REMOVAL OF HEAVY METALS USING HYBRID PRECURSOR PREPARED BY AGRO RESIDUE (RICE HUSK)

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ABSTRACT

Rice husk is an abundantly available waste material in all rice producing countries. In certain regions this low value agricultural by product is used as a fuel for parboiling paddy in rice mills, it produced 13-15MJ/kg of energy. The partially burned rice husk in turn contributes to more environmental pollution. This rice husk contains nearly 20 percent silica, can be made into adsorbent material, which is used, in environmental remediation. Developed countries have accepted and followed the concept of “no waste” and all such materials are termed as “new resources” for new material development through value addition. In the present study hybrid precursor, which contains both carbon and silicon, used for the removal of heavy toxic metals, such as lead, copper and zinc present in wastewater. The efficiency of the hybrid precursor in the removal of heavy metals is approximately 90%.

Key Words: Hybrid precursor, Rice husk, Agro-Residue, Adsorption, Flora and fauna.

INTRODUCTION

Water pollution is one of the most important environmental problems in the World. A large quantity of water, containing heavy metals is discharged by industrial activities and the activities, which involves processing of metals. These waste water disposal poses to the environment. These disposed heavy metals are very toxic and harmful to human being as well as Flora and Fauna.

Microbial degradation, chemical oxidation, photolysis and adsorption are used for the treatment of wastewater. Activated carbon are the most common adsorbent which can be made from different plants, animal residues, and bituminous coal. Silicon based adsorbents are also very effective in the removal of heavy metals. In present study Hybrid precursor is used which contains both carbon and silicon.

The production of hybrid precursor from agricultural by product serves a double purpose, first it converts unwanted surplus waste of which billons of kilogram are produced annually, to value added adsorbent. It is reported that

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for every ton of rice produced, approximately 0.23 tons of rice husk is formed and accordingly during 1999-2000, the production of rice husk in India is reported to be nearly 127 million tones\textsuperscript{10}. So the disposal of this huge amount of by product (rice husk) has been a major, costly waste disposable problem. Second activated carbon and hybrid precursor are increasing used in removing organic compounds and heavy metals of environmental or economic concern\textsuperscript{1,2}.

Hybrid precursor prepared by rice husk chooses to be used as an adsorbent due to its amorphous structure (high surface area), insoluble in water, chemical stability, high mechanical strength and local availability at almost no cost of rice husk\textsuperscript{8}.

**MATERIAL AND METHODS**

**Materials**

The rice husk used in the present studies for making hybrid precursor of silicon and carbon was obtained from M/S Rice Mills, Bhopal, India. The rice husk after washing with distilled water was used as such, without further grinding and or carbonization. The chemicals used were ethylene glycol (L.R. grade S.D. Fine Chem. India), sodium hydroxide (A.R. grade’s. Fine Chem., India) and ammonium nitrate (A .R.grade, S.D. Fine Chem., India).

**Synthesis of Hybrid Precursor**

The preparation of hybrid precursor of silicon and carbon was carried out by refluxing 100 gm of rice husk with 1000 ml solution of sodium hydroxide of different concentrations i.e. 3, 6, 9 and 12 M separately in the presence of 250ml. ethylene glycol. The refluxing duration was maintained for a fix period of 4 hours in each experiment. The temperature of the reaction solution could be maintained at 198-200\(^{\circ}\)c because this being the boiling point of ethylene glycol. At the end of four hours duration, the excess quantity of ethylene glycol was recovered back by distillation. The reaction between various constituents resulted in the formation of sodium glycol /glucolato silicates. To prepare hybrid precursor, the sodium glycol /glucolato silicates so obtained was then dissolved in 250 ml double distilled water. The pH of this solution was found to be 13-14. To this highly alkaline solution, 25 % ammonium nitrate solution was then slowly added under constant stirring condition at room temperature till the pH of the solution is reached to a value of 8.0. This led to the formation of hybrid precursor in the form of gel on allowing the solution undisturbed for duration of 24 hours. The hybrid precursor gel was then filtered using what man filter paper No.40 and dried at room temperature in order to preserve the gel matrix of hybrid precursor.

**Techniques used for characterization studies**

The hybrid precursor was characterized by (i) chemical analysis to determine the carbon and silicon content as per the procedure reported by Raman et al\textsuperscript{11}. The sodium content was estimated using Flame photometer The X-ray diffraction technique (X-ray diffraction Model no.1710 of Philips make) was used to identify the presence of various phase present in the hybrid precursor and The thermal analysis for TGA and DTA was carried out (using Linseis Thermowaag L 81) to study the thermal behavior of the hybrid precursor. The cation exchange capacity of hybrid precursor is also determined\textsuperscript{9}.

**Preparation of Pb\textsuperscript{2+}, Cu\textsuperscript{2+} and Zn\textsuperscript{2+} sample solution**

Stock solution of Pb\textsuperscript{2+}, Cu\textsuperscript{2+} and Zn\textsuperscript{2+} (1000mg/L) were prepared from Lead nitrate (Pb(NO\textsubscript{3})\textsubscript{2}), Copper Nitrate (Cu(NO\textsubscript{3})\textsubscript{2}) and Zinc Nitrate (Zn(NO\textsubscript{3})\textsubscript{2}) using double distilled water. The stock solutions were serially diluted to prepare experimental solutions of desired concentration.

**Experimental Procedure**

A fixed amount of hybrid precursor was equilibrated with 100ml of 5.0, 10.0, 50.0, 100.0, 200.0 mg/l of Pb\textsuperscript{2+}, Cu\textsuperscript{2+} and Zn\textsuperscript{2+} sample solutions respectively. The suspensions were
shaken continuously on a mechanical shaker for 5 minutes and allowed to stand for 30 minutes followed by filtration through what man filter paper no. 42. The filtrates were analyzed for the concentration of unabsorbed metal ions using Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

Studies on synthesis of Hybrid precursor

The percentage of silica content in rice hulls, generally is found to vary between 13-29 % and is reported to depend up on the soil-mineral strata and climatic conditions of the locations, wherein the rice hulls is grown\(^1\). The silica in rice hulls is present in a hydrated amorphous form either opal or silica gel. This reactive form of silica is mainly localized in the outer layer of epidermis of rice hulls. The rice hulls used in the present studies were analyzed for its silica content and it is found that the percentage of silica lies in the range of 27-28 %. The typical organic constituents present in Rice hulls on weight basis arereported by various investigators\(^12,13\) and it is shown in Fig.1 and percentage of silica, carbon and sodium present in hybrid precursor is reported in Table-1.

![Fig.1. Typical organic constituents present in rice husk](image)

**Table 1. Summarizes the silica, sodium and carbon content is prepared hybrid precursor**

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Percentage (weight basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>27.60%</td>
</tr>
<tr>
<td>Carbon</td>
<td>16.41%</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.21 %</td>
</tr>
</tbody>
</table>

Characterization studies on hybrid precursor gel

The X-ray powder diffraction pattern of hybrid precursor has shown in Figure-5 exhibits amorphous characteristics by the presence of broad and weak peak pattern. The presence of alkali glycolato silicate species is confirmed\(^14\) by the presence of peaks at dA\(^0\) value 4.92, 4.78, 4.08 nms and 3.88 nm. The peaks at d A\(^0\) values 3.88, 3.04, 2.79 nms are attributed to sodium ammonium nitrate (JCPDS file no. 28-490) and very minor peaks at dA\(^0\) values 4.30 3.88 and 2.79 are ascribed to hexa and nano hydrated sodium silicate (JCPDS file no. 16-815). The peaks at d A\(^0\) values 2.71, 3.23 and 4.30 are attributed to the presence of L-Arabinose and at d A\(^0\) values 4.76, 4.08 and 3.55 to the \(\alpha\)-D Galactose (JCPDS file...
no.3-0157) and at 0 values 4.78, 5.16 and 4.19 are ascribed to the presence of and D-Xylose (JCPDS file no. 3-0154) respectively. These various organic compounds are incorporated on the surface and as well as in the matrixes of silica-carbon gels i.e. hybrid precursor.

The thermal analysis was carried out in air atmosphere at a heating rate of 10°C per minute from ambient up to 1200°C only as the major changes expected to be completed in this temperature regime itself. The TGA-DTA thermogram of the hybrid precursor is shown in Fig. 6. The TGA studies of hybrid precursor show a total weight loss of 72.52% up to 900°C in four steps. These weight losses are attributed to the evaporation of absorbed water, oxidative removal of various glycol ligand and carbonaceous materials to yield silanol groups that ultimately leads to the reordering sintering of the silica network. The weight loss becomes constant above 900°C. The weight of remaining mass i.e. due to silica is found to be 27.48%, which is in close agreement with the results obtained by chemical analysis. The DTA of the hybrid precursor shows a small endothermic peak in the temperature range of 86 to 150°C and is accompanied with a weight loss of 9.5%. This is attributed to the loss of absorbed water. Next, there is an exothermic peak in the temperature range of 180-195°C and is associated with highest weight loss of 25.4% in the whole temperature regime. Manocha et al. have also observed similar phenomenon and have attributed it to the reaction between organic and inorganic species of the various constituents of the hybrid precursors. The major organic removal occurs by combustion in air as shown by two exothermic peaks centered at 300 and 400°C. The sharp exothermic peak at 300°C is attributed to partial decomposition of Si-O-R groups and is associated with 9.2% weight loss. Further there is broad exothermic peak in the temperature range of 380-495°C with a weight loss of 7.2% and is attributed to decomposition of residual organic matter and conversion of Si-O-R groups to Si-OH groups and latter to the siloxane bond. These two exothermal effects suggest two types of organic contents in the hybrid precursor matrix. The steady weight loss above 500°C is assigned to the condensation of silanol groups and formation of inorganic network of silica.

**Removal of Copper (II), Lead (II) and Zinc (II) from the solution**

The percentage removal of Pb²⁺, Cu²⁺ and Zn²⁺ present in the solution was determined by batch experiment for different initial concentrations viz. 5.10, 50, 80, 100, 200, 500 mg/L using 100ml solution and 0.5 gm of hybrid precursor by equilibrating the solution with the adsorption at 30°C for 30 minutes.

![Fig. 2. Percentage removal of Pb²⁺ metal ions from aqueous solution.](image-url)
Fig. 3. Percentage removal of Cu$^{2+}$ metal ions from aqueous solution.

Fig. 4. Percentage removal of Zn$^{2+}$ metal ions from aqueous solution.
The removal efficiency of zinc is higher than copper and lead. If the concentration of above three metals lies in the range of 5 mg/L the removal efficiency is higher i.e. approximately 97 percent. As the concentration of metal ions increases the removal efficiency decreases.

**TECHNO – ECONOMIC FEASIBILITY OF THE ADSORBENTS**

The comparative study of the cost of various adsorbents have been evaluated for understanding the cost effectiveness of the hybrid precursor prepared by using rice husk and the data are given in Table-2

**Table 2. Summarizes the cost of various adsorbents**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Name of adsorbent</th>
<th>Price in Rs./ 100g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Hydroxyapatite</td>
<td>5500 approx.</td>
</tr>
<tr>
<td>2.</td>
<td>Activated carbon</td>
<td>600 approx.</td>
</tr>
<tr>
<td>3.</td>
<td>High grade rock phosphate</td>
<td>0.40* approx.</td>
</tr>
<tr>
<td>4.</td>
<td>Zeolite</td>
<td>1.5 approx.</td>
</tr>
<tr>
<td>5.</td>
<td>Low grade rock phosphate</td>
<td>0.22* approx.</td>
</tr>
<tr>
<td>6.</td>
<td>Pyrophyllite</td>
<td>0.20* approx.</td>
</tr>
<tr>
<td>7.</td>
<td>Hybrid precursor</td>
<td>0.50* approx</td>
</tr>
</tbody>
</table>

**CONCLUSION**

From the studies carried out for the synthesis of hybrid precursor using rice husk and its use for the removal of toxic heavy metals i.e. Cu²⁺, Pb²⁺ and Zn²⁺ the following conclusion can be drawn

Firstly the synthesis of hybrid precursor containing silicon and carbon can be carried out using rice husk by novel low temperature method involving simple refluxing of various reactants at 200°C only. Secondly this hybrid precursor is useful for the removal of toxic

![Fig. 5. XRD spectra of the hybrid precursor gel](image-url)
metals like Cu^{2+}, Pb^{2+} and Zn^{2+}. Removal capacity came out to be approximately 90 percentages. From the cost data given in table 1, it is found that the use of hybrid precursor as adsorbent can be a techno-economical option for application in removal of toxic metals ions namely lead, copper and zinc.

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REFERENCES


