CHAPTER 5

PREPARATION AND CHARACTERIZATION OF NATURAL ION EXCHANGER, REMOVAL OF HEXAVALENT CHROMIUM, COPPER AND LEAD FROM WASTE WATER AND INDUSTRIAL EFFLUENTS BY NATURAL ION EXCHANGER
CHAPTER: 5

5.0 PREPARATION AND CHARACTERIZATION OF NATURAL ION EXCHANGER:

INTRODUCTION

The increased population and industrialization may cause discharging of heavy metals in environment, which is responsible for pollution of water and soil. Many industrial operations, agricultural practices and human activities are increase concentration of heavy metals in water and soil. These heavy metals are essentials for living organism up to proper limits above these they become hazardous. Hence there is necessity to remove them from water and soil (Rane et al., 2010). A number of technologies have been developed over the years to remove heavy metals from industrial waste water. The most important technology includes adsorption and coagulation ion exchange, electro coagulation (Dermentzis et al., 2011), adsorption (Talla et al., 2010), bio sorption (Mane et al., 2010) and zeolite (Kragovic et al., 2012). Ion exchange can be used to remove heavy metals from waste water using an ion exchange resin as synthetic ones derived from Dowex HCR-S (Fil et al., 2012), D-151 weak acid resin (Xiong and Yao, 2011), amberlite 200 (Alguacil, 2003). The natural ion exchangers are Attapulgite (Zhang et al., 2009), Kudzu (Pueraria lobata Ohwi) (Brown, 2000), activated carbon (Ghazy and El-morsy, 2009), fly ash (Ozturk and Kavak, 2005), fungal biomass (Loukidou et al., 2003), Tamarindous indica seeds (Kuchekar et al., 2011), rice husk (Gopal Krishnan and Jeyadoss, 2011).

In the present study, adsorption of hexavalent chromium, copper and lead by naturally occurring Tamarindous indica seeds powder is examined. The purpose of the study is to examine heavy metal removal by natural ion exchanger. The parameters that influence adsorption viz. pH, ion exchanger dose, temperature, contact time were investigated.
**EXPERIMENTAL**

**Preparation of resin:**

The 5 kg of seeds of Tamarindousindica was pulverized after drying it in sun light in open air for one week. Small size piece of dried seed has been grinded for 200 mesh powder. This powder is treated with 39% formaldehyde and 0.2N. Sulphuric acid at 80° c. for half an hour, after cooling and washing with double distilled water substrate allow drying for overnight in open air. Dried powder is used for adsorption studies.

**Scheme:**

Seed powder → formaldehyde 700 ml → 0.1 mol L^-1 sulphuric acid 10 ml heat for 30 min at 80° C → Cool the substrate → filter → wash with double dist. water → Dried at open air and use this substrate as an insoluble natural ion exchange resin.

![Scheme Diagram](image-url)
Table 1: Characteristic properties of ion exchange resin.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical form</td>
<td>Spherical</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.15 m/cm³</td>
</tr>
<tr>
<td>Ash content</td>
<td>10.4 %</td>
</tr>
<tr>
<td>Moisture content</td>
<td>8.7 %</td>
</tr>
<tr>
<td>Matter soluble in water</td>
<td>8.4 %</td>
</tr>
<tr>
<td>Matter soluble in acid</td>
<td>18 %</td>
</tr>
<tr>
<td>Water holding capacity</td>
<td>80.32 %</td>
</tr>
</tbody>
</table>

Plant profile:

Table 2: Botanical classification of Tamarindous indica.

<table>
<thead>
<tr>
<th>Kingdom</th>
<th>Plantae</th>
</tr>
</thead>
<tbody>
<tr>
<td>Division</td>
<td>Magnoliphyta</td>
</tr>
<tr>
<td>Class</td>
<td>Magnolipsida</td>
</tr>
<tr>
<td>Order</td>
<td>Fibulas</td>
</tr>
<tr>
<td>Family</td>
<td>Fabaceae</td>
</tr>
<tr>
<td>Subfamily</td>
<td>Caesalpinoideae</td>
</tr>
<tr>
<td>Tribe</td>
<td>Detarieae</td>
</tr>
<tr>
<td>Genus</td>
<td>Tamarinouds</td>
</tr>
<tr>
<td>Species</td>
<td>Indica.</td>
</tr>
</tbody>
</table>
Instrumentation:
Ellico MAKE MODEL SL-159 spectrometer was used absorbance measurement. Equiptronic make digital PH meter was used for measurement of PH.

Reagents: All chemical were used of analytical grade

Characterization of ion exchange resin:

FTIR Analysis:
The FTIR spectra of raw seeds powder, Formaldehyde treated resin are shown in Fig. 1 and 2. The fact that broad peak in between 3462 and 3281 cm⁻¹ is indicates presence of phenolic – OH group in both resin. IR absorption at 2924 cm⁻¹ so indicates presence of = C – H group on the benzene ring. The 1600 – 1500 cm⁻¹ absorption peak clearly indicates the presence of aromatic double bonds in both resin. The IR bonds in the region of 1149 – 1066 cm⁻¹ indicate C – O bond in raw resin. One characteristic peak at 1739 – 1743 cm⁻¹ indicates presence of ester group in both resins. Some peaks in the region of 1670 – 1612 cm⁻¹ also are of due to olefinic bonds in raw and treated resin. The IR frequency at 2924 cm⁻¹ is due to stretching vibration of – CH₂ – group in alkane. IR absorption at 2022 cm⁻¹ in treated resin also suggest presence of – CH₂ – group in between two phenolic rings which is lower frequency than that of raw seeds powder.
Fig. 1: FT-IR spectrum of raw seed powder.

Fig. 2: FT-IR spectrum of phenol formaldehyde resin.
SEM and EDX Analysis:

The morphological analysis of raw resin and phenol formaldehyde resin was performed by SEM as shown in Fig. 3 and 4. Many small pores and particles > 5\(\mu\)m diameter are observed on the surface of resin. EDX spectrum from Fig. 5 and 6 does not showed any peak of metal ions.

Fig. 3: SEM photograph of raw seed powder.

Fig. 4: SEM photograph of phenol-formaldehyde resin.
Fig. 5: EDX spectra of raw seed powder.
Fig. 6: EDX spectra of phenol-formaldehyde resin.
5.1 Removal of hexavalent chromium from industrial effluents by
natural ion exchanger:

Introduction

Rapid industrialization affects to rise up disposal of heavy metals in environment. The exceeding increase in the use of heavy metals leads to environmental as well as public health problems (Gaikwad et al., 2010). Toxic heavy metal ions discharge in waste water through various industrial activities as mining, refining of ores, fertilizer industries, tanneries, batteries, paper industries, pesticides, nuclear power plant and textile industries (Rane et al., 2010).

The electroplating and metal finishing plants discharge waste water contains hexavalent and trivalent chromium. Hexavalent chromium requires high cost chemicals for reduction, so was usually treated with ion exchange resin which offers greater advantages (Sapari et al., 1996). Trivalent chromium is essential in human nutrition (glucose metabolism). Most of the hexavalent compounds are toxic cause’s lungs cancer. Chromium (VI) moves readily through the soil and aquatic environment which was strong oxidizing agent, being absorbed through the skin. The maximum concentration limits for chromium (VI), discharge in to ground water is 0.1 mg/l and in potable water is 0.05 mg/l (Nomanbhay and Palanisamy, 2005). A number of technologies have been developed over the years to remove heavy metals from industrial waste water. The most important technology includes adsorption and coagulation ion exchange electro coagulation (Dermentzis et al., 2011), adsorption (Talla et al., 2010), bio sorption (Mane et al., 2010) and zeolite (Kragovic et al., 2012). Ion exchange can be used to remove heavy metals from waste water using an ion exchange resin as synthetic ones derived from Dowex HCR-S (Fil et al., 2012), D-151 weak acid resin (Xiong and Yao, 2011), amberlite 200 (Alguacil, 2003). The natural ion exchangers are Attapulgite (Zhang et al., 2009), Kidzu (PuerariaLobataOhwi) (Brown, 2000), activated carbon (Ghazy and El-morsy, 2009), coconut husk (Dave et al., 2012), fly ash (Ozturk ang Kavak, 2005). fungal
biomass (Loukidou et al., 2003). *Tamarindous indica* seeds (Kuchekar et al., 2011), rise husk (Gopal Krishnan and Jeyadoss, 2011), al., 2008).

In the present study, adsorption of chromium (VI) by naturally occurring *Tamarindous indica* seeds powder is examined. The purpose of the study is to examine heavy metal removal by natural ion exchanger. The parameters that influence adsorption viz. pH, ion exchanger dose, temperature, contact time were investigated.

**Experimental**

**Seed powder:**

*Tamarindous Indica* seeds were pulverized after drying in sunlight and open air for one week. Small size pieces of dried seeds were ground and passed through the mesh size 200 unit. This powder was treated with 39% formaldehyde and 0.1 mol L⁻¹ sulphuric acid at 80°C for 30 min. After cooling and washing with double distilled water, substrate was allowed to dry for overnight in open air. Dried powder was used for adsorption studies. The properties of resin were reported in Table 1.

**Scheme**

| Seed powder | → formaldehyde 700 ml | → |
| 0.1 mol L⁻¹ sulphuric acid 10 ml | → heat for 30 min at 80°C |
| Cool the substrate | → filter | → wash with double dist. water |

dried at open air and use this substrate as a insoluble natural ion exchange resin.
Sorbet:

For adsorption study stock solution of chromium (1000 mg/l) was prepared by dissolving 4.8 g of chromium sulphate [Cr₂(SO₄)₃·6H₂O] in double distilled water (DDW). The various concentrations were then obtained by diluting the stock solution with double distilled water.

Method for Separation of Chromium:

25 ml chromium solution [Cr₂(SO₄)₃·6H₂O] having concentration 1.0 mg/l was transferred to a beaker. pH of this solution was adjusted to 6.5 ± 0.1 and was transferred to a 250 ml conical flask. In this solution, 3.5 g natural adsorbent was added with successive shaking for 30 min. Solution is filtered using what man filter paper no. 41 and concentration of chromium remain in solution was determined using Shimadzu UV-visible spectrophotometer by standard method (Cotton et al., 1999). In a method, 0.6 mL of 7.0 mol L⁻¹ hydrogen peroxide solution, 0.2 mL of 10⁻¹ mol L⁻¹ potassium cyanide and 5.5 mL of buffer solution (pH 6.5) were transferred in 25 ml standard volumetric flask. This solution is warmed at 60°C in a water bath for 10 min. The effluent from column was transferred in it after mixing the solution. absorbance were measured at 360 nm. The initial concentration C₀ (mg/l) and equilibrium concentration at various time intervals Cₑ (mg/l) were determined and metal uptake qₑ (mg/l) was calculated from the mass balance equation as:

\[ qₑ = (C₀ - Cₑ) \frac{v}{m} \]  

Where, \( C₀ \) and \( Cₑ \) are the initial and equilibrium concentration of chromium solution (mg/l), \( v \) is the solution volume (ml), and \( m \) is the adsorbent weight (g). The adsorption capacity was calculated using the equation (Badmus et al., 2007)

\[ \text{adsorption capacity} = \frac{(C₀ - Cₑ)}{C₀} \times 100 \]  

The sorption equilibrium data for chromium on Tamarindousindica seeds powder was analyzed in terms of the Freundlich and Langmuir isotherm models. The Langmuir isotherm equation could be written as:
\[ \frac{q_e}{q_m} = \frac{K_i C_e}{1 + K_i C_e} \]  

Where

\( q_e \) = the equilibrium concentration on adsorbent (mg/g)

\( C_e \) = equilibrium concentration in solution (mg/l)

\( q_m \) = maximum adsorption capacity (mg/l)

\( K_i \) = adsorption equilibrium constant (mg/l)

This method is based on the assumption that the forces of interaction between sorbed molecules are negligible and once a molecule occupies a site no further sorption take place.

Also, the logarithmic form of Freundlich equation may be written as:

\[ q_e = K_F C_e^{\frac{1}{n}} \]  

Where.

\( q_e \) = the equilibrium concentration of adsorbent (mg/g)

\( C_e \) = equilibrium concentration in solution (mg/l)

\( K_F \) = adsorption capacity

\( n \) = reaction energy

The Freundlich equation can be described by assuming a heterogeneous surface with adsorption on each class of sites. Although this expression is empirical, \( 1/n \) reflects the curvature in the isotherm and may represent the energy distribution of adsorption sites.

The liberalized form of Freundlich sorption isotherm is:
\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\] 

By plotting \( \ln q_e \) versus \( \ln C_e K_F \) and \( n \) can be determined, if a straight line is obtained.

To study the effect of important parameters like contact time, resin amount, pH, initial metal concentration and temperature on the removal of Cr (VI) by natural ion exchanger, experiments were conducted at room temperature except those in which the effect of temperature. The parameters chosen in the experiments were reported in Table 2.

**Results and Discussion**

**FTIR Analysis:**

The FTIR spectra of raw seeds powder, Formaldehyde treated resin and Cr (VI) adsorbed resin are presented in Fig. 1-3 respectively. The fact that broad peak in between 3462 and 3281 cm \(^{-1}\) indicates presence of phenolic – OH group in both resin. IR absorption at 2924 cm \(^{-1}\) also indicates presence of \( = \text{C} - \text{H} \) group on the benzene ring. The 1600 – 1500 cm \(^{-1}\) absorption peak clearly indicates the presence of aromatic double bonds in both resin. The IR bonds in the region of 1149 – 1066 cm \(^{-1}\) indicate \( \text{C} - \text{O} \) bond in raw resin. One characteristic peak at 1739 – 1743 cm \(^{-1}\) indicates presence of ester group in both resins. Some peaks in the region of 1670 – 1612 cm \(^{-1}\) also are of due to olefinic bonds in raw and treated resin. The IR frequency at 2924 cm \(^{-1}\) is due to stretching vibration of \( - \text{CH}_2 - \) group in alkane. IR absorption at 2022 cm \(^{-1}\) in treated resin also suggest presence of \( - \text{CH}_2 - \) group in between two phenolic rings which is lower frequency than that of raw seeds powder. Hence due to adsorption of Cr (VI) ion color of product change because of d – d transition (Hommaid and Hamdo, 2014).
SEM and EDX Analysis:

The morphological analysis of phenol formaldehyde resin was performed by SEM as shown in Fig. 4a – 4c. Many small pores and particles \( \geq 5 \mu m \) diameter are observed on the surface of resin. Pores are not observed in Fig. 4c, clearly indicates that biosorption of chromium on phenol formaldehyde resin. EDX spectrum from Fig. 5c, also showed a peak at 0.5 KeV, which confirmed that Cr (VI) was adsorbed on phenol formaldehyde resin, which was absent in Fig. 5a and 5b. It supports that the reaction of metal ion and phenolic –OH group on phenol formaldehyde resin surface may be partly ion exchange or complexation (Mulani et al., 2013).

Effect of pH on ion exchange process:

In order to establish the effect of pH on the ion exchange of chromium (VI) ion on natural resin, the batch equilibrium studies at different pH values were carried out in the range of 1.0 - 7.0 for a constant ion exchanger of 3.5 g/l and initial metal concentration of 25 mg/l at 298 K (Fig. 1). The high values of pH were not studied because of precipitation of metal ion take place. Fig.6 shows the change in metal uptake by natural ion exchange resin at different pH levels. It can be seen from Fig. 6, the pH of the aqueous solution is important control parameter in the ion exchange process (Dekhilet et al., 2011). The percentage removal of metal increased with pH 1.0 - 7.0 with maximum binding at pH 6.5. At this pH 99 % removal of chromium was observed.

Effect of initial metal concentration on ion exchange process:

The 25 ml of chromium (VI) metal solution of different concentrations ranging from 25 to 250 mg/l with 3.5 gm of ion exchanger was stirred with ambient temperature (298K) for a contact period of 30 min. The result obtained is shown in Fig. 7. It was also realized that the capacity of metal removed by natural ion exchanger at the equilibrium increased with the initial concentration of metal but the percent removal decreased with the increase in initial metal concentration. Apparently, the initial heavy metal ion concentration played an important role in affecting the capacity of metal exchange on natural resin. The higher the heavy metal concentration,
stronger the driving forces of the concentration gradient and therefore the higher the adsorption capacity (Rezaee et al., 2005).

**Effect of solution temperature on ion exchange process:**

The effect of solution temperature on chromium (VI) metal removal is shown in Fig. 8. The removal of metal ion increased slightly increasing temperature from 273 K to 348 K. It is seen from Fig. 8, when natural ion exchanger used for chromium (VI) removal with an increase in temperature from 273 K to 348 K, the ion exchange capacity increased from 52.36 % to 99 % with initial metal concentration. This indicated that the exchange reaction was endothermic and ion exchange mechanism favors high temperature. An increase the removal with the rise in temperature may be explained by active site on natural ion exchanger being more active at high temperature (Egilal et al., 2011).

**Effect of resin dose on ion exchange process:**

The percentage efficiency of chromium (VI) ion at different doses of ion exchanger was strongly acidic and shown in Fig. 9. The degree (%) of removal efficiency increased as the resin dose was increased. It might be concluded that by increasing the resin dose, the removal efficiency of heavy metal ion increased, while ion exchange density decreased with increase in resin dose. The decrease in ion exchange density may be due to the fact that some adsorption site may remain unsaturated during the adsorption process, whereas the number of sites available for adsorption increased by increasing the resin dose and that results in the increase of removal efficiency (Rafati et al., 2010). When increased resin dosage from 0.5 g to 3.5 g, removal efficiency increased from 80.55 % to 99 % for chromium (VI).

**Effect of contact time on ion exchange process:**

The removal efficiency increased with increase in contact time. Other parameter such as adsorbent dose, pH and temperature of solution was kept optimum. It can be seen that chromium removal efficiency increased from 60.00% to 99 %, when contact time increased from 10 min to 30 min. the result obtained are shown in Fig. 10. Optimum contact time for chromium (VI) removal was found to be 30 min. Hence the ion
exchanger requires shorter contact time. Greater availability of various functional
groups on the surface of resin, which are required for interaction with anions and
cations, significantly improved the binding capacity and the process proceeded
rapidly. The result is important as equilibrium time is one of the important parameters
for an economical wastewater treatment (Hani et al., 2012).

Sorption isotherm:

The sorption isotherm for the removal of Cr from effluent onion exchanger was shown
in Figs. 11 and 12, respectively. The isotherms are regular, positive and concave with
respect to the concentration axis. The results show efficiency of ion exchanger for
chromium removal from effluent. The sorption studies are carried out at 323 K to
determine the sorption isotherms.

The isotherm parameters were evaluated using Langmuir and Freundlich isotherm
models. The straight line obtained for two sorption isotherms indicated that the
sorption of chromium (VI) fit to investigate isotherm models. The corresponding Langmuir
and Freundlich parameters along with correlation coefficient are given in Table 4. The slope of the Freundlich isotherm was more linear than
Langmuir isotherm, hence sorption isotherm fit better with Freundlich model.

Conclusion

The purpose of this work was to study the possibility of removing hexavalent
chromium from effluent through sorption by modified natural ion exchanger. The data
reported here, show that *Tamarindousindica* seed powder is an effective sorbent for
removing Cr from effluent. The sorption capacity of natural adsorbent was higher
than the reported value of other adsorbents. Equilibrium studies were conducted for
the adsorption of chromium from effluent by surface modified natural ion exchanger.
The equilibrium data have been analyzed using Langmuir and Freundlich isotherm
models, and results showed that the sorption of hexavalent chromium occur at pH 6.5,
which is fit better to Freundlich isotherm model. It could be planned to use natural ion
exchanger to economic polluted water treatment.
Application

Removal of chromium (VI) from industrial effluents

In order to assess the practical performance of natural ion exchanger for removal of hexavalent chromium from industrial effluent, an experiment was carried out after adjusting the pH 6.5 at which the maximum adsorption of hexavalent chromium can be achieved. Developed method is applied for removal of hexavalent chromium from 5 different Pharmaceutical industrial effluents. The concentration of hexavalent chromium from these effluents was determined before treatment and after treatment with natural ion exchanger. It is observed that more than 99% of hexavalent chromium was removed from effluents. The results are reported in Table 3.

Table 1: Properties of ion exchange resin.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical form</td>
<td>Spherical</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.15 gm./cm$^3$</td>
</tr>
<tr>
<td>Ash content</td>
<td>10.4%</td>
</tr>
<tr>
<td>Moisture content</td>
<td>8.7%</td>
</tr>
<tr>
<td>Matter soluble in water</td>
<td>8.4%</td>
</tr>
<tr>
<td>Matter soluble in acid</td>
<td>18%</td>
</tr>
<tr>
<td>Water holding capacity</td>
<td>80.32%</td>
</tr>
</tbody>
</table>

Table 2: Experimental Parameters.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Studied ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial metal concentration (mg/l)</td>
<td>25, 50, 100, 250 and 500</td>
</tr>
<tr>
<td>pH</td>
<td>1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5</td>
</tr>
<tr>
<td>Solution temperature (K)</td>
<td>273, 298, 323 and 348</td>
</tr>
</tbody>
</table>
**Table 3:** Concentration of Chromium (VI) in industrial effluents before and after treatment of ion exchange resin of 3.5 gm at pH 6.5, time 30 min and temperature 25°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Effluent ml</th>
<th>Concentration before treatment (mg/l)</th>
<th>Concentration after treatment (mg/l)</th>
<th>% removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial sample 1</td>
<td>25</td>
<td>5.0</td>
<td>0.03</td>
<td>99.40 %</td>
</tr>
<tr>
<td>Industrial sample 2</td>
<td>25</td>
<td>4.5</td>
<td>0.02</td>
<td>99.55%</td>
</tr>
<tr>
<td>Industrial sample 3</td>
<td>25</td>
<td>4.5</td>
<td>0.02</td>
<td>99.55 %</td>
</tr>
<tr>
<td>Industrial sample 4</td>
<td>25</td>
<td>2.2</td>
<td>0.01</td>
<td>99.54 %</td>
</tr>
<tr>
<td>Industrial sample 5</td>
<td>25</td>
<td>3.5</td>
<td>0.01</td>
<td>99.70 %</td>
</tr>
</tbody>
</table>

**Table 4:** Isothermal parameters of Cr (VI) adsorption.

<table>
<thead>
<tr>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_m$ (mg/l)</td>
<td>$K_L$(mg/l)</td>
</tr>
<tr>
<td>3.94</td>
<td>0.018</td>
</tr>
</tbody>
</table>
Fig. 1: FT-IR spectrum of raw seed powder.

Fig. 2: FT-IR spectrum of phenol formaldehyde resin.
Fig. 3: FT-IR spectrum of phenol formaldehyde resin after Cr (VI) adsorption.

Fig. 4a: SEM Image of raw seed powder.
Fig. 4b: SEM Image of phenol-formaldehyde resin.

Fig. 4c: SEM Image of phenol formaldehyde resin after Cr (VI) adsorption.
Fig. 5a: EDX spectrum of raw seed powder.
Fig. 5b: EDX spectrum of phenol-formaldehyde resin.
Fig. 5c: EDX spectrum of Chromium adsorbed resin.
Fig. 6: Effect of pH on ion exchange process (293 K solution temperature, 1 mg/l initial metal concentration and 3.5 g resin dose).

Fig. 7: Effect of initial metal concentration on ion exchange process (pH 6.5, 293 K solution temperature and 3.5 g resin dose).
Fig. 8: Effect of solution temperature on ion exchange process (pH 6.5, 1 mg/l initial metal concentration, 3.5 g resin dose).

Fig. 9: Effect of adsorbent dose on ion exchange process (pH 6.5, 293 k solution temperature, 1 mg/l initial metal concentration).
Fig. 10: Effect of contact time on ion exchange process (pH 6.5, 293 K solution temperature, 1 mg/l initial metal concentration, 3.5 g resin dose).
Fig. 11: Linear plot of Langmuir isotherm for the adsorption of Cr (VI) on ion Exchanger.

Fig. 12: Linear plot of Freundlich isotherm for the adsorption of Cr (VI) on ion Exchanger.
5.2 Removal of copper from industrial effluents with natural Adsorbent:

Introduction

The accumulation of wastes and toxic metals in water is worldwide problem. Heavy metals are widely used in industrial activity such as metal finishing, electroplating, drying, photography, surface treatment, printed circuit and board manufacturing, which cause pollution of water. The extensive use of heavy metals in industrial activities results large concentration in effluents, which need sufficient treatments. Several method of effluent treatment such as electrolysis, precipitation, crystallization and filtration are available but these methods produce new side products. However new method has been developed based on biomass. In this method biological material is derived from living or recently non living organism. The bio sorption of zinc (II) by *callymperes erosum* was studied (Babarinde et al., 2008) at pH range 2.0 - 7.0 with contact time 60 min and temperature is 27°C. Heavy metals ions viz. copper, cadmium, nickel, lead and chromium are mainly found in industrial wastes and cause acute toxicity to the aquatic and terrestrial life including human being. Most of the industrial process generates waste water containing heavy metals contaminants. Now a day’s environmental researcher has been focused on heavy metal, due to their high toxicity. Water pollution is major environmental problem that leads to ecological imbalance. Commonly employed treatments for water purification are ion exchange, electrolysis, evaporation, chemical reduction, osmosis and electro dialysis. These techniques are expensive and not remove heavy metals completely. The resent technique bio sorption (Gopalakrishnan & Jeyadoss, 2011), which is more effective, cheaper and simple. In this study biosorption of Zn (II), Cu (II) and Cr (VI) was carried out from textile dye effluents using rice husk and coconut fiber at pH range 1.0-3.0 with contact time 300 min. These study show 64 %, 67 % and 72 % removal of Zn (II), Cu (II) and Cr (VI) respectively. Bio sorption has a property of certain types of inactive dead microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solution. It exhibits a property just as a chemical substance as an ion exchanger and was from biological origin. It has particularly a cell wall
structure of certain algae, fungi and bacteria, which was found responsible for this phenomenon (Hee et al., 2001). Removal of heavy metals from industrial waste water and effluents is important because it causes many health problems such as nephritis scaring, damage of liver, brain, nervous and reproductive system. Some metals are essential to living organism up to proper limit and above this it become hazardous. The industries such as chemical, dye, fertilizer, cement, paper, textile, paint and pigment are using heavy metals, as raw materials, some of which discharge in the forms of effluents and cause pollution of ground water as well as surface water. These heavy metals are accumulating in living organism. Lead was removed from aqueous solution by phenol formaldehyde resin as ion exchanger by (kuchekar et al., 2011). In this study lead was removed at pH 6.5 having resin dose 5 gm at 20 min contact time. Large surface area and non-toxic plant adsorbent was used is oak sawdust by (Mehmet et al., 2007), which remove heavy metals. This type of work achieved in field of the removal of heavy metals. The use of several types of supports were sawdust (Deli et al; 2011), cystoseira stricta biomass (Abdelkader et al., 2011). Cellulose acetate polymer and attapuligate clay (Reem & Athraa, 2011), agricultural biproduct like soya bean hulls, sugar cane bagasse, corn stover (Wayne & Lynda, 2008), activated carbon (Ilhan & Fual, 2000), Typha domingensis leaf powder (Ghani et al., 2009) and Leca (Malakootian et al., 2009), were used for removal of heavy metals.

Copper is the major toxic pollutant in waste water and effluent. Extensive use of copper results in large copper concentration (Yavuz et al., 2008). Biosorption is occurs in presence of biomass of living or non-living organism or microorganism like plant, agricultural bi-product, bacteria, microalgae and fungi. The bio mass when properly dried and screened can be used as a sorbing material (Musad et al., 2004; Schneider et al., 1999). Copper is a toxic to the human biosystem and among the common global pollutants arising from increasing industrialization. According to the WHO, the maximum permissible limit (MPL) of copper in drinking water is 0.003 mg/l (WHO, 2011). In present investigation Tamarindous indica seed powder used as a novel bio-sorbert for removal of copper (II) from aqueous solution. The aim of this work is to use Tamarindous indica seed powder for removal of copper (II) from industrial effluents.
**Materials and Methods:**

*Tamarindous Indica* seeds were pulverized after drying in sunlight in open air for one week. Small size pieces of dried seeds were grinded and pass through the mesh size 200 unit. This powder was treated with 39% formaldehyde and 0.1 mol l⁻¹ sulphuric acid at 80° C, for 30 min. After cooling and washing with double distilled water, substrate was allowed to dry for overnight in open air. Dried powder was used for adsorption studies.

**Metal ion solution:**

For adsorption study stock solution of copper (1000 mg/l) was prepared by dissolving 3.929 g of copper sulphate pentahydrate (CuSO₄·5H₂O) in double distilled water (DDW). The various concentrations were then obtained by diluting the stock solution with double distilled water.

**Method for separation of copper:**

25 ml copper solution (CuSO₄·5H₂O) having concentration 1.0 mg/l was transferred in beaker. pH of this solution was adjusted to 8.5 ± 0.1 and was transferred in 250 ml conical flask. In this solution 4.0 g natural adsorbent was added and kept for 30 min with successive shaking at interval of 10 min. Solution is filtered using whatman filter paper no. 41 and concentration of copper remain in solution was determined using Shimadzu UV-visible spectrophotometer by standard method. The amount of copper (II) uptake was calculated by difference in concentration. The initial concentration C₁ (mg/l) and metal concentration at various time intervals Cᵢ (mg/l), were determined and metal uptake qₑ was calculated from the mass balance equation as (Kathiresan & Rosemal, 2010).

\[ qₑ = \frac{(C₁ - Cᵢ)V}{W} \]  

(1)

Where, \( V \) is the volume of solution in ml and \( W \) is mass of adsorbent in gm
Characteristic properties of ion exchange resin:

The physical forms and characteristics properties of phenol formaldehyde resin were studied as per (Gaikwad et al., 2009) and results are reported in Table 1.

Result and discussion

Effect of initial pH on bio sorption:

The pH of the solution is important parameter in the bio sorption of copper (II). To understand the adsorption mechanism, the bio sorption of copper (II) as a function of pH was measured and the results are plotted in Fig. 1. It was observed that by increase in pH bio sorption capacity was increased from pH 1.0 to 11.0. As a result net negative charge on the cell wall of bio sorbent above the isoelectric point, ionic strength of ligands hydroxyl group favors reaction with copper (II). On the other hand decrease in pH the net charge on cell wall is positive inhibiting approach of positively charged ions. As pH increases the ligand in Tamarindous indica would be exposed, increasing the attraction of metal ions with positive charge and allowing the biomasses to bio sorption on cell wall surface. The results suggests that optimum bio sorption is obtained in basic region and that pH would play a vital role in removal of copper (II) from aqueous solution using Tamarindous indica (Ghani et al., 2008).

Effect of contact time on bio sorption:

The effect of contact time on the bio sorption of copper (II) by Tamarindous indica was studied and results were plotted in Fig. 2. From a figure it is observed that the bio sorption capacity of Tamarindous indica for copper (II) increased as contact time increased. The bio sorption process was rapid at first 25 min, and equilibrium was nearly reached at 30 min. Hence in present study 30 min was chosen as the equilibrium time. The initial fast phase occurs due to surface adsorption on biomasses. The subsequent slow phase occurs due to diffusion of the metal ions in to the inner part of the biomass. The copper bio sorption rate was high at beginning but plateau values were obtained in 60 min. similar to that was reported earlier (Ghani et al., 2008).
**Effect of solution temperature on bio sorption:**

The effect of solution temperature on bio sorption is shown in Fig. 3. The bio sorption increased with slight increasing temperature from 293 K to 353K. When temperature increases from 293 K to 353 K, the efficiency of bio sorption increases from 52.66 % to 95.00 % for initial metal concentration at pH 8.5. This indicated that the bio sorption was endothermic in nature and its mechanism favors high temperature (Gupta et al., 2011).

**Effect of bio adsorbent dosage on bio sorption process:**

The percentage efficiency of metal uptake at different dosage of bio adsorbent is plotted in Fig. 4. The adsorption of metal ion increases with increase in adsorbent dose. The decrease in ion exchange density may be due to the fact that some adsorption site may remain unsaturated during the adsorption process, whereas the number of sites available for adsorption increased by increase in adsorbent dose and that results in the increase in efficiency (Mane et al., 2010). It could be observed from fig. 4, when increased resin dosage from 0.5 to 4.0 gm, adsorption efficiency increase from 22.41 % to 95.00 % for copper (II) ion.

**Adsorption isotherms:**

The adsorption capacity at the bio-materials was towards the copper (II) in aqueous solution at pH 8.5, have been calculating by using the Langmuir and Freundlich isotherm models. It is expressed by the following equation:

\[
\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_0}{q_{max}}
\]  \hspace{1cm} (2)

Where \( q_e \) refers to the metal ion sorbed (mg g\(^{-1}\)) amount of copper (II), \( q_{max} \) is the maximum adsorption capacity of the biomaterial (mg/l), \( C_0 \) is the equilibrium concentration of copper (II) (mg/l) and \( b \) is the constant related to the adsorption energy (Gonen & Serin, 2012). The results were reported in Table 2. The plots of the sorption isotherm according to the linearized Langmuir model, (Eq.2) at the 30\(^{0}\) C temperature. In the considered concentration range, it appears that the results obtained (Fig. 5) are in good compliance with this model. The maximum adsorption capacity found is more important in the case of biomass. It is treated with a solution of 0.1 mol L\(^{-1}\) sulphuric acid and 39% formaldehyde solution (\( q_{max} = 25.71 \) mg/l). To explain the
adsorption of the observed equilibrium in better way the Freundlich isotherm model is also used. It is represented by the following equation:

\[ q_e = K_f C_e^{1/n} \]  (3)

A linear form of this expression is given as

\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \]  (4)

Where \( K_f \) the Freundlich constant and \( n \) is the adsorption intensity. The plot of the adsorption isotherms according to the Freundlich model (Eq. 4), (Fig. 6), (Tashauoei et al., 2010). The constant \( K_f \) and \( 1/n \) were determined by linear regression from the plot of \( \ln C_e \) against \( \log C_e \). \( K \) is a measure of the degree or the strength of adsorption, while \( 1/n \) is used as an indication of whether adsorption remain constant (at \( 1/n = 1 \)). It is appears that Freundlich model best fits the experimental results than Langmuir (Fig. 3), over the experimental range with good correlation coefficient (\( R^2 = 0.94 \)). The constant of both Langmuir and Freundlich along with correlation coefficient values are reported in Table 2.

Applications

**Removal of copper from industrial effluents:**

In order to assess the practical performance of *Tamarindus indica* seeds powder for removal of copper (II) from industrial effluents, an experiments was carried out after adjusting the pH 8.5, at which the maximum adsorption of copper (II) can be achieved. Developed method is applied for removal of copper (II), from various industrial effluents viz. Cipla plant-1, Cipla plant-2, Mcure pharmaceuticals, Task chemicals and Glenmark pharmaceuticals. The concentration of copper from these effluents was determined before treatment and after treatment with natural ion exchangers. It is observed that more than 75% copper is removed from effluents. The results are reported in Table 3.
Conclusion

The present study focuses on the use of *Tamarindus indica* seeds powder for the adsorption of copper (II) from industrial effluents. Adsorption was found to be pH dependent with maximum adsorption at pH 8.5. Fast adsorption is observed for copper (II), which suggests the adsorbent to be used effectively for continuous flow water system. Phenolic group present in the resin were found to be the active sites of metal adsorption. Adsorption was enhanced due to presence of micro pores, voids and fissures. Equilibrium isotherm were attempted with Langmuir and Freundlich models, among which Freundlich model are in good arrangement with the experimental data with high correlation coefficient values. The result proves that the adsorption of metal ions occurs by a physicochemical process rather than an ion exchange mechanism. The results also prove the potential for the treatment of industrial waste water.

**Table 1:** Characteristics properties of the ion exchange resin.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical form</td>
<td>Spherical</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.15 gm/cm³</td>
</tr>
<tr>
<td>Ash content</td>
<td>10.4 %</td>
</tr>
<tr>
<td>Moisture content</td>
<td>8.7 %</td>
</tr>
<tr>
<td>Matter soluble in water</td>
<td>8.4 %</td>
</tr>
<tr>
<td>Matter soluble in acid</td>
<td>18 %</td>
</tr>
<tr>
<td>Water holding capacity</td>
<td>80.32</td>
</tr>
</tbody>
</table>

**Table 2:** Langmuir and Freundlich Parameter.

<table>
<thead>
<tr>
<th>Langmuir isotherm parameters</th>
<th>Freundlich isotherm parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>q_{max} (mg gm⁻¹)</td>
<td>K_f (mg gm⁻¹)</td>
</tr>
<tr>
<td>b ( L mg⁻¹)</td>
<td>n</td>
</tr>
<tr>
<td>R²</td>
<td>R²</td>
</tr>
<tr>
<td>25.71</td>
<td>1.25</td>
</tr>
<tr>
<td>3.1</td>
<td>2.44</td>
</tr>
<tr>
<td>0.85</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Condition - pH=8.5.
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Effluent, ml</th>
<th>Concentration before treatment (mg/l)</th>
<th>Concentration after treatment (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cipla-1</td>
<td>25</td>
<td>3.5</td>
<td>0.4</td>
<td>88.0</td>
</tr>
<tr>
<td>Cipla-2</td>
<td>25</td>
<td>4.6</td>
<td>1.0</td>
<td>78.3</td>
</tr>
<tr>
<td>M-cure</td>
<td>25</td>
<td>4.0</td>
<td>0.7</td>
<td>82.0</td>
</tr>
<tr>
<td>Task chem</td>
<td>25</td>
<td>5.0</td>
<td>1.4</td>
<td>72.0</td>
</tr>
<tr>
<td>Glenmark</td>
<td>25</td>
<td>5.9</td>
<td>1.4</td>
<td>76.3</td>
</tr>
</tbody>
</table>

**Condition** - pH= 8.5, Contact time 30 min., Adsorbent dose 4.0 g.
Fig. 1: Effect of pH on % Cu (II) removal.
Adsorbent dose (gm) = 4.0; Contact time = 30 min.

Fig. 2: Effect of contact time on bio sorption of Cu (II) removal.
Adsorbent dose (gm) = 4.0; pH = 8.5.
Fig. 3: The effect of solution temperature on bio sorption.

Adsorbent dose (gm) = 4.0; pH = 8.5; Contact time = 30 min

Fig. 4: Effect of bio sorbent dosages on ion exchange process.

Adsorbent dose (g) = 4.0; pH = 8.5; Contact time = 30 min; Temp. = 333 K.
Fig. 5: Langmuir plot for copper bio sorption.

Adsorbent dose (gm) = 4.0; pH (333K) = 8.5; Contact time = 30 min;
$q_{\text{max}}$ (mg/g) = 25.71; $b$ (L mg$^{-1}$) = 0.0129; $R^2$ (333 K) = 0.85.

Fig. 6: Freundlich plot for copper bio sorption

Adsorbent dose (gm) = 4.0; pH (333 K) = 8.5; Contact time = 30 min:
$K_f$ (mg/g) = 1.25; $n$ = 2.44; $R^2$ (333 K) = 0.95
5.3 Removal of Lead from aqueous solution using Tamarinouds indica seeds as a natural Adsorbent:

Introduction:

Now days the mercury of heavy metal from industrial process, solution has attracted a great attention owing to the gradual rise in the environmental protection and the disposal of toxic substance. Numerous process are available for extraction and recycle of metal from industrial influence such as coagulation, chemical perception, slow sand filter membrane technology adsorbing natural products and ion exchange resin. Adsorption and ion exchange are potential alternative for aqueous solution (Erdem et al., 2004)

The high concentration of lead is caused pollution of water soil above affection living organism. The chief source of atmospheric lead is combustion engine. Lead is the important industrial health hazardous metal. It acts as poison and remains in bone for long ad bent of years. Poisoning of lead causes shrinking of kidney, tissue and premature loss of teeth (Raman and Shinde, 1989) Major source of lead pollutant is continuous discharge of industrial effluent in to surface water. Human activity and many agricultural operations. Leads to the increase in concentration of lead Pb (II) in water. air. soil. These toxic Pb (II) is removed from water and effluent sample is necessary (Abdel-Ghani et al., 2007)

Many other techniques for removal of Pb (II) from aqueous solution have alternative studies. Such as activated carbon, silica, aluminum, magnesium, etc. (Kamble et al., 2010) In advance countries removal of heavy metals in water is normally achieved by advanced technologies such as ion exchange, chemical precipitation. ultra filtration or electrochemical deposition do not seems to be economically facile for such industries because of their relative high cost. Therefore there Is a need to look alternative and economic and can be used by such industries to overcome this difficulties there is a strong need to develop new cheapest method for removal of heavy metals ions. Therefore it is desired that simple economic removal method which could be practiced in developing countries is established. Although precipitation, filtration method is cheap but its operation is complicated, on other hand adsorption method such as ion exchange is simple for metal removal (Xiong and Yao. 2011)
In present study of removal of Pb (II) from waste water and from industrial effluent further carried out by adsorption with powdered seeds of tamarindous indica at PH 6.5 with 20min interval of time.

**Reagents:**

All chemical were used of analytical reagents grade. 1% PAR 4 (2-pyridylazo) resorcinol was prepared by dissolving 1 g PAR and diluting it to 100 ml by distilled water.

Lead (II) solution (1 mg/ml); It was prepared by dissolving 1.599 g lead nitrate in distilled water and transferred it in 100 ml volumetric flask and diluted up to mar. Buffer solution having pH 6.5 was prepared by dissolving 16.4 g of sodium acetate and 11.5 ml acetic acid and diluted to 1 litter.

**Determination method of lead:**

The PH of Pb (II) solution was adjusted to 6.5 ml of .01% aqueous solution of PAR was added and dilated to 25 ml. The absorbance of the orange colored complex was measured at 520 nm against a regular blank. The amount of lead present in solution was determined by calibration curve (Devi et al., 2010).

**Effect of PH on removal of lead from aqueous solution:**

To study the effect of pH on removal of lead, 25 ml of (1 mg/ml lead (II) solution was shaken with 5.0gm resin for 20 min by varying the pH from 4 to 11. The result indicate a maximum at adsorption at PH = 6.5. The decrease in adsorption at higher pH 9 may be due to negative change on surface of adsorbent (Tall et al., 2010).

**Result and discussion**

**Conclusion:**

The powdered seeds of tamarindous indica can be used as an efficient adsorbent for the removal of Pb (II) from aqueous solution. The adsorption of Pb (II) was found to be concentration dependent. Percentage removal of Pb (II) increased with decrease in pH. It was found that it is maximum at pH 6.5
This technique is efficient, economic and eco-friendly for removal of Pb (II) form waste water and effluents sample. Raw material used for the preparation of substrate is widely available and in expensive hence method helps to solve water pollution problem.

**Table 1:** Fixation of resin amount and time (min).

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Pb^{2+} Soln. (ml)</th>
<th>Resin (gm)</th>
<th>Time(min)</th>
<th>O.D.</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>5.0</td>
<td>10</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>5.0</td>
<td>20</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>5.0</td>
<td>30</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>5.0</td>
<td>40</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>5.0</td>
<td>50</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>6</td>
<td>25</td>
<td>5.0</td>
<td>60</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**Table 2:** Concentration of Pb (II) from water sample before resin treatment.

<table>
<thead>
<tr>
<th>sample site</th>
<th>Pb (II) solution, reagent ml</th>
<th>PH</th>
<th>O.D</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>6.5</td>
<td>0.10</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>6.5</td>
<td>0.10</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>6.5</td>
<td>0.12</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>6.5</td>
<td>0.08</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>6.5</td>
<td>0.05</td>
<td>1</td>
</tr>
</tbody>
</table>
Table 3: Concentration of Pb (II) from water sample after resin treatment.

<table>
<thead>
<tr>
<th>sample site</th>
<th>Pb (II) solution (ml)</th>
<th>Resin (gm)</th>
<th>Time (min)</th>
<th>PH</th>
<th>O.D</th>
<th>Conc.</th>
<th>% removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>5.0</td>
<td>20</td>
<td>6.5</td>
<td>0.01</td>
<td>0.2</td>
<td>98.25</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>5.0</td>
<td>20</td>
<td>6.5</td>
<td>0.01</td>
<td>0.2</td>
<td>98.25</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>5.0</td>
<td>20</td>
<td>6.5</td>
<td>0.00</td>
<td>0.4</td>
<td>94.56</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>5.0</td>
<td>20</td>
<td>6.5</td>
<td>0.00</td>
<td>0.00</td>
<td>99.00</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>5.0</td>
<td>20</td>
<td>6.5</td>
<td>0.00</td>
<td>0.00</td>
<td>99.00</td>
</tr>
</tbody>
</table>

Table 4: Conc. of Pb (II) from industrial effluent before resin treatment.

<table>
<thead>
<tr>
<th>Name of industry</th>
<th>Effluent reagent ml.</th>
<th>PH</th>
<th>O.D</th>
<th>conc.</th>
<th>% removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cipla-1</td>
<td>25</td>
<td>6.5</td>
<td>0.064</td>
<td>2.4</td>
<td>86.45</td>
</tr>
<tr>
<td>Cipla-2</td>
<td>25</td>
<td>6.5</td>
<td>0.079</td>
<td>2.9</td>
<td>84.56</td>
</tr>
<tr>
<td>Task chem.</td>
<td>25</td>
<td>6.5</td>
<td>0.079</td>
<td>2.9</td>
<td>84.56</td>
</tr>
<tr>
<td>Emeure</td>
<td>25</td>
<td>6.5</td>
<td>0.07</td>
<td>3.0</td>
<td>82.0</td>
</tr>
<tr>
<td>Glemark</td>
<td>25</td>
<td>6.5</td>
<td>0.066</td>
<td>2.6</td>
<td>85.55</td>
</tr>
</tbody>
</table>

Table 5: Conc. Of Pb (II) from industrial effluent after resin treatment.

<table>
<thead>
<tr>
<th>Name of industry</th>
<th>Effluent (ml)</th>
<th>Resin (gm)</th>
<th>Time (min)</th>
<th>PH</th>
<th>O.D</th>
<th>conc.</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cipla-1</td>
<td>25</td>
<td>5.0</td>
<td>20</td>
<td>6.5</td>
<td>N.D.</td>
<td>ND</td>
<td>95</td>
</tr>
<tr>
<td>Cipla-2</td>
<td>25</td>
<td>5.0</td>
<td>20</td>
<td>6.5</td>
<td>0.03</td>
<td>0.6</td>
<td>83.65</td>
</tr>
<tr>
<td>Task chem.</td>
<td>25</td>
<td>5.0</td>
<td>20</td>
<td>6.5</td>
<td>0.03</td>
<td>0.6</td>
<td>83.66</td>
</tr>
<tr>
<td>Emeure</td>
<td>25</td>
<td>5.0</td>
<td>20</td>
<td>6.5</td>
<td>0.03</td>
<td>0.6</td>
<td>83.55</td>
</tr>
<tr>
<td>Glemark</td>
<td>25</td>
<td>5.0</td>
<td>20</td>
<td>6.5</td>
<td>0.01</td>
<td>0.2</td>
<td>92.45</td>
</tr>
</tbody>
</table>
**Fig. 1:** Calibration curve for Pb (II). 1mg/ml obeys Beers law.

**Fig. 2:** Effect of pH on absorbance.