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Biosorption of Zinc by Chemically Modified Biomass of Corncob (*Zea mays* L.)

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Abstract: In the studies corncob (CC) biomass was utilized as a new adsorbent to remove Zn (II) from aqueous solution. Corncob was modified with $KMnO_4$, H_2O_2, HNO_3, Na-Sul, Oxalic Acid and Ascorbic Acid to investigate the effect of chemical modification on Zn (II) binding capacity. The adsorption behavior Zn (II) was studied under different conditions, including metal ion concentration 25-400 (mgLG^1), pH values were 2, 3, 4, 5, 5.5, 6, 7 for Zn (II) and contact time was 1440 minutes. The sorption capacity of pretreated corncob was in following order: $KMnO_4$-CC (41) > Na-Sul-CC (37) > H_2O_2-CC (34.75) > OA-CC (32.75) > AA-CC (27.7) > HNO_3-CC (27.42) > Nat-CC (25.4) for Zn (II).The optimize pH for Zn (II) was 5.5. Kinetic studies revealed that adsorption was rapid in first fifteen and thirteen minutes and equillibrium was achieved after 120 minutes. The equilibrium adsorption data were fitted to Langmuir and Freundlich adsorption isotherm models. $KMnO_4$ pretreated CC show best metal uptake in comparison to others. These findings demonstrate that CC (corncob) is cost effective, potential and a novel biosorbent for the removal of heavy metals such as Zn (II) from the aqueous solution.

Key words: Biosorption % Zinc % Corncob % Pretreatment % Uptake % Biomass

INTRODUCTION

Heavy metal pollution is one of the most important environmental problems today. Various industries produce and discharge wastes containing different heavy metals into the environment, such as mining and smelting of metalliferous, surface finishing industry, energy and fuel production, fertilizer and pesticide industry and application, metallurgy, iron and steel, electroplating, electrolysis, electro-osmosis, leatherworking, photography, electric appliance manufacturing, metal surface treating, aerospace and atomic energy installation etc. Thus, metal as a kind of resource is becoming shortage and also brings about serious environmental pollution, threatening human health and ecosystem. Three kinds of heavy metals are of concern, including toxic metals (mercury, cromium, zinc etc), precious metals (such as Pd, Pt, Ag, Au, Ru etc.) and radio-nuclides (Uranium, thorium, radium etc [1]. Heavy metals have been greatly released into the environment due to rapid industrialization and have created a major universal concern. Cadmium, Zinc, Copper, Nickel, Lead, Mercury and Chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, printing and photographic industries [2]. Heavy metal toxicity can result in damage or reduced mental and central nervous function, lower energy level and damage to blood composition, lungs, kidneys, liver and other vital organs [3]. Zn (II) may be found in wastewater discharges from acid mine drainage (AMD), galvanizing plants, as a leachate from galvanized structures and natural ores and from municipal wastewater treatment plant discharges. Zn (II) travels through the food chain via bioaccumulation. Hence, there is significant interest regarding Zn (II) removal from wastewater streams. Traditional methods for removal of Zn (II) ions from solution are often expensive and ineffective at low metal concentrations. Therefore, there is a need for a cost effective treatment method that is capable of removing low concentrations of Zn (II) from solution [4].

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Zn (II) may be found in wastewater discharges from acid mine drainage (AMD), galvanizing plants, as a leachate from galvanized structures, natural ores and from municipal wastewater treatment plant discharges. According to world health organization (WHO) more than 3mg L^{-1} of zinc in drinking water is unacceptable. Too much intake of Zn (II) can lead to respiratory incapacitation, as indicated by increased respiratory activity such as breathing rate, volume and frequency of ventilation, coughing, decrease in oxygen uptake efficiency [5]. Contamination of environmental by heavy metal is a serious problem and this has led to the development of new and improved methods for treating wastewaters. The conventional methods used to remove heavy metals from wastewaters are precipitation, coagulation, reduction and membrane processes, ion exchange. However, industrial application of such processes is often restricted because of technical and or economic constraints. Adsorption is an effective technique for removal of heavy metal [6]. Biosorption is a term that describes the removal of heavy metals by the passive binding to non-living biomass from an aqueous solution. This implies that the removal mechanism is not metabolically controlled. In contrast, the term bioaccumulation describes an active process whereby removal of metals requires the *metabolic* activity of a living organism. In recent years research on the mechanisms of biosorption has intensified since biomass can be employed to sequester heavy metals from industrial effluents (e.g. from the mining or electroplating industry) or to recover precious metals from processing solutions of the many types of biosorbents [7]. A corncob is the central core of a maiz (*Zea mays ssp. mays L.*) ear. The corn plant's ear is also considered a "cob" or "pole" but it is not fully a "pole" until the ear is shucked, or removed from the plant material around the ear. Every row of corn on a corncob has the same number of kernels. Corn is one of the largest production crops in the world, especially in china. Corncob, corn husk, corn leaf and corn stalk are abundant agriculture residues form corn, but most are burnt without utilization [8]. *Zea mays* powder is responsible for biosorption. Sorption efficiency of Zea *mays* is increased by introducing Carboxyl, phenolic, amino and hydroxyl groups in biomass because these groups have better affinity towards metal ions [9]. Studies were carried out to evaluate the biosorption potential of *Zea mays* (corncob) and to know the the effect of different experimental parameters like pH, initial metal concentration and contact time.

MATERIALS AND METHODS

Corncob biomass was procured from the Rafhan Maize Products Co. Ltd, Faisalabad, Pakistan. It was washed with distilled water, dried, ground, sieved and finally stored in air tight jars at room temperature. Biosorbent for all experiments was pretreated by using $KMnO_4$ (0.1 M), Ascorbic acid (0.1M), Sodium Sulphite (0.1 M), Oxalic Acid (0.1 M) and HNO_3 (0.1 M) on native corncob biomass to enhance its biosorption capacity. Stock Cu (II) solution (1000 ppm), was prepared by dissolving 3.93g copper sulphate in deionized water. After preparation of solution, different parameters like pH, metal initial concentration and contact time dependency were studied in batches experiments. In all sets of experiments fixed volume of Cu solutions (100 mL) were thoroughly mixed with desired biosorbent dose 0.1 g at 30°C and 100 rpm up to 24 hours. To check the influences of pH, metal initial concentration and contact time on sorption of Cu by *Zea Mays* Biomass at different conditions of initial metal concentration (25, 50, 100, 200 and 400 ppm) and for pH (2, 3, 4, 5 and 6) and for contact time (0, 15, 30, 45, 60, 120, 240, 360, 1200 and 1440 minutes) were selected. For the adjustment pH of the medium 0.1 N solution of H_2SO_4 and NaOH was used. The flasks were covered with aluminum foils and placed on rotating shaker (PA 250/25. H) with a constant rate of 100 rpm. After 24 hours samples were filtered with filter paper. Metal ion concentration was measured by Atomic Absorption Spectrophotometer using an air acetylene flame and single element hollow cathode lamp. The instrument was calibrated with standard solution before analysis of sample solution. Instrumental setting for Cu (II) analysis were Copper hollow cathode lamp, current 15mA and Wave length 324.5nm, Slit 0.7 and air acetylene flame. Uptake of Zinc ion was calculated from a mass balance equation ($q = \frac{(Ci - Ce)V}{M} x1000$); q, Zinc uptake capacity (mg Zn (II) g^{-1} *Zea Mays* biomass).

RESULTS AND DISCUSSION

Heavy metal pollution has become one of the most serious environmental problems today. Unlike organic pollutants, these heavy metals (Cu, Zn, Zn, Ni, Cd) are non-biodegradable and so removal of these heavy metals is extremely important for the health of living organisms. Biosorption is an alternative process for the removal of heavy metals, metalloid species, compounds and particles from aqueous solution by biological material.

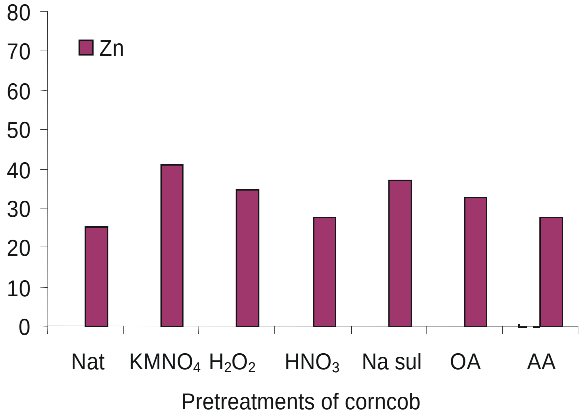

Fig. 1: Effect of Pretreatments on biosorption of Cu (II) and Zn (II) by *Zea mays*

Biosorption is found to be the effective method for the removal of heavy metals. In this research work, biomass of *Zea mays* was used along with original and pretreated biomass (Fig. 1). This research work determines the effect of native as well as pretreated Z*ea mays* on biosorption of Zn (II) from aqueous solution. Under the influence of different experimental variables such as effect of pretreatments, pH, initial metal concentration and contact time which is conventionally being used to optimize the suitable experimental conditions for the maximum metal uptake by the selected biosorbent is described comprehensively.

Effect of pretreatment: To evaluate the effect of pretreatments on Z*ea mays* 100 mg LG^1 of Zn (II) solutions were shaken at 100 rpm with 0.1gm of pretreated corncob. The size of the biomass was 0.25 mm at the pH of 5.5 for Zn (II). Effect of chemically pretreatment Corncob (CC) has been indicated that the q (mg gG^1) values were in the following order: KMnO$_4$-CC (41) > Na-Sul-CC (37) > H$_2$O$_2$-CC (34.75) > OA-CC (32.75) for Zinc (Fig. 1). The above results depicted that the removal of surface impurities and exposure of available binding sites for metal biosorption after pretreatments may be the reason for the increase in metal biosorption [10]. In case of plant origin biomaterial active binding sites for metals are supposed to be functional groups of hydroxyl and carboxyl in cellulose and pectin, chemical modification has shown great promise in improving the cation exchange capacity due to the increase of functional groups [11]. The pretreatments modify the cell surface either by removing or masking the groups or exposing more metal binding sites. Chen *et al*., [12] used treated alga for the biosorption of nickel and copper from aqueous solution and they got the same trend for the effect of pretreatments. Results showed that KMnO$_4$ pretreatments of the biomass exposed more functional groups of the biomass and introduce more sorption sites on biomass surface hence has increased the biosorption capacity of the CC. H$_2$O$_2$ pretreatment also increases the sorption capacity of biomass but less than KMnO$_4$ pretreatment. The HNO$_3$ pretreatment decreased the metal uptake by damaging most of the sorption sites. Numerous studies show that pH is an important factor affecting adsorption of heavy metals by biosorbents [11]. The change in pH values can usually result in the change of the surface charge on the biosorbent. At high pH values, electrostatic repulsion decreases owing to the reduction of positive charge density on the biosorbent, which leads to an increase in metal adsorption capacity. Therefore, Zn adsorption capacity increased with increase in pH value [13].

The results showed that Zn (II) uptake at pH range of 2-7 for original and pretreated biomasses. The absorption capacity (mggG^1) in case of Zn (II) increased from 11.9 to 49.4, 25.5 to 63, 22 to 59, 20 to 59.5, 21.5 to 53 and 20 to 52 for Nat-CC, (KMnO$_4$-CC), (H$_2$O$_2$-CC), (HNO3-CC), (Na-sul-CC), (OA-CC) and (AA-CC) (Fig. 1). It would be plausible to suggest that at lower pH value, the surface of the adsorbent is surrounded by hydronium ions (H$^+$), thereby preventing the metal ions from approaching the binding sites of the sorbent. This means that at higher H$^+$ concentration, the biosorbent surface becomes more positively charged such that the attraction between biomass and metal cations is reduced [14, 15]. Lee and Chang [11] reported the same results regarding the biosorption of heavy metals from aqueous solution by Spirogyra and Cladophora filamentous macro-algae.

Effect of metal ion concentrations: When an adsorbate come in contact with an adsorbent surface, adsorbate molecules adsorb to the surface in quantities that depend on their bulk concentration [16]. The effect of metal concentration on the removal of Zn (II) and Cu (II) from the aqueous solutions by *Zea mays* in its native as well as pretreated form were studied at pH 5.5 by changing the concentration of the system from 25 to 400 mg LG^1. The data showed that the metal uptake increased and percentage adsorption of the Zn (II) decreased with increase in initial Zn (II) concentrations. It indicated the relation between metal uptakes capacities q (mg gG^1) and the metal ion concentration (mg LG^1) for the removal of Zn (II). Results showed that sorption capacity increased with increased in initial metal ion concentration of Zn (II) on the biomass and % age removal decreased with increased in initial metal concentration. The sorption capacities (mggG^1) for Zn (II) (mg gG^1) increased from 8 to 86.74, 12.88 to 95.4,17.16 to 86.12, 7.76 to 59.76, 15.44 to 78.2, 12.88 to 78.14 and 11.3 to 79.22 while % removal decreased from 32-21.68, 51.52-23.85, 68.64-21.53, 31.04-14.94, 61.76-19.55, 51.52- 19.53 and 45.2-19.80 for (Nat-CC), ($KMnO_4$-CC), (H_2O_2-CC), (HNO3-CC), (Na-sul-CC), (OA-CC) and (AA-CC) as concentration increased from 25 to 400 mgLG^1 (Fig. 1). All the biosorbents has a limited number of active sites, which would have become saturated at a certain concentration. It can be explained by the fact that at very low concentration of metal ions, the ratio of sorption surface area to the total metal ions available is high and there is a greater changes for metal removal [5]. At high concentration low adsorption is due to the saturation of adsorption sites. Kinetic study reported that sorption capacities increased by increasing concentration (mgLG^1) by using *Syzygium cmini*, for the removal of lead from aqueous solution.

Langmuir isotherms were 4.7 for Zn (II) which was plots of C_e/Q_e gLG^1 verses C_e mgLG^1 under different concentrations of metals. Straight lines with R^2 values of Zn (II) sorption, 0.826, 0.963, 0.917, 0.973 0.804 and 0.827 by Nat-CC, $KMnO_4$-CC, H_2O_2-CC, HNO_3-CC, Na-Sul-CC, OA and AA-CC were obtained. Linearization of graph and theoretical monolayer capacity (q_{max}) calculated for Zn (II) on the Nat-CC, $KMnO_4$-CC, H_2O_2-CC, HNO_3-CC, Na-Sul-CC, OA and AA-CC found to be agreed with the experimentally determined sorption which is an indication of the applicability of the Langmuir isotherm for Zn (II) (Fig. 2). Validation of Langmuir isotherm model on the system under observation showed that the monolayer sorption of metals on to surface containing a definite number of identical sites. The linear plot of the Freundlich isotherm model for Zn (II) were 0.990, 0.990, 0.955, 0.979, 0.925, 0.973 and 0.948 with Nat-CC, $KMnO_4$-CC, H_2O_2-CC, HNO_3-CC, Na-Sul-CC, OA nad AA-CC respectively, these values were greater than R^2 values obtained in case of Langmuir model. For Zn (II) metal ion sorption, the value of K_f (Freundlich constant) is 5.9 with H_2O_2-CC whish is greater than Nat-CC (3.1), $KMnO_4$-CC (3.0), HNO_3-CC (1.2), AA-CC (2.9) and OA-CC (3.6) and Na-Sul-CC (5.1) which indicated high sorption ability of H_2O_2-CC. These results indicated that Freundlich and Langmuir isotherm models satisfied well the experimental data Zn (II). Reddy *et al*. [16] studied the biosorption of Zn (II) from aqueous solutions using chemically modified *Moringa oleifera* tree leaves which have quoted the same drift in results.

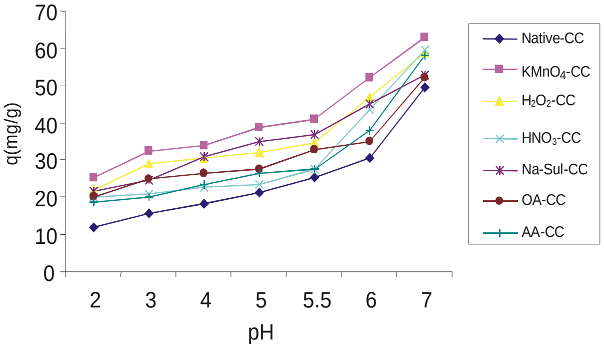

Fig. 2: Effect of pH on biosorption of Zn (II) by *Zea mays*

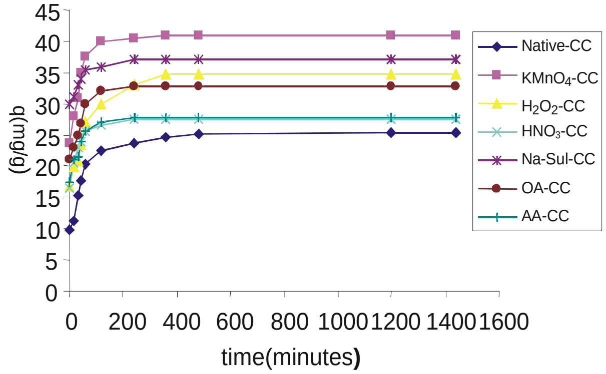

Fig. 3: Effect of time on biosorption of Zn(II) by *Zea mays*

Influence of contact time: Contact time was one of the important parameter for an economical wastewater treatment. The biomass of *Zea mays* were used as biosorbing agent for removal of Zn (II). The rapid initial sorption was likely due to extra cellular binding and because adsorption sites are open, the metal ion interacts easily with the sites and hence a higher rate of adsorption is observed. During the first few minutes, adsorption rate of material was extremely sharp then the rate began to drop toward a steady state and reached maximum at 1440 minutes with insignificant levels of adsorption [11]. For the sorption mechanism of Zn (II) metal cations on to (Nat-CC), ($KMnO_4$-CC), (H_2O_2-CC), (HNO_3-CC), (Na-sul-CC), (OA-CC) and (AA-CC), a kinetic investigation with different time intervals ranging from 0 to 1440 minutes (0, 15, 30, 45, 60, 120, 240, 360 and 1440) was conducted having metals concentration 100 mgL^{-1} (Fig. 2). The effects of contact time on the biosorption of Zn (II) on the original and pretreated biomasses. For Zn (II) uptake capacity q (mg gG^1) increased from 9.9-25.4, 23.6-41, 16.8-34.75, 16.6-27.42, 29.9-37, 21-32.75 and 17.5-27.7 for (Nat-CC), ($KMnO_4$-CC), (H_2O_2-CC), (HNO3-CC), (Na-sul-CC), (OA-CC) and (AA-CC) respectively as time increases from 0 to 1440 minutes.

As observed in the adsorption curve, the rapid adsorption of Zn (II) in the first 120 minutes may be due to physical adsorption or ion adsorption on the surface of *Zea mays*. Slower adsorption that followed may have involved other mechanisms, such as complexation, micro-precipitation and binding site saturation. After the equilibrium period the amount of biosorbed metal ions did not change significantly with contact time and it is thus fixed as the optimum contact time. This trend for metal ions in binding suggests that the binding may take place through interactions with functional groups on the surface of the biosorbent. Amarasinghe and Williams [3] explained the same trend by using biosorbent tea waste. At the beginning, metal ions in the solution were rapidly adsorbed by the native and pretreated biomasses. After a very rapid adsorption, the adsorption rates of metal ions slowly declined. Initially, the adsorption sites are open and the metal ions interacts easily with the site and hence a higher rate of adsorption is observed. Nadeem *et al*. [10] and Lee and Chang [11] reported the same trend by using fish (*Labeo rohita*) scales for Pb (II) and Spirogyra and Cladophora filamentous macroalgae biomass for Pb (II) and Cu (II).

It is clear from the results that pseudo-first order kinetic equation fails to predict the experimental adsorption capacity (q_{exp}) because R^2 values of pseudo-first order kinetics are relatively lower then pseudo-second order kinetics. The adsorption kinetics data were further analyzed using pseudo-second-order kinetic model. The model is based on the assumption that the rate of sorption is proportional to the square of the number of unoccupied sites. It was expressed as, $T/q = 1/k_2q_e^2 + t/q_e$; where $k_{2,}$ is the equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). The slopes and intercepts of plots t/q versus t were used to calculate the pseudo-second-order rate constants k_2 and q_e. The results depicted that the q_{exp} (experimental capacity) (25.40, 41.00, 34.75, 27.42, 37, 32.75 and 27.7) for Zn (II) sorption values with Nat-CC, $KMnO_4$-CC, H_2O_2-CC, HNO_3-CC, Na-Sul-CC, OA and AA-CC respectively for all the initial metals concentration used (Fig. 2). This confirms that pseudo-first order kinetic model is not accurate for sorption kinetics of Zn (II) sorption by Nat-CC, $KmnO_4$-CC, H_2O_2-CC, HNO_3-CC, Na-Sul-CC, OA and AA-CC. The coefficient of correlation for the second order kinetic model was approximately equal to 1.0 and the estimated values of qe mg g^{-1} for Zn (II). Both facts suggest that the sorption of Cu (II) and Zn (II) ions follows the 2nd order kinetic model, which relies on the assumption that biosorption may be a rate-limiting step. The initial concentration, equilibrium concentration and contact time were the experiment variables during contact time study [15]. Hanif *et al*. [17] have quoted the same results in kinetic studies for Ni (II) biosorption from industrial waste water by *Cassia fistula* biomass.

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