Academic View

Analysis of Biosorption of Zn (II) ions onto Chemically Modified Saw Dust By using Various Parameters

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Abstract

This study explored biosorption study of Zn (II) onto raw saw dust (RSD) and modified saw dust (MSD) prepared by using saw dust. The adsorption capacity was determined at equilibrium with the help of batch adsorption technique using different parameters like pH of solution, contact time of adsorbent, initial concentration of metal ions and biosorbent dose. Spectrophotometric analysis of resultant sample shows that the loading capacity of adsorbent increases as the pH value increases attaining maximum adsorption at pH 6. The zinc adsorption on both raw and modified adsorbent was found to follow pseudo second order kinetics. The contact time at equilibrium for the adsorption was found to be at 60 and 120 mins respectively. Maximum percentage removal of Zn (II) was found to be 54.23% for RSD which increases up to 66.6 % for MSD maximum at 0.15g of adsorbent in 20 ml metal solution. The results indicate that the chemically modified saw dust can be a low cost alternative to commercial adsorbents for the Zn (II) removal from its aqueous solution.

Keywords: *Adsorption, Chemical modification, Equilibrium, Saw Dust, Zinc ions*

Introduction

Metals are considered as the essential elements for the life processing of the living organisms. They are required for the biochemical and metabolic activities of the living organisms. Metals including Zn, Cu, Fe, Mg are required for the living organisms for their life processes. Even though metals are required for the development of the living organisms, high dose of such metals may pose a toxic effect on living organism (Bhattacharya *et al*., 2006). Similarly, other metals with no biological importance may enter living system and cause damage to the living cell.

Heavy metals (As, Rd, Cr, Ni, Zn, Pb, Hg) are those elements which have specific gravity at least 5 times that of the water and have toxic effect on living cells even at low concentration. They are distributed widely in economically important mineral, so the main source of the heavy metals on the environment is the extraction of the minerals. Similarly, different industries like electroplating industries, carpet industries, electronic equipment and manufacturing processes are the sources of the heavy metals. Due to the rapid increment in industrialization, the level of heavy metals in waste water is gradually increased. As the heavy metals are highly soluble in water their level in food chain is also increased (Babel and Kurniawan, 2003).

Health effect of heavy metals toxicity ranges from mild headache, nausea, vomiting to the life threatening diseases. Compared to other metals Zn (II) is less toxic but exposure to higher concentration pose a harmful effect causing acute zinc related toxicities, a rare events. In addition to the acute intoxication, high dosages and longtime supplementation of zinc causes reduction in copper adsorption. Some of the harmful effects caused by high concentration of zinc are discussed below (Chen *et al*., 2009).

- The metal fume fever which causes pain in chest, cough dyspnea, reduced lung volumes nausea, chills, malaise and leukocytosis are most common effect of zinc toxicities. Higher concentration of corrosive $ZnCl_2$ inhalation causes mucous membrane damage of respiratory tract without causing metal fume fever.
- Exposure to lower dose for long time (~0.5-2 mg zinc/kg/day) of compounds of zinc results in the decreased adsorption of copper. The symptoms of low copper adsorption include anaemia which is manifested by the low concentration of electrolytes. High doses of zinc causes the reduction of leucocytes number and function.
- Consumption of zinc for long time may also reduce in the decrease in the iron.
- Exposure of skin to the zinc chloride and other zinc salts may causes skin irritation which is characterized by hyperkeratosis, inflammatory changes in the epidermis and acanthosis of the follicular epidermis.
- Several remediation techniques for the removal of the heavy metals are available, which ranges from traditional physiochemical to bioremediation processes. As they are expensive and inadequate, the search for efficient and cost effective remedies can be fulfilled by biosorption (Zwain *et al*., 2014).
- Biosorption process involves passive uptake of metal ions by inactive biological materials through different physiochemical mechanisms. The metal removal usually involves physical adsorption on the surface of adsorbent, ion exchange mechanism, chelation of metal ions, complexation, and micro-precipitation process (Pavasant *et al*., 2006).

Different types of bio-adsorbents have been investigated. The agricultural residues are found effective and efficient for adsorptive removal of heavy metals. These materials are mainly composed of cellulose that can remove heavy metals present in aqueous solution. Different agricultural waste biomass sources with good adsorption properties have been reported e.g. dust of saw, rice husk, waste tea and coffee, orange peel, peanut shells, activated carbon, dry leaves of tree and barks (Naik and Aruna, 2019).

Toona ciliata, commonly known as Red cedar or Tooni is a deciduous tree, bark with dark grey or reddish brown in color. They are found in countries like Nepal, Bangladesh, Thailand and China. In Nepal it is found in Terai upto the height of 1700 m, mostly in forest near river or moist surface. Red cedar is mostly used as fodder, timber and medicine.

Saw dust is waste material obtained during wooden furniture making process. It is lignocellulosic or tannin rich waste material having great potential as an adsorbent. So it attractes scientist dealing with wastewater purification by using low-cost biosorption process. Chemical modification of saw dust with sulphuric acid increases the surface area and porosity of the saw dust thus increasing the adsorption capacity (Bellir *et al*., 2013). The main components of saw dust are cellulose, hemicellulose, and lignin. Sulphuric acid treatment increases the cellulose content of the saw dust by removing lignin and increasing the solubility of the hemicelluloses. The modified saw dust have higher active sites, better ion exchange properties and have new functional groups that favors the metal uptake. It removes low molecular weight compounds and increases the concentration of active sites.

Experimental Methods

Preparation of stock solution

Stock solution was prepared by dissolving 0.50 g of hydrated zinc sulphate crystals in 250 mL volumetric flask in 0.1 N nitric acid solution to give 500 mg/L solution. Other working solutions were prepared by diluting the stock solution in distilled water.

Zincon (2-carboxy-2-hydroxy-5-sulfoformaxylbenzene) Stock Solution

Zincon stock solution was prepared by dissolving 0.087 g of chelator (Na^+ salt, 85% dye content) in 2 mL of NaOH (1M) and diluted to 100 mL with distilled water.

Buffer Solutions

Buffer tablets of pH 4 and 9.2 were dissolved in distilled water in different 100 mL volumetric flask to prepare 4.0 and 9.2 buffer solution

Preparation of Adsorbents

Saw Dust of *Toona cilitate* was washed several times with distilled water to get clear filtrate and left in sunlight for 2-3 days to dry. It was sieved to the size of 100 and 200 ASTM at department of Geology in Tri Chandra Campus. Thus obtained saw dust adsorbent was used for removal of Zn (II) ions. It was packed in air tight vessel and marked as raw saw dust (RSD) for remaining experiments.

The RSD was then subjected to chemical modification using conc. H_2SO_4. About 100 g of RSD was treated with 150 mL of conc. H_2SO_4. The mixture was left for 24 hours at room temperature to complete the reaction. It was washed several times with distilled water to remove excess acid until neutral pH was obtained. This chemically modified saw dust (MSD) was dried in sun light for 4-5 hours and then at temperature of 60-70^o C in oven for about 8 hours.

Determination of Metal Ion concentration and Calibration Curve

The stock solution of 500 mg/L zinc sulphate was diluted to make 10 mg/L solution. Then 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5 and 7.0 mL of this solution was added in separate 25 mL volumetric flasks and 1 ml of buffer was added in each volumetric flask.

Then 1 mL of zincon chelator solution was added to each volumetric flask and volume was made up to the mark by adding distilled water and shaken well. After the complete reaction the intense blue color was observed. The absorption spectra of intensive blue color was recorded in the spectrophotometer against the blank solution. The solution gave the maximum absorption at wavelength of 615 nm, which was determined as λmax and other solution were measured in the spectrophotometer against reagent blank at this wavelength. The calibration curve was used for calculation of metal concentration in solution.

Adsorption Study

For Batch adsorption experiment 20 mL of metal solution with known concentration was taken in a conical flask containing 25 mg of the adsorbent. The mixture was shaken in a shaker for 24 hours at room temperature to attain equilibrium. The mixture was filtered and that filtrate was analyzed using a spectrophotometer at their optimized wavelength (λmax). The value of metal ion concentration before and after equilibrium gives the remaining concentration of metal ions.

Effect of pH

Adsorption of Zn (II) is highly dependent on pH of solution because pH affects the solubility of the metal ions, functional group on the adsorbent and the degree of ionization of the adsorbent during the reaction.

Batch experiment for pH analysis were carried out by shaking 20 mL of 50 mg/L metal solution with 25 mg of RSD and MSD for 24 hrs with various initial pH values ranging from 1.0, 2.0, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5 and 8.0. The mechanical shaker was used to shake samples in 100 mL conical flasks. The initial and final pH levels were measured, and the optimum equilibrium pH was calculated. Similarly the initial and equilibrium metal ion concentration were measured spectrophotometrically.

Effect of Initial Concentration of metal ions

The analysis of adsorptive removal of Zn (II) in various initial concentration was investigated by varying concentrations at optimum pH 6. In 50 mL conical flask 20 mL of metal solution with 10 to 150 mg/L concentration was shaken with 25 mg of adsorbent for 24 hrs. The initial and final concentration of solution were determined by using spectrophotometer.

Effect of Contact Time

After determining the optimum pH, the equilibrium time for metal ion adsorption onto adsorbents was determined. In a 100 mL conical flask with 25 mg adsorbent, 20 mL of 25 mg/L Zn (II) ions solution was added and was shaken for 5- 240 min. The concentration of Zn (II) before and after treatment were determined using spectrophotometer.

Results and Discussion

Effect of pH

The variation in adsorption of Zn (II) at different pH values onto RSD and MSD at initial concentration 50 mg/L is shown in the figure 1. Since pH value of the solution is responsible for charge on adsorbent surface and ionization of the adsorbate so it has significant impact on the uptake of zinc. To analyze effect of pH, sample solution with different pH values ranging from 1 to 8 were taken. The percentage removal of Zn (II) by RSD and MSD increased from 4.62% to 42.94% and 6.65% to 83.03% respectively when pH was increased from 1 to 6 and on further increase in pH causes decrease in adsorption of zinc.

At low pH, hydrogen ions compete with metal ions for sorption sites which causes low sorption of zinc at lower pH. Another effecting factor is that at low pH hydrogen ion concentration is higher and the surface of biosorbent becomes positively charged. It reduces the attraction between adsorbent and metal ions. At higher pH, the surface of biosorbent becomes negatively charged that facilitates greater metal ion sorption. It suggests that sorption take place according to cation exchange mechanism. At high pH value, the decreasing adsorption is due to precipitation of zinc ions as their hydroxides.

From this study maximum pH was found to be 6 for both RSD and MSD. Similarly, % adsorption for RSD was 42.94% and that for MSD was 79.28%. Hence, optimum pH for further studies has been investigated as 6 for Zn (II) onto saw dust adsorbent.

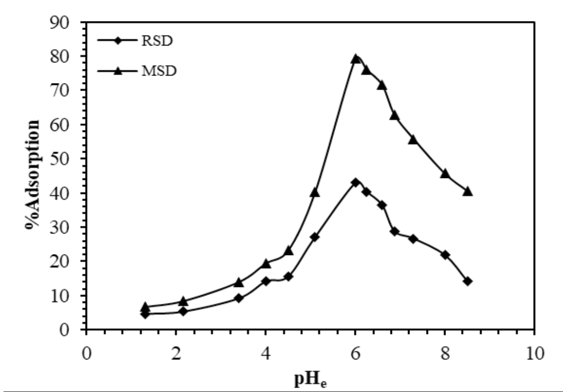

Figure 1*:* *Effect of pH on Adsorption of Zn (II) onto RSD and MSD*

Effect of initial concentration

The adsorption isotherm of zinc (II) on RSD and MSD are shown in the figure 2. For RSD when the concentration of zinc was increased from 10-150 mg/L, the adsorption increases but after certain time adsorption tends to remain constant even with increase in concentration. Similarly, for MSD the adsorption increases upto17.15 mg/g increasing the concentration of zinc from 10 to 150 mg/L. Further increase in concentration does not significantly increase the adsorption capacity.

Initially zinc ions uptake increases as the metal ion concentration increases and eventually reaches to equilibrium. This may be attributed to the fact that adsorbent surface have fixed number of adsorption sites which get saturated with increase in metal ion concentration, hindering further adsorption of ions. It indicates monolayer or Langmuir types of adsorption.

At the same time, adsorption of MSD is more than the adsorption of the RSD, this may be due to the enhancement of functional group by treatment with sulphuric acid. The acid treatment dissolves low molecular weight soluble substances and it breaks down the larger molecular weight polymers. This results in the exposure of adsorption sites on the surface of biosorbents.

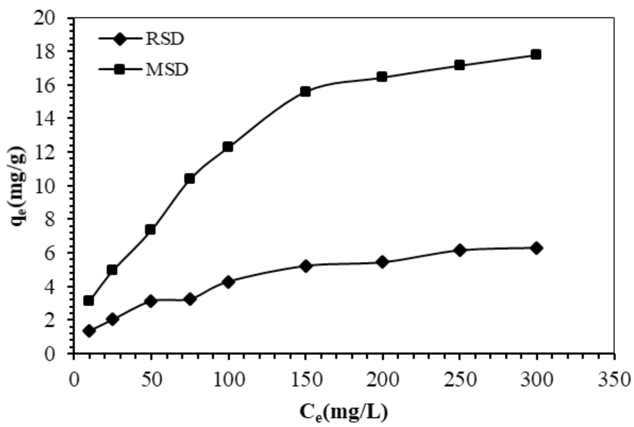

Figure 2: *Adsorption Isotherm for adsorption of Zn (II) onto RSD and MSD*

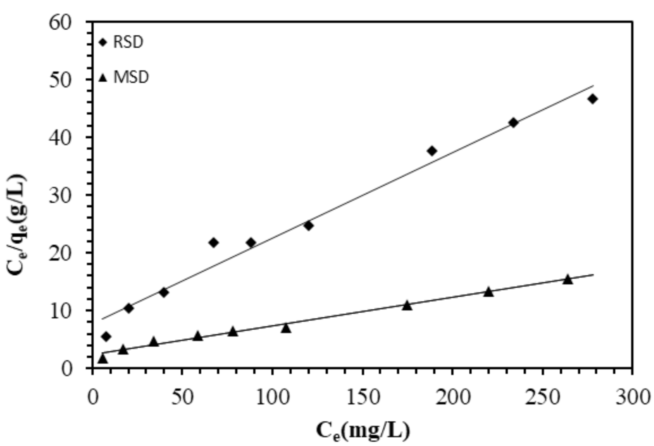

Figure 3: *Langmuir plot for adsorption of Zn (II) onto RSD and MSD*

Above results, to large extent matches with the previous studies. In most of the studies experimental data were fitted in both Langmuir and Freundlich isotherm model but in this study the data are best fitted in Langmuir adsorption isotherm as shown in Figure 3**.**

Effect of Contact Time

In order to analyze the adsorption kinetics of metal ions, the adsorption process were obtained for contact time between 5 to 240 mins. To study the kinetic parameter initial concentration of 25 mg/L was taken and pH was maintained at their respective optimum pH. The removal of Zn (II) by MSD and RSD adsorbents increases with increase in time until a certain equilibrium point reaches after that no significant increases in adsorption occurs as shown in figure 4. The data obtained were fitted with different kinetic models, pseudo first order and pseudo second order.

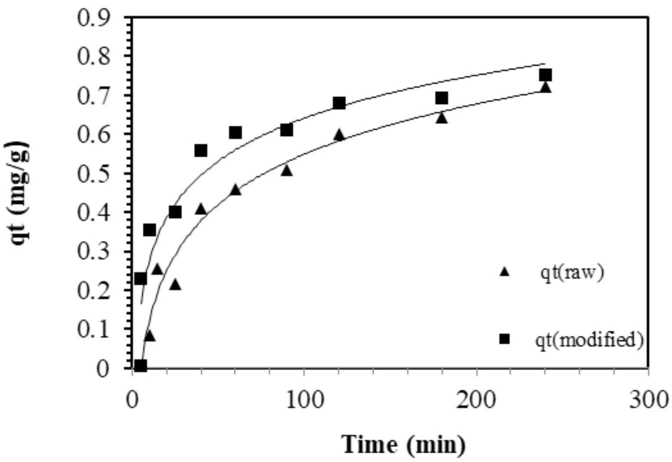

Figure 4*: Adsorption Kinetics for Adsorption of Zinc (II) onto MSD and RSD*

Figure 5 shows the fitting of pseudo-second order kinetics model for adsorption of Zn (II) onto RSD and MSD. This experiment shows the uptake of zinc (II) ions on the surface of adsorbent at various time intervals for fix concentration of 25 mg/L of metal ions solution.

These data shows that, at initial state the rate of metal adsorption by RSD and MSD were rapid and followed by slow phase sorption process and equilibrium is reached in 60 min and 120 min for the adsorption of Zn (II), indicating that no more metal ions were further removed from solution. The removal of metal ions was rapid in first hour because of the presence of large number of vacant sites in the adsorbent. After certain time, it gradually decreases due to decrease in active sites on the adsorbent surface until it reaches equilibrium. Comparing this result with other literature survey it was found that equilibrium time for Zn (II) was around 60 min and 120 min adsorption of Zn (II) onto bioadsorbent was also nearly same.

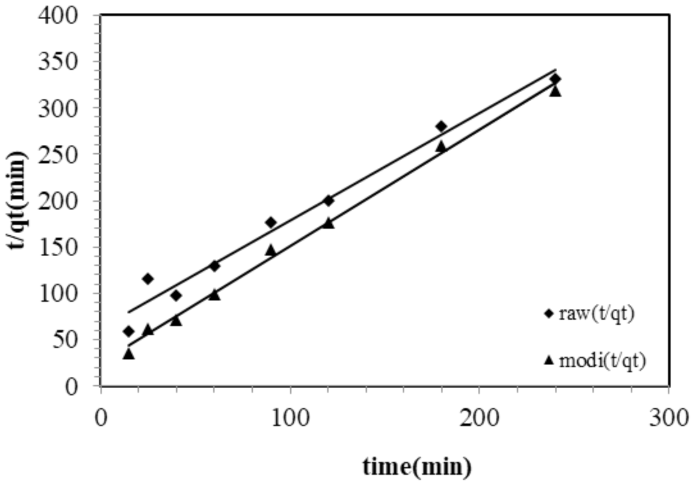

Figure 5*: Pseudo second order kinetic plot for Adsorption of Zn (II) onto MSD and RSD*

Effect of Adsorbent Dose

Another parameter used to evaluate the adsorption capacity at a given concentration of adsorbate is dose of adsorbent. To study the effect of adsorbent dose on the adsorption efficiency of the RSD and MSD, the experiment were carried out by varying the amount of adsorbent dosage from 0.01g to 0.5g in 20mL of the prepared solution and the other parameter like pH and initial concentration were kept at optimum condition. Then the mixture was shaken at mechanical shaker for 24 hours and filtered. The metal ions remained in solution was measured by using spectrophotometer and percentage of adsorption of zinc ions was calculated. The result was found to be follows.

The adsorption efficiency of the RSD and MSD increases with increasing the dosage of adsorbent from 0.01g to 0.15g as given in figure 6. The highest values of Zn (II) removal are 55.23% and 66.81% at 0.15 g dose for RSD and MSD respectively. It is seen that the removal of Zn (II) ions increases with increasing amount of the adsorbent which increases available exchangeable site. Due to availability of more binding sites it is easy for complexation of metal ions so percentage removal of metal ions also increases with increase in adsorbent dose. As the adsorbent dose increased, the adsorption process becomes faster, thus increasing the efficiency of the processes. But further increase up to 0.5 g it was found to decrease in percentage removal of metal ions. The higher dose of adsorbent may cause aggregation of adsorbent particles and consequently, the available adsorption sites may decrease.

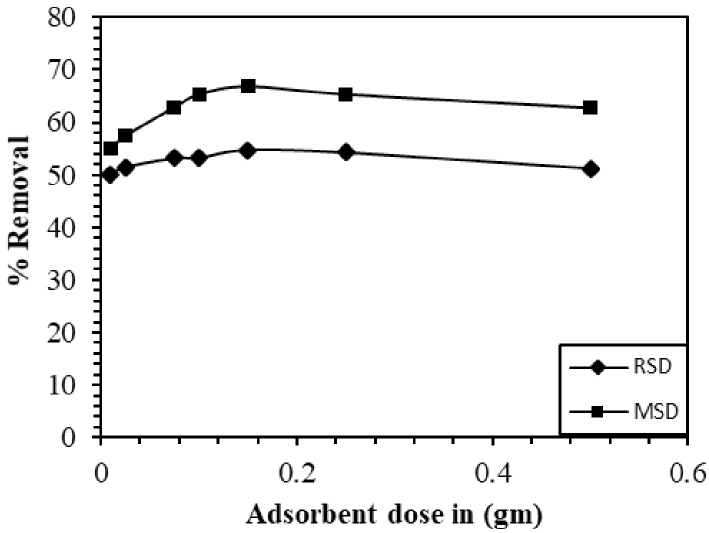

Fig. 6: Effect of Adsorbent Dosage on Removal of Zn (II)

In figure 6 it is observed that there is slightly increase in percentage removal of metal ions with increase in adsorbent dosage from 0.01g to 0.15g and slightly decreases and almost constant further increasing from 0.15g to 0.5g of adsorbent. The maximum removal of Zn (II) for RSD and MSD was 55.23 % and 66.81% respectively at 0.15 g of adsorbent and 20 mL metal solution.

Conclusion

In this research, adsorption of zinc (II) ions on raw saw dust (RSD) and modified saw dust (MSD) has been compared using batch adsorption technique. The adsorption study of Zn (II) ions were conducted at different pH values, various initial concentration of metal ions, time and dose of the adsorbent. Spectrometric analysis of resultant sample shows that the maximum absorbance of zinc occur at pH 6 and % removal of zinc was 42.94% and 79.28% for raw and modified sample respectively. The uptake of Zn (II) ions on both raw and modified adsorbent was found to follow pseudo second order kinetics. The optimum time for the adsorption was found to be 60 mins and 120 mins for RSD and MSD, respectively. Maximum percentage removal of Zn (II) was 54.23% for RSD which increases up to 66.6 % for MSD at 0.15g of adsorbent at 20 mL metal solution. In summary, the results indicate that charred saw dust can be used as an effective and efficient alternative to commercial adsorbents for the removal of Zn (II) ions from its aqueous solution.

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