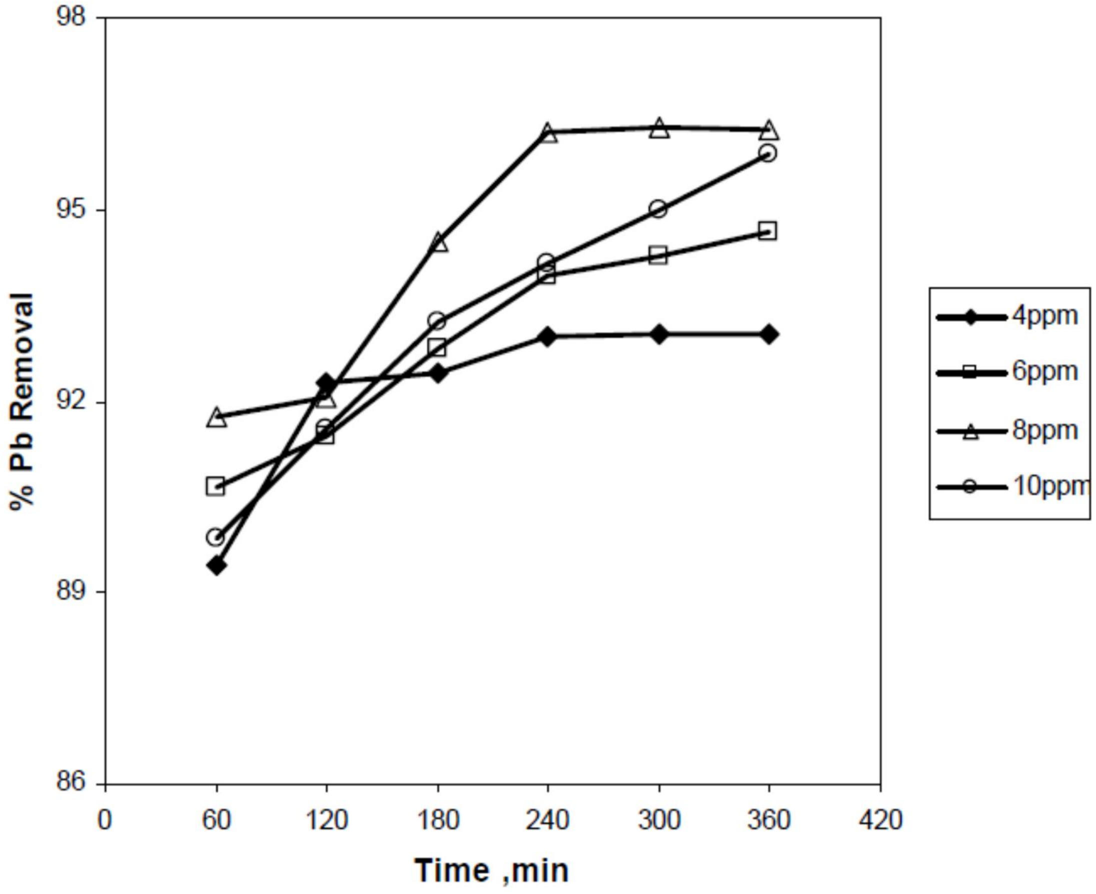

Figure 2: % of Pb(II) Removal vs Contact time with NSP

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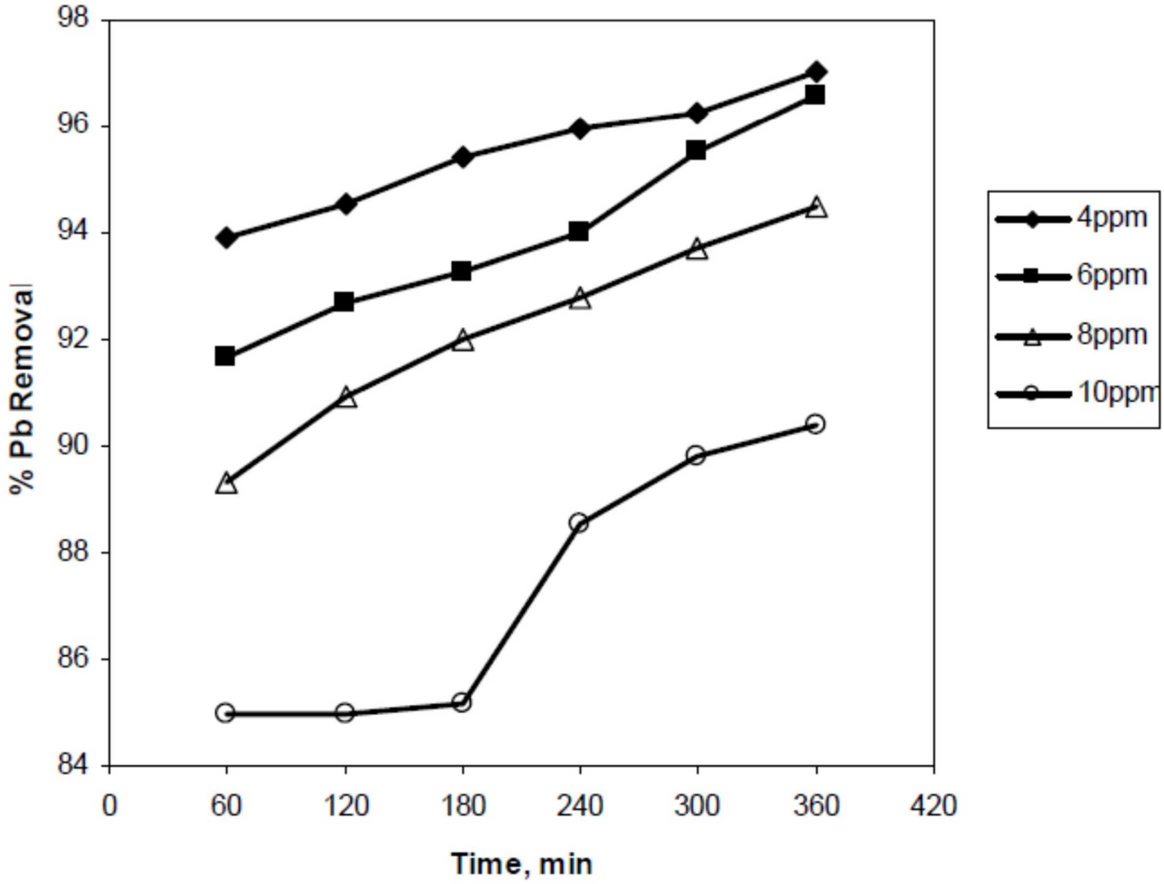

Figure 3: % of Pb(II) Removal vs Contact time with JSP

3. 1. 1. 2 Effect of Adsorbent Dosage

The effect of adsorbent dosage on the removal capacity was also studied for NLP, NSP and JSP. The removal capacity of Pb(II) ion was determined by passing Pb(II) solutions of different concentrations (4.0 mg/L- 10.0mg/L) through the column using a fixed amount (1g) of adsorbent. Secondly, the data were collected for varying amounts of the adsorbent (NLP) at a fixed concentration of (6.0 ppm) Pb(II) ion-solution. The Pb(II) ion concentration was then measured in the outlet to calculate the percent of removal as shown in Table 1. It was observed that 1g NLP adsorbed Pb(II) ion from 100 ml Pb(II) solution of 4.0 ppm, 6.0 ppm, 8.0 ppm and 10.0 ppm and percentage of adsorption were 93.64%, 96.27%, 95.83% and 93.96%, respectively. Similarly, NSP and JSP were studied and the data are given in Table 1 The relation between the percentages of removal of Pb(II) with adsorbent dosage is shown in Figure 4. From this curve, it is clear that the percent of removal of Pb(II) increased with the increase of adsorbent dosage and reached almost saturation with 96.27%, 94.45% and 95.57% removal for NLP, NSP and JSP, respectively when the amount of adsorbent was ≥ 2g of adsorbents for the 6.0 ppm Pb(II) in 100mLsolution.

Table 1: Data for the fixed amount of adsorbent dosage of NLP, NSP and JSP equilibrium at 360 minutes

Amount Adsorbent (g)	Initial metal Conc., *Co* (ppm)	% of Pb Removal		
		NLP	NSP	JSP
1g	4	93.64	93.05	96.26
	6	96.27	94.27	95.50
	8	95.83	96.27	93.71
	10	93.96	95.00	89.81

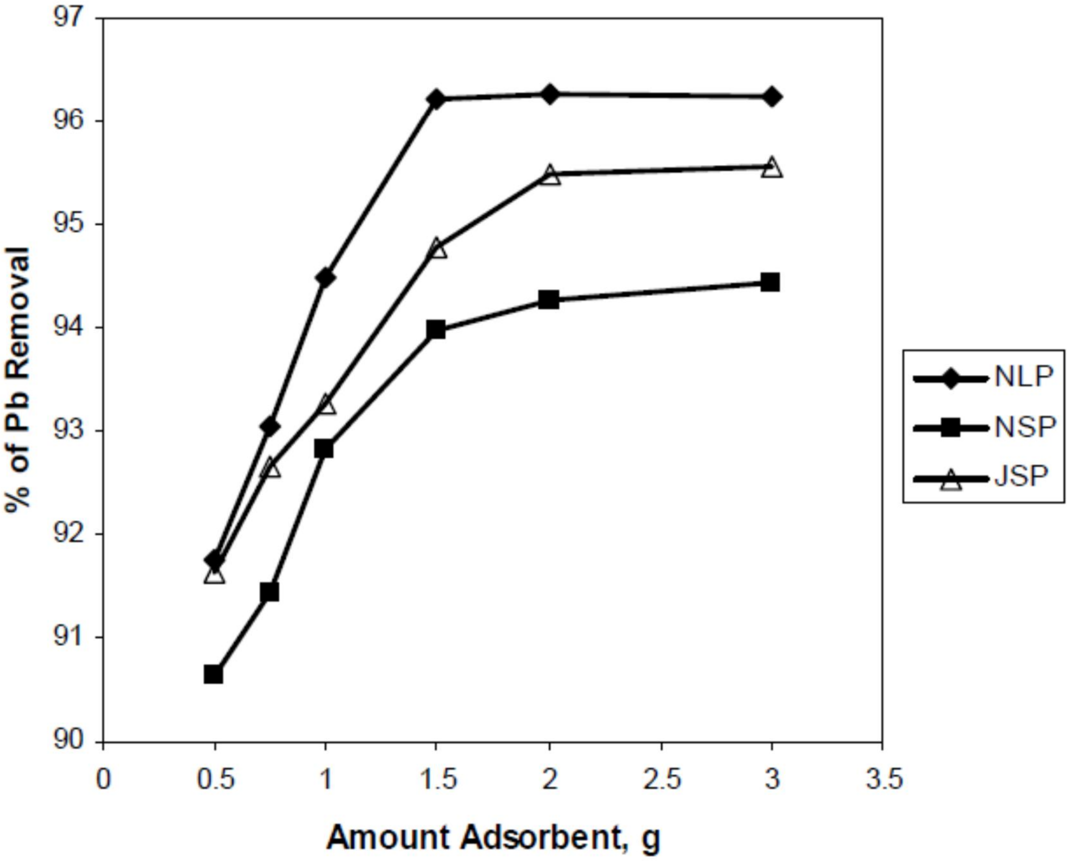

Figure 4: Effect of adsorbent dosage (NLP, NSP, and JSP) on the removal of Pb(II) with fixed concentrated solution (6.0 mg/L) and contact time 360 minutes

3.1.1.4 Effect of pH

The experiments carried out at different initial pH show that the adsorption percentage increases with increase in initial pH of the medium up to 7 and then decreases as depicted in the Figure 5. This behavior can be explained using pH of the adsorbent. In addition the decrease in adsorption of metal ions at low pH can be attributed to the competition between H^+

and metal ions. It is thus clear from Figure 5 that at lower pH, the adsorption of Pb(II) ion studied is drastically reduced. This observation was made to use of to desorb the Pb(II) ion from the adsorbed material.

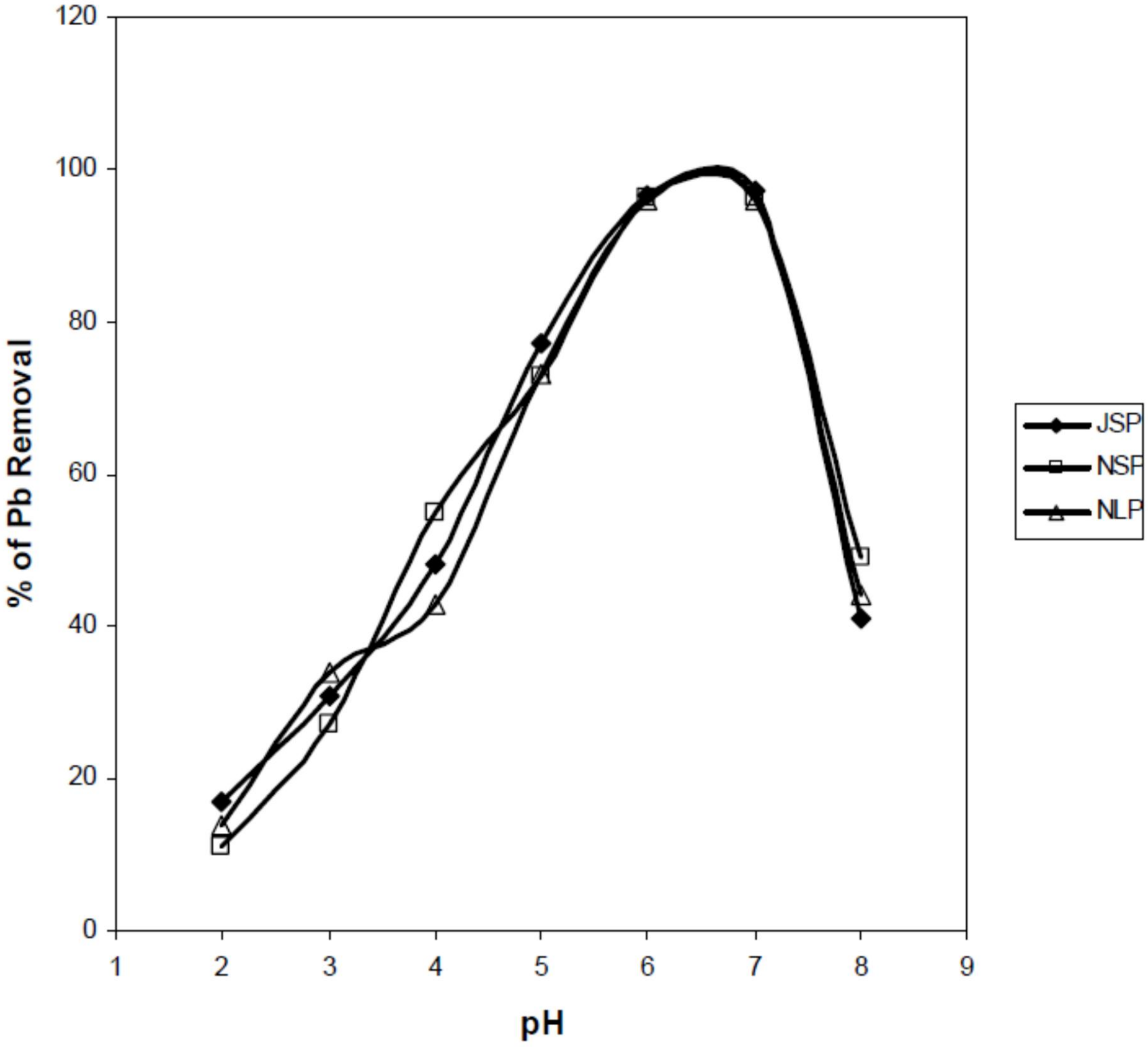

Figure 5: Effect of pH for removal of Pb(II) ion onto NLP, NSP, JSP, contact time 360 minutes, Pb(II) ion 6.0 mg/L and adsorbent 1.0 g.

3.1.1.5 Desorption Studies

In metal ion removal process, it is important to study desorption of the adsorbed metal ions under suitable conditions. In the desorption studies deionized water was used as a desorbing agent. The NLP, NSP and JSP samples loaded with different adsorbed amount of Pb(II) ions (initial Pb(II) concentration are 4.0, 6.0, 8.0 and 10.0 mg/L) were placed in 100 ml deionized water and the amount of Pb(II) ions desorbed were measured from 0.5 g of different adsorbents after two hours contacted time. Table 2 shows the data of the adsorbed and desorbed amount of Pb(II).ions. The data showed that there was small amount Pb(II) ions desorbed from different adsorbent surface indicating the strong contact between Pb(II) ion and NLP, NSP and JSP surfaces. But when we use 0.1M HCl as a desorbing agents, the percentage of desorption is higher. The desorption indicate that hydrochloric acid is a better reagent for desorption of Pb(II) ion from NLP, NSP and JSP. The reversibility of adsorbed Pb(II) ions in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of Pb(II) ions by mineral acid medium indicates that the Pb(II) ions were adsorbed onto the NLP, NSP and JSP through by physisorption mechanisms.

Initial Conc. C_o (mg/L)	Amount Adsorbed, C_{ads} (mg/g)			% Desorption with deionized water			% Desorption with 0.1M HCl		
	NLP	NSP	JSP	NLP	NSP	JSP	NLP	NSP	JSP
4	3.688	3.691	3.881	0.050	0.056	0.052	2.356	1.019	1.763
6	5.542	5.487	5.794	0.064	0.051	0.057	2.012	1.243	1.080
8	7.398	7.365	7.560	0.061	0.066	0.063	3.079	2.064	1.983
10	9.015	9.157	9.037	0.043	0.065	0.065	2.874	1.704	2.045

Table 2: Adsorption and Desorption data for Pb(II) on NLP, NSP, and JSP

3.1.1. 3 Evaluation of Bio-sorption Efficiency

Sequestering of metallic species by biomass has been traced mainly into the cell wall of the fungal biomass. The cell wall is not necessarily the only site where the sequestered metals might be situated. They may also be found within the cell, coupled with various organic parts or may crystallize in the cytoplasm or may interact with DNA and RNA. The drying and then grinding of bio-adsorbent, following heating at around 65ºC unveiled the sites where metal ion could be sequestered, increasing the probability of encountering metal ions at such sites.

The biosorption data for the removal of Pb(II) ions were correlated with Langmuir and Freundlich models . The Langmuir equation (Eq.1) is valid for monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies. Using the Langmuir equation (Eq.1), the linear plots of $1/C_{ads}$ versus $1/Ce$ were obtained which suggest the applicability of the Langmuir isotherm was shown in Figures 6, 7 and 8 for NLP, NSP and JSP, respectively. Values of K_L and b were determined from slope, $1/K_L b$ and intercept $1/K_L$ of the plots and were presented in Table 3.

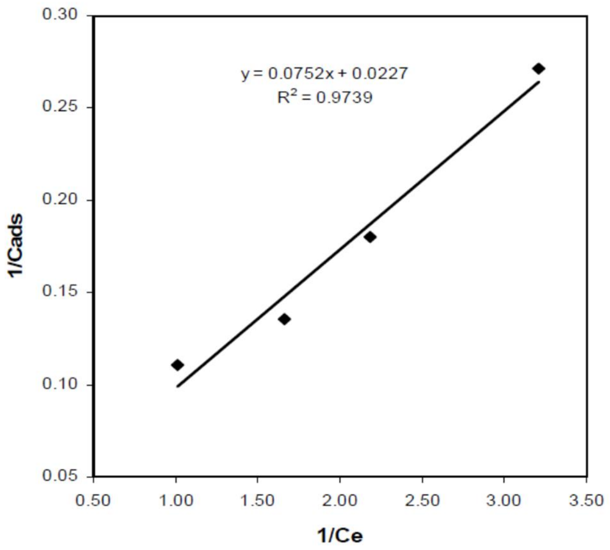

Figure 6: Langmuir isotherm model for adsorption of Pb(II) ion onto NLP.

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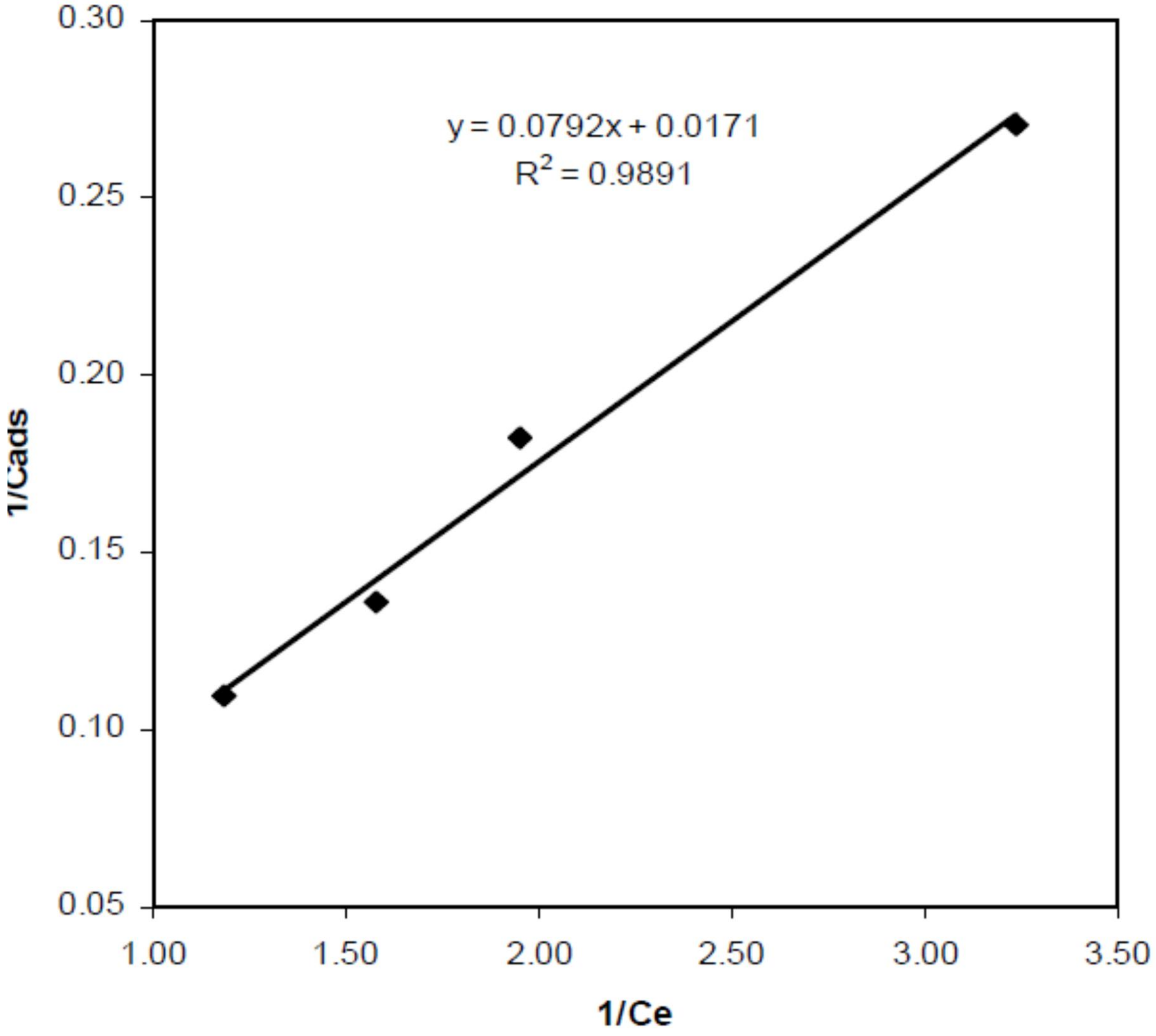

Figure 7: Langmuir isotherm model for adsorption of Pb(II) ion onto NSP

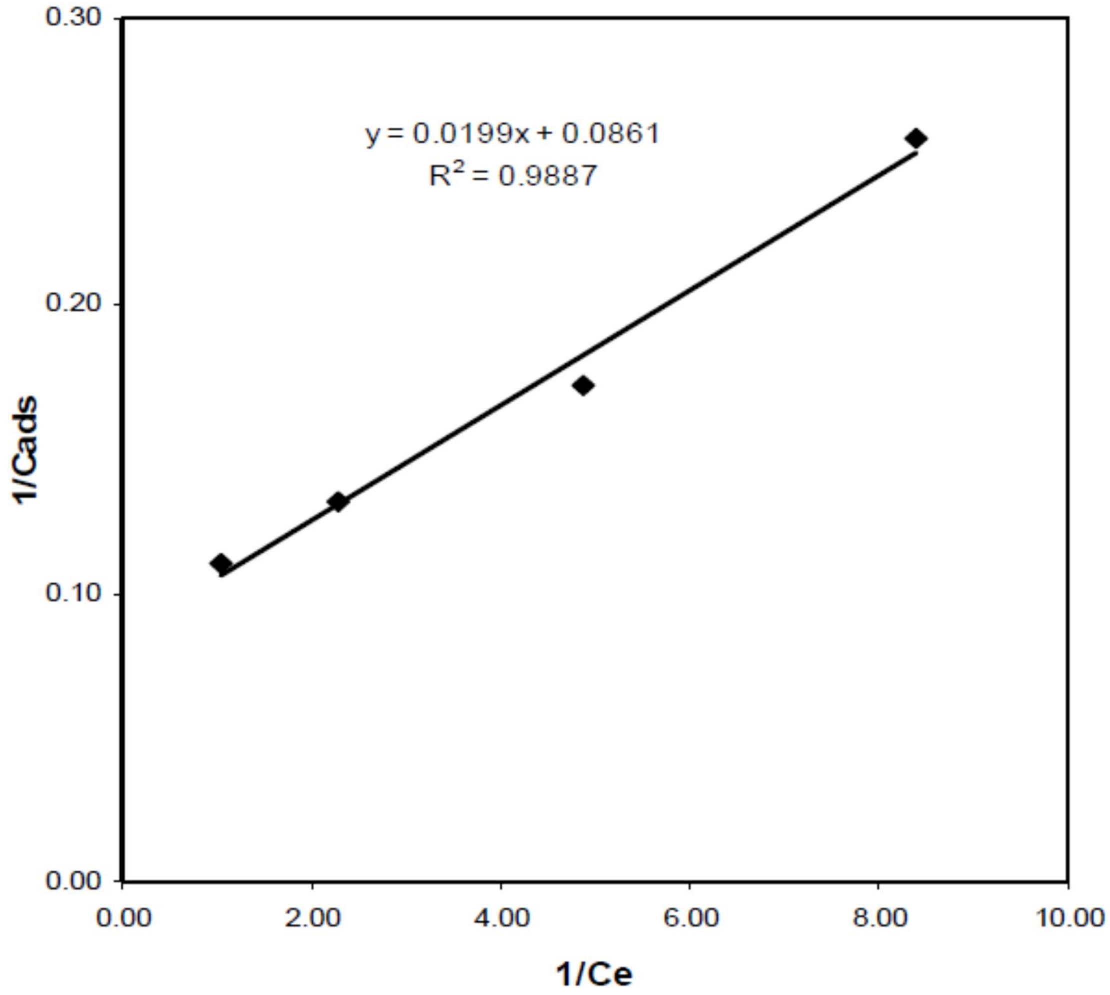

Figure 8: Langmuir isotherm model for adsorption of Pb(II) ion onto JSP.

Table 3: Langmuir constants for adsorption of Pb(II) ion onto NLP, NSP, JSP

Langmuir Constants			
Different Adsorbents	K_L kg/kg (Pb(II)/Ads)	b m^3 /kg	R^2
NLP	4.405×10^{-3}	302	0.9739
NSP	5.848×10^{-3}	216	0.9891
JSP	1.161×10^{-3}	4327	0.9887

The observed K_L values suggest that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface .characteristics, when ion exchange is the predominant mechanism takes place in the adsorption of Pb(II) ion. Further, the essential features of the Langmuir adsorption isotherm can be expressed in terms of dimensionless constant, called separation factor or equilibrium parameter (R_L) which can

V. CONCLUSIONS

Our goal was to find a process for the removal of Pb(II) ions from industrial wastewater, which would be easier, readily available and better from the economic point of view compared to the other processes. NLP, NSP and JSP are very effective adsorbent for the removal of toxic metal ions such as Pb(II) even when their concentration is as low as 4 ppm. These bio-adsorbents are cheap, abundant and above all biodegradable. Furthermore the adsorbents show maximum removal capacity at pH 6. This indicates that no additional reagent is required to control the pH of the medium. So, they may be replaced most conventional adsorbents in the removal and recovery of metal ions from industrial wastewater. From the results, it is possible to conclude that:

- The experimental data produces good fits with both Langmuir and Freundlich isotherms and the adsorption coefficients agree well with the conditions supporting favorable adsorption.
- Neem leaf powder (NLP), Nut shell powder (NSP) and Jute stick powder (JSP) have very good potential for utilization as an adsorbent for Pb(II) from aqueous medium. But for Cr(III), they show less potential adsorption capacity. Above 95% Pb(II) and Cd(II) can successfully be removed by using NLP, NSP and JSP as adsorbents.
- The kinetics of adsorption of Pb(II) on NLP, NSP and JSP are complex and while the results were tested with models based on pseudo first order and Pseudo second order equation, close conformity could be obtained with pseudo second order mechanism.
- The adsorption is influenced by pH of the medium, initial concentration of the metal ions and the amount of the adsorbent.
- The adsorption process is spontaneous at room temperature and normal pressure.
- Desorption studies indicate that hydrochloric acid is a better reagent than deionized water for desorption Pb(II) ions from NLP, NSP and JSP.

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