Moringa Oleifera Seed as Low Cost and Effective Biosorbent for Cu (II) Removal From Acid Mine Drainage

Abstract

Acid mine drainage (AMD), has been a major environmental problem resulting from the microbial oxidation of iron pyrite in presence of water and air, affording an acidic solution that contains toxic metal ions. The main objective of this study was to remove metal ions from acid mine drainage (AMD) by using Moringa oleifera seed powder (MOSP). Moringa oleifera an agricultural solid waste by-product has been developed into an effective and efficient biosorbent for the removal of Cu (II) from acid mine drainage wastewater. The experimental equilibrium adsorption data were analyzed by two widely used two parameter equations - Langmuir, Freundlich isotherms. Langmuir model offered a better fit with the experimental data than others four isotherm models. The kinetic data were fitted the model with correlation coefficient greater than 0.99. The result of the present investigation indicates that Moringa Oleifera seed can be effectively used for removal of Cu(II) from aqueous solutions.

1. Introduction

Acid mine drainage (AMD) is a serious environmental problem resulting from the weathering of sulfide minerals, such as pyrite (FeS2) and its polymorph marcasite (α-FeS). It is characterized by a low pH-value and high levels of sulfate and metals [1,2]. AMD usually contains high concentration of metals such as iron, manganese, zinc and smaller amount of cadmium, lead, copper, and nickel. The oxidation of sulfide releases dissolved ferrous iron and acidity into water which subsequently releases...
other metal ions. AMD’s typically contain high concentration of dissolved iron which may exists either in reduced form (Fe2+) or in the oxidized form (Fe3+). Acidity in AMD is comprised of hydrogen ion acidity and mineral acidity (iron, aluminum, manganese, and other metal ions depending on the specific geologic setting and metal sulfide). There are 20,000–50,000 abandoned mines in the United States. Many of these mines produce acid mine drainage (AMD). These AMD contains a variety of heavy metals, which adversely affect over 23,000 km of streams in the United States [3]. Pennsylvania alone has over 25% of all abandoned mine sites listed by the office of Surface Mining that generates mine drainage. More than 3000 miles of rivers in Pennsylvania alone are polluted with mine drainage in the nation. If left untreated, the acid drainage can contaminate surface and ground water, damaging the health of plants, wild life, and fish [4]. When acid mine waters mix with surface waters there is potential for gross pollution. An ochre (ferric oxide) precipitate can blanket the receiving water source and kill aquatic flora and fauna. The loss of biological activity could in some instances devastate the food chain and lead ultimately to fish kills and loss of amenity [5]. The industrial sources of manganese are steel alloy, dry cell battery, glass and ceramic, paint, ink, dye and fertilizers It also occurs in metal mines, mine drainage, especially in coal fields [6]. The best available technology discharge limits for acid mine wastewater (mg/l) is provided elsewhere [7]. The current technologies for the removal of copper include chemical precipitation, ion exchange, or electrochemical processes. Many of these methods are not economical, especially when used for the reduction of heavy metal ions to low concentrations. Hence, there is a need to develop cost-effective technologies for treating the acid mine drainage wastewater that reduce metal ion concentrations to environmentally acceptable levels.

Biosorption has the potential to contribute to the achievement of this goal. Biosorption is a process that uses inexpensive biomaterials to sequester metals from aqueous solutions and the biomaterials used in this process are termed as biosorbents. The by-products from agricultural, food and pharmaceutical industries provide economically viable sources of biosorbents; this makes biosorption an inexpensive alternative treatment method. Several workers have reported on the potential use of agricultural by-products as good substances for the removal of metal ions from aqueous solutions and wastewaters [8, 9,10,11, 11,12,13,14,15], Moringa oleifera belongs to the family Moringaceae, which is native to the sub-himalayan tracts of India. Moringa oleifera seed is abundantly available in India with no commercial use. Since its fruits and leaves are edible and consumed in all the seasons, trees are widely cultivated species in India. Due to this, massive amount of seed is produced, which is being disposed off as waste. The plant contains various amino acids, fatty acids, vitamins and nutrients [16], glucosinolates and phenolics (flavonoids, anthocyanins, proanthocyanides and cinnamates) which are the functional groups that are capable of anchoring metals. The bark tissue of M. oleifera contains 4-(α-L-rhamnopyanosyloxy)-benzyglucosinolate [17]. Every glucosinolate contains a central carbon atom which is bonded to the thioglucose group (making a sulfated ketoxime) via a sulfur atom and to a sulfate group via a nitrogen atom. These functional groups containing sulfur and nitrogen are good metal sequesters from the aqueous solution. Because of the composition of Moringa oleifera seed powder and its availability Moringa oleifera seed was chosen as a biosorbent for the removal of Cu (II) from acid mine drainage wastewater .

In the present study, an easy and economic preparation of the adsorbent was carried out and adsorption experiments have been performed to determine the metal biosorption mechanism. The main objectives of the present study include is to study the sorption potential of MOS for copper removal from acid mine drainage wastewater under equilibrium conditions and to understand the
kinetics of it. The data from the experimentation were matched with different kinetic models to recognize the adsorption mechanism.

2. Materials & Methods

2.1 Chemicals

All reagents used were of AR grade. Deionized double distilled water was used during the experimental studies. Stock solution (1000 mg L^{-1}) was prepared by dissolving CuSO\textsubscript{4}·6H\textsubscript{2}O. This was further diluted to obtain the desired concentration for practical use. BDH reagent grade HCl, NaOH and buffer solutions were used to adjust the solution pH.

2.2 Preparation of the biosorbent

*Moringa oleifera* seeds were collected from local market of Loni (Maharashtra, India), it was dried and ground in a mill to obtain fine powder. The powder was washed twice with deionized water and dried at 50^\circ\text{C} for 24 h, then boiled in double distilled water by changing the water repeatedly until water becomes colorless, which specify the removal of water soluble color compounds. The washed and boiled powder was oven dried at 70^\circ\text{C} for 24 h and stored in desiccators to prevent moisture adsorption before its utilization. This treated *Moringa oleifera* seed powder is called as MOS.

2.3 Characterization of the adsorbent

Characterization of biosorbent surface and structure hold keys to understanding the metal binding mechanism onto biomass. The proximate and ultimate analysis of MOSP is presented in Table 1. The proximate analysis of the coal was carried out by using standard methods (ASTM D 5142-90).

<table>
<thead>
<tr>
<th>Characteristics of <em>moringa oleifera</em> seed (MOS)</th>
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<tr>
<td>Bulk density (g/cm\textsuperscript{3})</td>
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<tr>
<td>Moisture content (%)</td>
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<tr>
<td>Ash content (%)</td>
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<tr>
<td>Fixed carbon (%)</td>
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<tr>
<td>Carbon (%)</td>
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<td>Hydrogen (%)</td>
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<td>Nitrogen (%)</td>
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<td>Sulphur (%)</td>
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<td>Oxygen (%)</td>
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Percent ash content, moisture content, fixed carbon, and bulk density are also given in Table 1. Elemental analysis results showed that MOS is composed of 45 % carbon, 6 % hydrogen, 0.9 % nitrogen, 0.8 % sulphur and 48 oxygen.

2.4 Biosorption procedures

Batch biosorption studies were executed by taking 50 mL of Cu (II) solution with known pH in a 250 mL flask and by adding 200 mg of MOS. The sealed flask was placed in a shaking incubator at a
speed of 350 rpm and temperature of 25°C. After 3h, biosorbent was separated using filter paper and the concentration of metal ion in solution was analyzed by AAS.

A Cyberscan -500 pH meter was used for pH measurements. The pH meter was calibrated using buffer standard solutions of pH 4.0, 6.0 and 9.0. The metal concentrations in the samples were determined using atomic absorption spectrophotometer (AAS, Chemito 201 India).

The effect of pH on Cu (II) biosorption was determined by equilibrating the suspensions in solutions of different pH ranging from 2.0 to 9.0. For the adsorption isotherm studies, the initial metal ion concentration was varied over a range of 20 to 200 mg L⁻¹. The concentration of MOS was varied between 25 to 700 mg to determine the ratio required for optimum biosorption. The interference caused by the presence of other cations that are normally present in water was checked by the addition of monovalent Na and K, and divalent Mg and Ca metal solution ranging from 0 to 400 µg mL⁻¹.

The quantity of metal ion adsorbed onto the MOS, \( Q_e \), was computed by the following equation:

\[
Q_e = \frac{V}{m} (C_0 - C_e)
\]  

Where, \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of Cu(II) in solution whereas \( V \) and \( m \) are solution volume in dm³ and mass of adsorbent in grams(g), respectively.

3 Result and discussion

3.1 Effect of pH

It is distinguished that pH is the most important factor that controls the biosorption process [18]. The pH level affects the system of negative charge on the surface of the biosorbing cell walls, as well as physicochemistry and hydrolysis of the metal. Therefore, initial experiments have been performed to find out the optimum pH for the metal removal. Percentage removal of the metal ion as a function of pH is shown in Fig. 1. It has been examined that under highly acidic conditions (pH ≈ 2.0) the amount of Cu (II) removal was very small, while the sorption had been increased with the increase in pH from 3.0 to 6.0 and then decreased in the range 7.0 and 8.0. The lower removal efficiency at low pH is apparently due to the presence of higher concentration of H⁺ in the solution which compete Cu (II) ions for the adsorption sites of the MOS. With increase in pH, the H⁺ concentration decreases leading to increased Cu(II) uptake.

Decreased biosorption at higher pH (pH>6) was due to the formation of soluble hydroxylated complexes of the metal ions and their competition with the active sites, and as a consequence, the retention had been decreased again. Therefore further experiments were carried out with initial pH value of 6. Previous studies also reported that the maximum biosorption efficiency for Cu(II) metal ion on biomass was observed at pH 6 [19,20,21].

3.2. Effect of biosorbent dose

Biosorption of Cu (II) onto MOSP was studied by changing the amount of sorbent from 0.1 to 0.8 g in the test solution while maintaining the initial concentration 50 mg mL⁻¹, pH 6 and contact time 2 h constant. Biosorption of Cu (II) as a function of biomass shown in Fig. 2, indicates the effect of sorbent dose on the Cu (II) biosorption by MOSP. Obviously, the biosorption efficiency increased as the sorbent dose increased, but it remained almost constant when the sorbent dose reached 0.4 g. When sorbent ratio is small, the active sites for binding metal ions on the adsorbent surface is less, so
the adsorption efficiency is low; when biosorbent dose increased more metal ions were adsorbed. Thus it results in the rise of adsorption efficiency until saturation.

Figure 1 Effect of pH on the removal of Cu(II)

Figure 2 Effect of Dose of Moringa Oleifera Seed Powder on the removal of Cu(II)

3.3 Effect of Initial Concentration
For practical applications, the process design and operation control, the sorption kinetics were very important. Sorption kinetics in wastewater treatment was significant, as it provides valuable insights into the reaction and the mechanism of the sorption reactions. Biosorption of Cu(II) onto MOSP at various initial concentrations had been carried and shown in Fig. 3.
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3.4 Biosorption isotherm

The successful representation of the dynamic adsorptive separation of solute from solution onto an adsorbent depends upon an appropriate description of the equilibrium separation between two phases [22]. In order to determine the mechanism of Cu(II) biosorption onto MOS and to evaluate the relationship between biosorption temperatures, the experimental data was applied to the two-parameter non-linear isotherm models, i.e. Langmuir, Freundlich.

The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface [23].

\[
\frac{1}{q_e} = \left( \frac{1}{K_{aqm}} \right) \frac{1}{Ce} + \frac{1}{q_m}
\]

In eq. (2) \( q_m \) is the monolayer biosorption capacity of the biosorbent (mg g\(^{-1}\)), \( q_e \) is the equilibrium metal ion concentration on the biosorbent (mg g\(^{-1}\)), \( C_e \) is the equilibrium metal ion concentration in the solution (mg L\(^{-1}\)), and \( K_L \) is the Langmuir biosorption constant (L mg\(^{-1}\)) related to the free energy of biosorption. The constant \( q_m \) and \( K_L \) increased with increase in temperature. The essential features of the Langmuir biosorption isotherm can be expressed in terms of a dimensionless constant separation factor (RL), which is defined in eq. (3).
where KL is the Langmuir constant (L mg⁻¹) and C0 is the initial adsorbate concentration (mg L⁻¹).

The value of RL indicates the type of isotherm [24]. The values of RL are all in the range of 0-1, which indicate the favorable biosorption of Cu (II) by MOSP.

\[
R_L = \frac{1}{1 + K_L C_0}
\]  

(3)

The Freundlich model assumes a heterogeneous sorption surface [25].

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

(4)

In eq. (4) Kf is a constant relating the biosorption capacity and 1/n is an empirical parameter relating the biosorption intensity, which varies with the heterogeneity of the material. From the graphs, Kf values were found to be 0.074 and the n values were found as 1.73. The 1/n values were between 0 and 1 indicating that the biosorption of Cu (II) onto the MOS was favorable at studied conditions. The high value of R² indicated that Freundlich model was altogether properly describing the relationship between the amounts of adsorbed metal ions and their equilibrium concentrations in the solution. Table 2 gives the statistical empirical data estimated from isotherm equation for the removal of Cu (II) using Moringa oleifera seeds.

**Table 2. Isotherm Constants**

<table>
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<tr>
<th>Isotherms</th>
<th>Constants</th>
<th>R²</th>
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<tr>
<td>Langmuir</td>
<td>a = 3</td>
<td>b = 4.9x10⁻³</td>
</tr>
<tr>
<td>Freundlich</td>
<td>n = 1.73</td>
<td>k = 0.074</td>
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</table>
4 Conclusion
The experimental investigation concluded that MOSP could be used as potential sorbent, for the removal of Cu (II) from acid mine drainage water. The batch study parameters; pH of solution, biomass concentration, were found to be effective on the biosorption processes. The isotherm studies revealed that the biosorption process followed the Freundlich model and it is the best fit model for the removal of Cu (II). The maximum biosorption capacity of copper was 32 mg g\(^{-1}\) at an optimum pH 6. Based on all results, the MOSP as a natural and low-cost biomass can be used as alternative biosorbent for treatment of waste waters containing Cu (II) ions.

References


BIOGRAPHY

Dr. Ravindra W. Gaikwad is a chemical engineer and a Professor of Chemical Engineering at Pravara Rural Engineering College, Loni, affiliated to University of Pune. Dr. Gaikwad has taught academic courses in mechanical operations, chemical engineering mathematics, process modeling & simulation, environmental engineering. His research has focused on Modeling, optimization and removal of heavy metals in Acid Mine Drainage wastewater, with emphasis in Environmental Technology (Wastewater engineering and solid waste management). The emphasis is both on the fundamental understanding and modeling of the key heavy metal removal that take place in environmental systems, and on the development of improved technologies for the treatment and management of liquid and solid wastes. Dr. Gaikwad has directed or co-directed research and training projects. He has had the opportunity to lead an extensive research effort involving field data collection and modeling of the chemical engineering system. Dr. Gaikwad has authored or co-authored 93 refereed journal articles, 34 professional proceedings papers, and 22 other articles and technical reports. In addition, he has served as an independent consulting engineer. He has designed and conducted numerous short courses and special training programs in process modeling & simulation and Environmental Engineering.