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Purification of Zn(II) Contaminated Waste Water by Using Chemically Modified Biosorbent

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Abstract

In this study the potential of chemically modified tea waste as a low-cost biosorbent for the purification of Zn(II) contaminated waste water was investigated. The surface morphology of biosorbent was characterized by SEM images and the surface charge was investigated by pH_{PZC} measurement. The surface functional groups responsible for adsorption were identified by FTIR spectroscopy. The influences of pH, contact time, initial metal concentration, were studied in batch experiments at room temperature. The optimum pH for maximum adsorption was found to be at pH 6. Langmuir model better explains the adsorption data, with correlation coefficient 0.99 and a maximum adsorption capacity of 58.13 mg/g. This indicates monolayer coverage on the adsorbent. The biosorption of Zn(II) was found to be rapid up to 100 min and equilibrium was reached within 120-170 min. Kinetic studies showed good correlation coefficient for a pseudo-second order kinetic model with higher value of correlation coefficient. These experimental results revealed that the biosorbent can be used as an efficient biosorbent for the treatment of Zn(II) contaminated waste water..

Keywords: *biosorption; heavy metal; Langmuir model; Pseudo-second order; waste water.*

1. Introduction

The metal contaminated waste water is a serious problem as it can easily find its way into surface as well as ground water. Different techniques have been developed for treatment of metal contaminated waste water including chemical precipitation, chemical oxidation or reduction, electrochemical treatment, ion exchange,

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reverse osmosis, filtration, evaporation recovery and ion exchange [1]. These treatment processes have some disadvantages like complicated treatment process, production of toxic chemical sludge. Moreover, such processes are also costly for treatment of waste water [2].

Zinc is an essential heavy metal, which is relatively non-toxic for human beings. It is second most abundant trace metal found in our body. It is a cofactor of many enzyme systems and found in active sites of various enzymes. Hence it is important for the physiological function of living tissues and helps to regulate many biological processes [3-4].

Zinc and its compounds are widely used in alloy production such as brass, German silver, delta metal, electrical devices, and rubber and tire industries. It is used in anticorrosion coating of steel and iron. It is also used for the manufacture of gold and silver in the cyanide method and for desilverization of lead in parks process. In electrical batteries it is used as negative plate. It is also used for roofing and gutter in buildings. Its oxide is used as a white pigment in water color and paints. Various zinc salts are used industrially in wood preservatives, catalysts, photographic paper, and accelerators for rubber vulcanization, ceramics and textiles. Compounds of zinc are used as pesticides [5-6].

Due to excessive use of Zn(II) in our daily life and in various industries, there is high possibility of zinc contamination in the aqueous environment. It can have severe toxicological effects on both humans and aquatic ecosystems. Zinc toxicity from excessive ingestion is uncommon but its exposure causes gastrointestinal distress, depression, lethargy, neurological signs and increased thirst and diarrhea. The most commonly reported effect of zinc includes metal fume fever which is characterized by chest pain. Longer term exposure to lower doses (~0.5-2 mg zinc/kg/day) of zinc compounds results in the decreased adsorption of copper. Dermal exposure to the zinc chloride and other zinc salts may causes irritation on skin.

Hence, it is essential to remove Zn(II) from industrial waste water to prevent its hazardous effect. Adsorption has been found to be superior to other techniques for waste water treatment in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. In recent years, the searches for low-cost agricultural by-products have been widely studied for Zn(II) removal from waste water.

In this study a biosorbent, prepared by using tea waste has been used as an adsorbent for treatment of Zn(II) contaminated waste water. It is composed of natural polymers like lignin, cellulose and hemicelluloses. These natural polymers can be used for sequestration of heavy metals. However, the biosorbent in raw form has very poor metal binding capacity. To enhance its capacity, it has been chemically modified. After chemical modification the polymeric network of the biosorbent is exposed for removal of heavy metals. For adsorptive removal of heavy metals, the amino-functional groups have been found to be more effective chelating group. The N atom of the functional group has greater metal complexation tendency by donating a lone pair of electrons. Hence there has been considerable interest for introduction of N-functional group on the surface of adsorbent to enhance the adsorption capacity [7-8]. To introduce N-functional groups, the biosorbent has been modified with dimethylamine.

2. Experiment

2.1 Preparation of biosorbent

Fifty grams of tea waste was washed with hot distilled water till the filtrate became clear. It was dried in an oven at 70°C and modified chemically to prepare an aminated biosorbent. The procedures used are similar to those earlier reported [9].

2.2 Adsorption experiments

The 1000 mg/l stock solution of Zn(II) was prepared by dissolving calculated amount of Zinc sulphate in 0.1 M HNO3. The stock solution was diluted to required dilution to prepare working solution of different concentration. The pH of experimental solutions were maintained using nitric acid and sodium hydroxide and [2-4-(2-hydroxymethyl)-1-piperazinyl] ethanesulphonic acid [HEPES] was used as buffer. Analytical grade reagents [AR] were used for all experimental works.

The biosorption studies were determined as a function of pH, contact time and initial metal ion concentration by using batch experiments. All the experiments were performed at room temperature and 150 rpm on a mechanical shaker with 25 mg of adsorbent in conical flask containing 20 ml of Zn(II) solution. After attaining equilibrium, the mixture was filtered through Whatman filter paper (no. 40). The concentration of Zn(II) in solution before and after equilibrium was determined by atomic absorption spectrophotometer (Agilent technologies AAS, model- 240FSAA, USA) using air acetylene flame.

The adsorption efficiency A% of the adsorbent was calculated by using equation (1)

$$A\ \% = \frac{C_i - C_e}{C_i} \text{ X } 100 \qquad (1)$$

where C_i and C_e are concentration of metal ions in mg/l before and after adsorption experiments.
The amount of metal adsorbed i.e. sorption capacity q_e (mg/g) was computed by using equation (2)

$$q = \frac{C_i - C_e}{W} \text{X V} \qquad (2)$$

where V is volume of metal solution (mg/L) and W is weight of adsorbent (g).

3. Result and Discussion

3.1 Characterization

The biosorbent was characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and elemental analysis. The elemental analysis shows percentage of carbon and nitrogen as 49.90 and 5.50, respectively.

3.1.1 Scanning Electron Microscopy

The scanning electron microscopic images were used to examine the surface morphologies of the biosorbent [10]. The images are given in Figure 1. The biosorbent is porous in nature which is clear in low magnification. The surface of biosorbent is rough with uniform microporous structure as seen in high magnification.

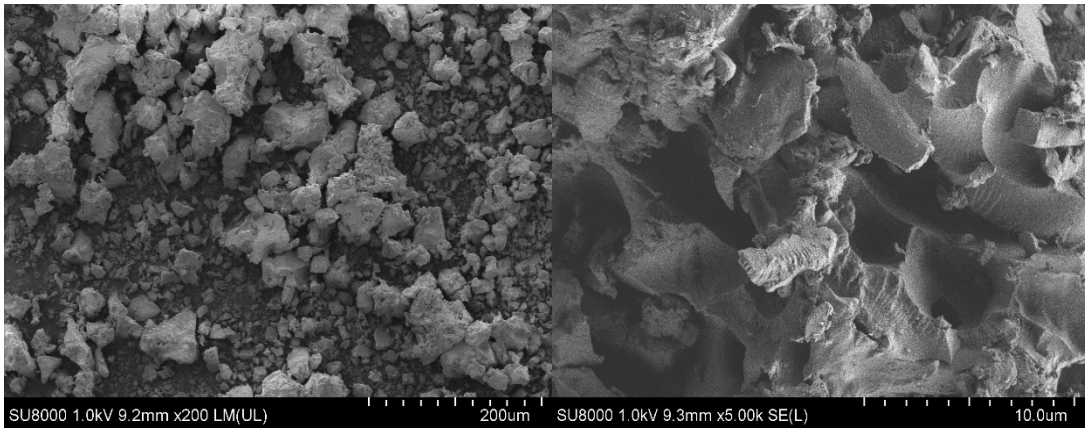


Figure 1. SEM images of biosorbent

3.1.2 Drift Reflectance Fourier-Transform Infrared Spectroscopy

To identify certain functional groups on the surface of the biosorbent DR-FTIR has been used as a useful tool[11]. The biosorbent surface is full of various functional groups. In this spectral analysis, each specific chemical bond often shows a unique energy absorption band. The DR-FTIR spectrum of the biosorbent is shown in Figure 2. The broad band ranging from about 3118 to 3650 cm^{-1} corresponds to the combination of stretching vibration bands of both OH and NH groups on the surface of the biosorbent. The peaks at 1450 cm^{-1} and 1033 cm^{-1} are due to the C-H bending and C-N stretching, respectively. The bands at 2924 cm^{-1} due to CH stretching in CH, CH_2 and CH3 groups, and 1078 cm^{-1} due to C-O stretching and 1646 cm^{-1} due to N-H bending in amines.

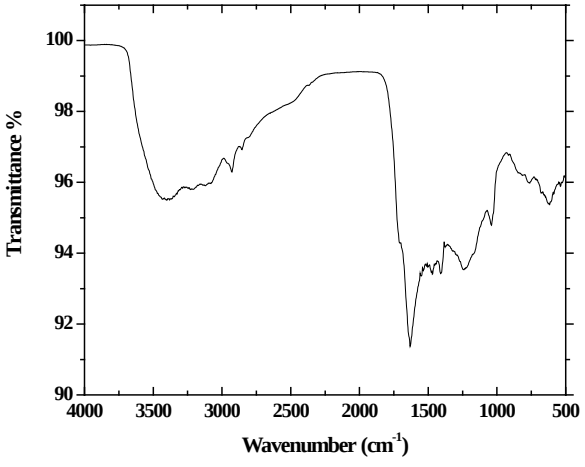


Figure 2. FTIR spectrum of biosorbent

3.2 Adsorption studies

3.2.1 Effect of pH

The adsorption of zinc ions onto the biosorbent was studied over a range of pH 1 – 6 for a fixed adsorbent dose (Figure 3). The pH was adjusted using 0.1 M hydrochloric acid and sodium hydroxide solutions. A general increase in adsorption with increasing pH of the solution was observed for the metal ion up to a pH value of 6 as maximum. The pH dependence of metal uptake could be related to the surface charge of the adsorbent and also the solution chemistry of the metal ions. At pH values less than 4, the metal is in the free ionic form Zn(II) and as such, there is decrease in metal uptake at low pH values. Low pH conditions allow hydrogen and hydronium ions to compete with zinc ions for metal binding sites uptake. At higher pH values, there are lower numbers of competing hydrogen ions and more binding sites are exposed, resulting in greater zinc sorption. The optimum pH was found to be at pH 6.

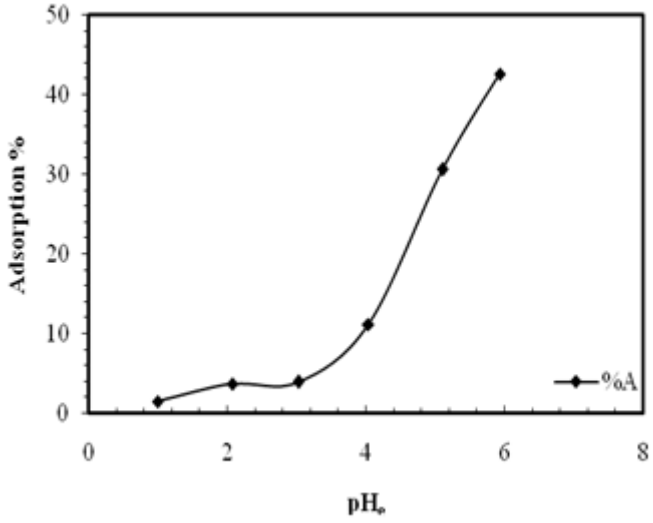


Figure 3. Effect of pH on adsorption percentage

3.2.2 Zeta potential

The zeta potential i.e. pH_{pzc} of biomaterial is an important character that determines the nature of the surface of biomaterial. It is the pH at which surface of biomaterial has net electrical neutrality. The zeta potential of TW in the solution of different pH values are shown in Figure 4. In the figure it is indicated that zeta potentials of raw biomaterial are positive at pH < 5.9 and negative at pH > 5.9. It indicates that the surface of biomaterial becomes positive below pH 5.9, while it becomes negative above pH 5.9. After chemical modification, the pH_{pzc} value shifts towards higher pH range. The pH_{pzc} value for MTW is above pH 9 as shown in Figure 4. The increase in pH_{pzc} values after amination is due to protonation of amino groups introduced onto the surface of biomaterial. Hence increase in pH_{pzc} values further confirms the successful amination onto the surface of biomaterial.

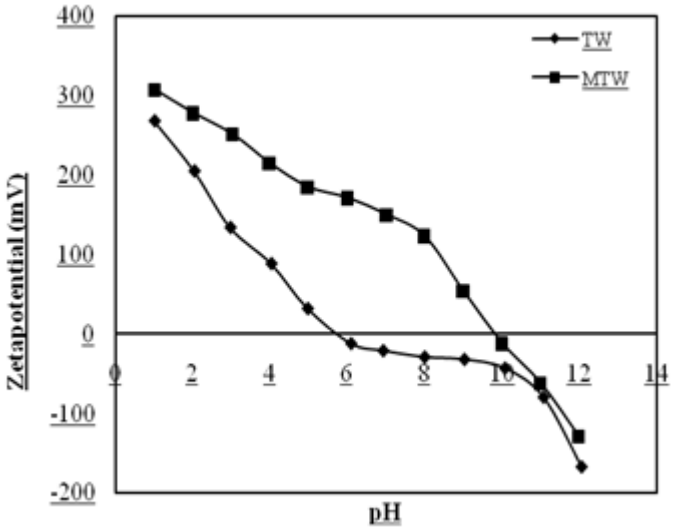


Figure 4. Zetapotential of biosorbents

3.2.3 Effect of initial metal ion concentration

The effect of initial metal ion concentration on the biosorption capacity of the biosorbent was studied under optimum conditions of pH and contact time as shown in Figure 5. In the plot, the metal uptake increases initially with increase in equilibrium metal concentration and eventually limited by the occupied active sites and results in a plateau.

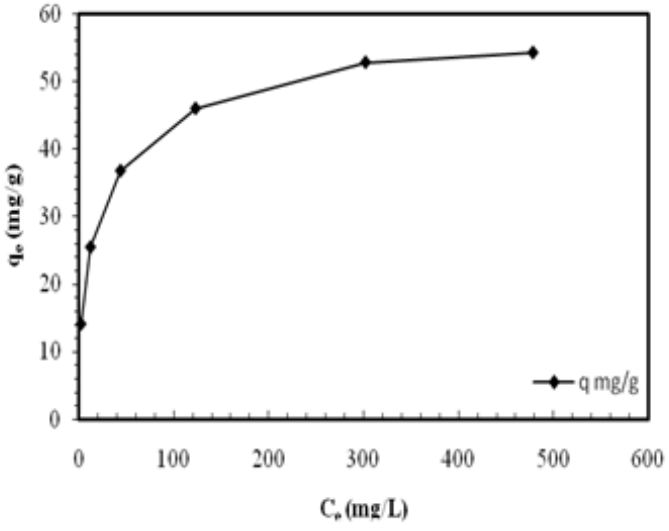


Figure 5. Effect of concentration of metal ions on adsorption of Zn(II)

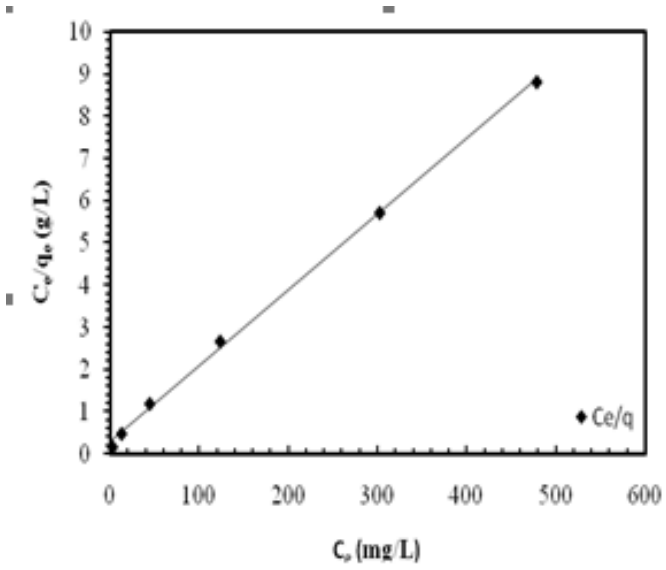


Figure 6. Langmuir Adsorption isotherm for adsorption of Zn(II)

From the isotherm plot it is clear that as the concentration of metal solution increases, the ratio of the metal ions and biosorbent increases and there is a decrease in biosorption efficiency. It is due to the saturation of the available binding sites on the surface of the biosorbent. As the number of metal ions competing for the fixed binding sites on the biosorbent increases, the resultant effect is reduction in the complexation of the metal ions with the biosorbent. Hence higher the concentration of metal solution, the more is the amount of metal ions that will be left in solution.

The sorption data have been subjected to Langmuir isotherm model. It suggests that metal ions are adsorbed according to Langmuir model. The linear form of Langmuir isotherm is given by equation (3)

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (3)$$

where q_e is amount adsorbed (mg/g), C_e is equilibrium concentration of metal ions (mg/L) and q_m and b are Langmuir constants. The linear plot of C_e/q_e versus C_e as shown in Figure 6, with high R^2 suggests the applicability of Langmuir adsorption model and indicates the formation of monolayer coverage of metal ions on the surface of adsorbent. The q_m and b values are found to be 58.13 mg/g and 0.02 L/mg. The values of these parameters show that the biosorbent is efficient for the removal of Zn(II) from the aqueous solution.

3.2.4 Effect of contact time - kinetics of adsorption

Figure 7 shows the effect of contact time on the biosorption of Zn(II) ions. The plot shows that the adsorptive capacity of Zn(II) increased with increase in contact time. The plot consists of initial rapid

adsorption phase and a slower phase where equilibrium uptake was achieved. The initial high rate of adsorption of metal ions is due to free active binding sites on the surface of the adsorbent. As the number of available sites decrease the rate of adsorption of metal ions also decrease. The biosorption of Zn(II) was rapid up to 100 min and equilibrium was reached with in120-170 min.

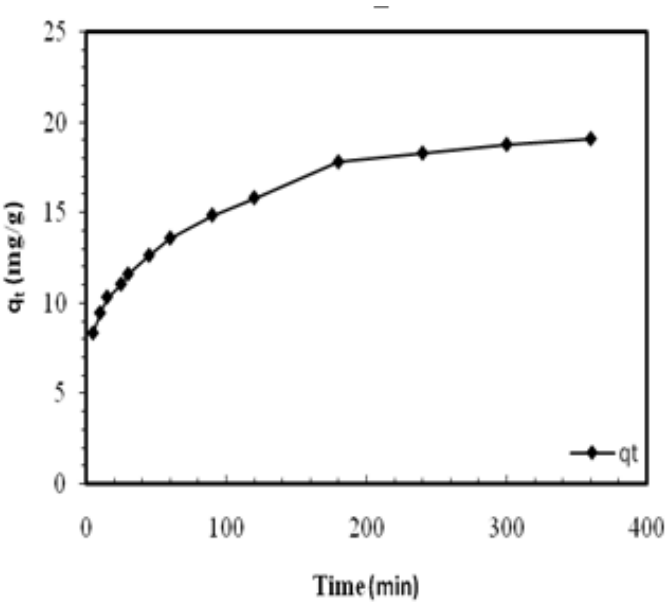


Figure 7. Effect of contact time on adsorption of Zn(II)

The experimental data were fitted to pseudo-second order kinetic model[12] to describe the kinetics of adsorption. It is expressed as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

where q_t is the amount adsorbed at time t (min) and k_2 (g/mg/min) is the rate constant of pseudo-second order kinetics of adsorption. The plot of t/q_t versus t is given in Figure 9. The plot is a straight line with high correlation coefficient value. It indicates that pseudo-second order kinetic model can be applied for adsorption of Zn(II) onto the biosorbent and also indicates the chemisorption of the metal ion.

5. Conclusion

FTIR spectra of the biosorbent prepared by amination of tea waste shows the presence of N-H, O-H, C-H and C-O stretching in the adsorbent. In this study effect of pH, contact time, initial Zn(II) ions concentration on the adsorption of Zn(II) were studied. The optimum pH for adsorption of Zn(II) ions was found to be at pH 6. The adsorption of Zn(II) was increased with increasing contact time and equilibrium was attained in 150 minutes of contact. The equilibrium data conformed well to the Langmuir isotherm with a high correlation

coefficient of 0.99, which indicates that the adsorption of Zn(II) onto surface of tea waste followed a monolayer pattern. The kinetic data obtained from this study fitted well with the pseudo-second order model. The maximum adsorption capacity determined from the Langmuir isotherm model was 58.13 mg/g. Hence it can be concluded that tea waste can be considered as an alternative biosorbent for the removal of Zn(II) ions since it is effective, low cost, abundant and can be obtained locally.

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