

Biosorptive removal of Lead(II) by the carbonaceous material obtained from industrial waste lignin



Chemistry

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ABSTRACT

For the removal of heavy metals such as lead from aqueous environments, adsorption process plays an important role. The applications of low cost sorbents have been widely studied for heavy metal ion removal from waste water. Natural materials have the potential to be used as low cost sorbents and are ecofriendly. However number of waste materials were investigated as the low cost adsorbent as a replacement for cost effective methods of removing lead ions from aqueous solution. This paper reports the study on performance of low cost adsorbent prepared from industrial waste lignin in removal of lead (II) ions. Lignin from pulp and paper industry was subjected to pyrolysis to obtain a porous carbonaceous material. The adsorption studies were carried out through various parameters such as adsorbent dose, pH and contact time. The maximum removal of Pb ions was observed at pH value 5 and contact time 3 hrs, also the adsorbent dose of 1g/50ml or 20g/L showed maximum uptake. The result of this study suggests that the industrial waste lignin could be a viable and potential sorbent for removal of Pb (II) from waste water. A series of isotherm studies was undertaken and the data evaluated for compliance was found to match with the Langmuir and Freundlich isotherm models.

Introduction

The removal of lead ions from sewage and industrial waste water is of great interest in the field of water pollution, which is a serious cause of water degradation [1,2]. Pollution by lead ions becomes a major issue worldwide due to its possible toxic effect. It is the significant heavy metal which is released into the environment in number of ways including lead acid batteries, petrochemicals, refineries, explosive manufacturing, effluents from plastics, textiles. It is harmful to aquatic ecosystems and water contaminated by lead creates a serious health problem to human being. A number of treatment processes have been applied for the removal of heavy metal ions such as precipitation, membrane filtration, ion exchange, adsorption and reverse osmosis. But due to high cost, these methods are not applicable for most of the industries, as well as they generate a lot of sludge or other waste products [3,4]. A lot of research work has been published on the use of agricultural waste products [5] such as onion skin, flour waste, paddy husk, paddy straw as potential adsorbents. A few work has been reported on the preparation of activated carbon from the waste materials like rice husk [6], coconut shell [7], paper waste [8] etc.

After cellulose, lignin is the second most abundant naturally occurring aromatic polymer found in plants. Lignin mainly comprise of about 15-30% of plant biomass. Lignin is a three dimensional amorphous polymer of high molecular weight. It is the natural product mainly derived from enzyme initiated dehydrogenative polymerization of three primary precursors [9] such as coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol. These basic units are linked by number of bonds which includes ether and carbon-carbon bonds, which rises to form highly complex structure of lignin in different plant species. A large amount of lignin is also obtained from black liquor, discharged as a waste from pulp and paper industries. A lot of research work has been reported for the utilization of industrial waste lignin e.g. alkali fusion, pyrolysis, ion exchanger [10], phenolic resin [11,12] and in polymers. Mostly a major amount of waste lignin is burnt to consume it. As the production of lignin is about 70 million tons per year, interest has arisen recently in the development of economically new applications of lignin. As lignin contains high carbon content (about 55-60%) and molecular structure similar to bituminous coal, it can be potentially considered as a precursor for activated carbon and their use as adsorbents [13].

Activated carbon is the most widely used adsorbent [14] because of its high surface area. But it cannot be used frequently due to its high cost. Therefore in this paper work, the carbonaceous residue obtained by pyrolysis of industrial waste lignin was tested for the uptake capacity of lead ions.

Materials and methods

All chemicals used were the AR grade from Merck. Sample solutions were prepared by dissolving required amount of lead acetate in distilled water. the concentration of the solution prepared was in the range of 45-50 ppm for lead solution.

Preparation of adsorbent

Industrial waste solid lignin was subjected to thermal degradation at about 500°C for 3 hrs in Nitrogen atmosphere. The carbonaceous material obtained was ground and sieved to get a particle size of 300 microns (industrial standard sieves). Then it was treated with 10% NaOH solution to remove the traces of undegraded lignin and then washed with distilled water and dried at 110°C. The carbonaceous material was used to study the removal of lead metal ions.

Adsorbent dosage

Adsorption of lead ions by different adsorbent dosage of carbonaceous material (0.5-2g) was carried out with 50ml of each aqueous lead solution containing defined amount of lead ions. Then the solutions were analyzed for the amount of lead ions uptaken, which was quantitatively determined by the difference between initial and final concentrations of Pb solutions by Atomic Adsorption Spectrometer.

pH studies

In order to select the pH range for maximum uptake, a series of solutions containing same initial concentration of Pb (II) ions with different pH was prepared. The uptake studies were carried out separately and the solutions were analyzed for the amount of Pb ions uptaken by Atomic Adsorption Spectrometer.

Contact time

Adsorption of lead (II) ions on the carbonaceous material obtained by pyrolysis of industrial waste lignin was studied at different time interval for 1g of adsorbent agitated with 50ml lead solution at pH 5 separately. Then the solutions were analyzed for the amount of Pb(II) ions uptaken by Atomic Adsorption Spectrometer.

Equilibrium studies of Pb (II) adsorption

Adsorption of Lead ions on the adsorbent obtained from industrial waste lignin with different dosage was studied by batch experiments. To facilitate estimation of the adsorption capacities the two well known equilibrium adsorption models -Langmuir and Freundlich were employed under the optimum conditions. The remaining concentration of Pb(II) after adsorption was measured using Atomic Adsorption Spectrometer and the amount of adsorption at equilibrium was calculated.

Results and Discussion

Effect of adsorbent dose

The influence of adsorbent dose on the removal of Pb has been investigated and represented in Fig.1. It is observed that the metal % removal is increased with increase in the adsorbent dose. This is because of the number of active sites available for metal uptake would be more as the amount of adsorbent increases. The maximum removal of 71.66% for Pb(II) was obtained for the adsorbent dose of 1g/50ml. However, it was observed that after the dose of 1g/50ml, there was no significant change in % removal of Pb.

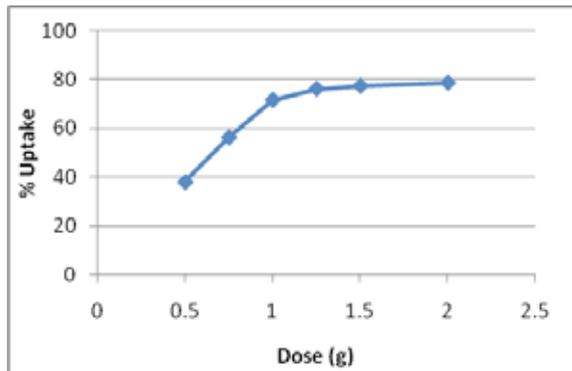


Fig.1. Effect of adsorbent dose for removal of Lead ions

Effect of pH

The pH of the solution has a significant impact on the removal of heavy metal ions, since it determines the surface charge of the adsorbent, the degree of ionization, speciation of adsorbate. The effect of pH on adsorption of Pb(II) under similar conditions of adsorbent dose and contact time is presented in Fig.2. The maximum removal efficiency reached to 75% for Pb(II) at pH 5. It was observed that there was a little uptake at pH lower than 3. It may be due to the H⁺ ions concentrations, which reverses the process of adsorption. The adsorption increases gradually with increase in pH from 3 to 6 and maximum adsorption is at 5-6 pH range.

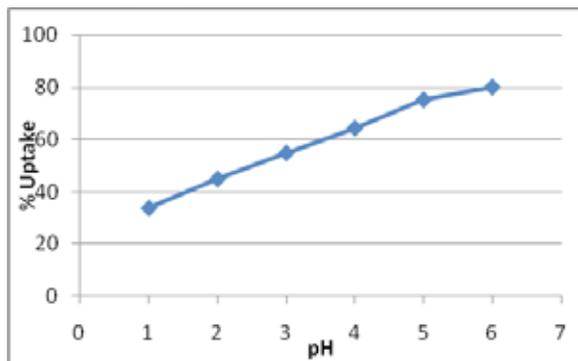


Fig.2. Effect of pH for removal of Lead ions

Effect of contact time

Adsorption of lead at different contact time was studied for 1g/50ml of the adsorbent at pH 5. For a fixed concentration of Pb and a fixed adsorbent dose, the retention of heavy metals increased with increasing contact time from 1hr to 3hrs. Fig.3 shows that the adsorption rate initially increased rapidly and that the optimal removal efficiencies were reached within 3hrs. The maximum removal of 67.85% for Pb was observed for contact time of 3 hrs. Removal is higher in the initial stages because adequate surface area of adsorbent is available for adsorption of lead. As time increase, more lead ions gets adsorbed onto the surface of the adsorbent and surface area available decreases. Thus the rate of % removal of lead becomes almost insignificant after 3 hrs.

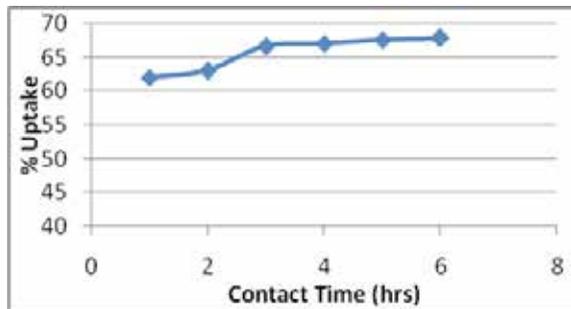


Fig.3. Effect of contact time for removal of Lead ions

Isotherm Analysis

The equilibrium study is important for adsorption process, as it shows the capacity of the adsorbent and describes the adsorption isotherm to express the surface properties and affinity of the adsorbent. In the present study, the equilibrium data for Pb(II) adsorption on the carbonaceous material prepared from industrial waste lignin were evaluated by the Langmuir and Freundlich models.

The Langmuir isotherm is based on assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecule on the adsorbent surface. The energy of adsorption is constant and there is no transmigration of adsorbate in the plane of the surface [15]. Whereas the Freundlich isotherm can be used for non-ideal adsorption that involves heterogeneous adsorption[16]. The linearized equations for the Langmuir and Freundlich isotherms are expressed as

$$\frac{1}{q_e} = \frac{1}{\theta b C_e} + \frac{1}{\theta} \quad (1)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

A linear graph of $\frac{1}{q_e}$ and $\frac{1}{C_e}$ for the carbonaceous material adsorbent was plotted. In the Eqⁿ (1), q_e is the amount of metal ion adsorbed per unit weight of the adsorbent (mg/g), C_e is the equilibrium concentration of the metal ion solution (mg/L), θ and b are the Langmuir constants related to the capacity and energy of adsorption (mg/g) and (L/mg) respectively.

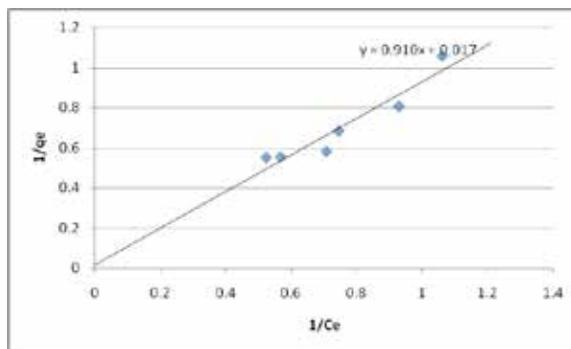


Fig.4. Langmuir Isotherm of Pb over carbonaceous material

For the analysis of Freundlich isotherm, a linear graph of $\log(q_e)$ was plotted by referring eqⁿ (2). The Freundlich constants, n and K_f , were determined from the slope and intercept of the plot respectively. The constant 'n' indicates the bond energies between metal ion and the adsorbent, whereas K_f (mg/L) is related to bond strength[17]. Thus the data of Pb(II) adsorption on the carbonaceous material may be concluded to perfectly fit both the isotherms.

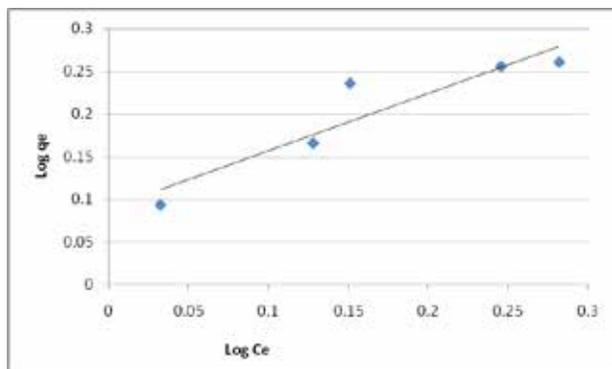


Fig. 5. Freundlich Isotherm of Pb over carbonaceous material

Conclusion

The present study reported the important parameters that determine the process of heavy metal adsorption using a new biosorbent obtained by pyrolysis of industrial waste lignin. The adsorption of Pb(II) ions was dependent on the following conditions: sorbate-sorbent contact time, pH and the adsorbent dosage. The optimum condition of 1g of the carbonaceous material and pH of 5 was obtained to remove 75% of Pb(II) from 50ml of aqueous solution in 3 hrs. In general, both the Langmuir and Freundlich models achieve good fittings. This study shows that the carbonaceous material prepared from pyrolysis of industrial waste lignin has high potential to be employed as an effective adsorbent in removal of lead ions and would be useful for the design of waste water treatment techniques for removal of other heavy metals.

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