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Exclusion of Zn(II) from aqueous solution using corncob (*Zea mays* stalk) after chemical modifications with inorganic acids and bases

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ABSTRACT

In the conducted research, corncob powder was pretreated with inorganic acids and bases. The consequence of different parameters such as initial metal concentration, pH, and contact time on Zn(II) biosorption from aqueous solution was deliberated. The order of maximum Zn(II) uptake $q_{\max}$ (mg g^{-1}) for different pretreated and raw corncob powder was $Ba(OH)_2$ (128.9) > H_3PO_4 (124.07) > NaOH (118.737) > H_2SO_4 (114.8) > HCl (93.41) > $Al(OH)_3$ (87.9) > Native (86.74). The percentage of Zn(II) removed on corncob biomass increased with increase in pH reaching a maximum at pH 5.5. Kinetics of Zn(II) biosorption described that Zn(II) sorption rate was high in first 15–30 min and equilibrium was established after 120 min. The maximum adsorption data of native and pretreated biomass was investigated using Langmuir, Freundlich equilibrium, and Pseudo-first and second-order kinetic models. It was accomplished that structural modifications onto corncob powder lead to the formation of novel biomasses with increased sorption efficiency and environmental stability for the abatement of Zn(II).

Keywords: Corncob stalk; Chemical modifications; Biosorption; Kinetics; Equilibrium modeling

1. Introduction

The discharge of heavy metals into the surroundings by industrial actions is a serious ecological problem, because these heavy metals have a tendency to exist indefinitely, streaming, and eventually gathering all over the food chain [1]. Water contamination by heavy metals transpires through industrial, military, and agricultural activities and disposal of waste; for example, power production industry and fuel produce average 2.4 million tons of heavy metals [2].

Zinc is twenty-third among the elements found in abundance. Zinc is a part of hundreds of enzymes and plays a very important role in reproduction, growth, taste, vision, immunity, and DNA metabolism [3]. The highest permissible concentration of zinc suggested by World Health Organization in drinking water is 5.0 mg L^{-1} [4]. Higher concentration of zinc can cause

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severe toxicity including vomiting, diarrhea, cholestatic jaundice, lethargy, hypermylasemia, neurological disturbances, and renal failure [5]. Zinc is not eco-friendly and it passes in the course of the food chain through bioaccumulation. Considerable interest has developed regarding the removal of zinc from wastewaters [6].

Different conventional approaches including ion exchange, ultrafiltration, reverse osmosis, eletrodialysis, chemical precipitation, and pytoremidiation present several limitations in the exclusion of heavy metal contaminants from water as they are expensive, not ecofriendly, have high-energy requirements, and are inefficient particularly when the heavy metal concentration is too low, as 1–100 mg L^{-1} [7]. These drawbacks lead to the need to develop more effective, eco-friendly, and economical process for the restoration of metals from wastewater [8]. Research interest has been focusing towards biological treatments for the handling of effluents such as bioaccumulation and biosorption [9].

Biosorption can be explained as the uptake of toxic heavy metals by passive diffusion with the help of any dead biological material. It is metabolism-independent and it only concerns with cell wall. So, it is better than other conventional methods and bioaccumulation. In this regard, a wide variety of dead biomass is being considered as an adsorbent for the treatment of industrial and domestic as well as natural waters including drinking water [10]. Some researchers have successfully conducted the modification of the biosorbent that enhance the binding capacity of biosorbents greatly [11].

Corn (*Zea mays* L.) is one of the three major cereals, after wheat and rice, in distinguished areas of Pakistan. In the entire world, maize is grown on 140 million hectares and in Pakistan average yield of corn is 1.86t/ha [12].

Corncob (*Zea mays* stalk) is one of the largest sources of available biomass in the corn processing industry. Corncob is either treated as waste or burnt as fuel causing environmental concern [13]. But corncob powder can be used as a biosorbent for heavy metals and sorption capacity of corncob powder can be increased by introducing carboxyl, phenolic, amino, and hydroxyl groups in biomass because these groups have better affinity towards metal ions [14].

2. Materials and methods

2.1. Preparation and treatment of biosorbent

Corncob (*Zea mays* stalk) was collected from Rafhan mills Faisalabad. To remove soluble impurities, dust and debris, they were repeatedly washed with water. Then they were sun dried for 24 h and ground. Biomass was pretreated with NaOH, $Al(OH)_3$, $Ba(OH)_2$, HCl, H_2SO_4, and H_3PO_4 having concentration of 0.1 M by taking 10 g of biomass/250 mL of each chemical's solution, and stirred for 24 h at room temperature at 200 rpm by using OCT- DIGITAL 4527-01 shaker. Modified biomass were filtered and washed constantly with distilled water up to neutral pH. Biomass was oven dried for 24 h at 50°C. All chemically pretreated biomasses were reweighed after the treatment to establish any mass loss or gain caused by modification. Reweighed corncob biomasses were then sieved through Octagon digital Siever (OCT-Digital 4527-01) to obtain different particle size. Biomass having homogenous particle size of 0.1–0.25 mm was used for the further experiments.

2.2. Preparation of solutions

4.38 g of zinc sulfate ($ZnSO_4{\cdot}7H_2O$) was dissolved into 1,000 mL of distilled water to prepare stock metal solution of zinc having concentration of 1,000 ppm. Working solutions were made by dilution of stander metal solution. The optimum pH for zinc was 5.5.

2.3. Batch biosorption studies

In all sets of experiments, fixed volume (100 mL) of Zinc solution were thoroughly mixed with fixed biosorbent dose (0.1 g) at 30°C and 200 rpm up to 24 h. To check the consequence of pretreatment, primary metal concentration, contact time, and pH on the biosorption of zinc using corncob at different conditions of initial metal concentration (25, 50, 100, 200, and 400 ppm), contact time (0, 15, 30, 45, 60, 120, 240, 480, 660, and 1440 min), and pH range (2, 3, 4, 5, 5.5, 6, and 7), respectively, were selected to study biosorption experiments. For adjusting the pH of the medium 0.1 N solution of NaOH and HCl were used. The flasks were roofed with an aluminum foil and were located on a revolving shaker with regular rate of 200 rpm. After 24 h samples were filtered with filter paper and stored in airtight sample bottles. The concentration of zinc was determined after diluting the sample solutions by (Hitachi polarized Z-8200) atomic absorption spectrophotometer.

3. Results and disscusion

In this research work, inorganic acids (HCl, H_2SO_4, H_3PO_4) and bases (NaOH, $Ba(OH)_2$, $Al(OH)_3$) were used for the modification of intact biomass of corncob and for representing results some abbreviations were used as HCl–PCC, H_2SO_4–PCC, H_3PO_4–PCC, NaOH–PCC, $Ba(OH)_2$–PCC, and $Al(OH)_3$–PCC, and native is represented as Nat–CC. “PCC” stands for pretreated corncob.

3.1. Effect of pretreatment

To evaluate the effect of pretreatment on biomass, 100 ppm of Zn(II) solutions were shaken at 200 rpm with 0.1 g/100 mL of biosorbent having size 0.1–0.25 mm at pH 5.5 for 24 h. Uptake capacity of corncob was significantly increased after pretreatments with inorganic acids and bases as shown in Fig. 1. After the acidic modification, the order of sorption capacity q (mg g^{-1}) of corncob was H_3PO_4–PCC (71.2) > HCl–PCC (55.4) > H_2SO_4–PCC (41.75) > Nat–CC (25.4), and the order of increase in sorption capacity q (mg g^{-1}) as a result of basic pretreatments was $Ba(OH)_2$–PCC (68.4) > NaOH–PCC (63.67) > $Al(OH)_3$–PCC (49.5) > Nat–PCC (25.4). Pretreatments of biomass with acids apart from the removal of mineral matter also resulted in the introduction of oxygen surface complexes which changes the surface chemistry by increasing the porosity and the surface area of original biomass [15]. Alkali treatments of biomass may destroy autolytic enzymes that may cause putrefaction of biosorbent, and remove proteins and lipids that bound the reactive sites [16].

3.2. Effect of pH

The solution pH is very imperative parameter in biosorption from aqueous solution because it disturbs equilibrium by affecting the solubility of metal ion, speciation of metal ion, extent to ionization of adsorbing material during process, and counter ions concentration on functional groups of the biosorbent [17]. The selected pH range for biosorption was 2, 3, 4, 5, 5.5, 6, and 7. As Fig. 2 indicated that sorption capacity q (mg g^{-1}) increased with increase in pH. But the maximum biosorption was observed at optimum pH of zinc was 5.5. Above 5.5, precipitation of zinc in the form of zinc hydroxide occurred which caused the sharp increase in sorption capacity. The results obtained in conducted research work were in agreement with the results reported in literature. Liu et al. reported the same results regarding the sorption of heavy metals from aqueous solution by orange peel cellulose [18].

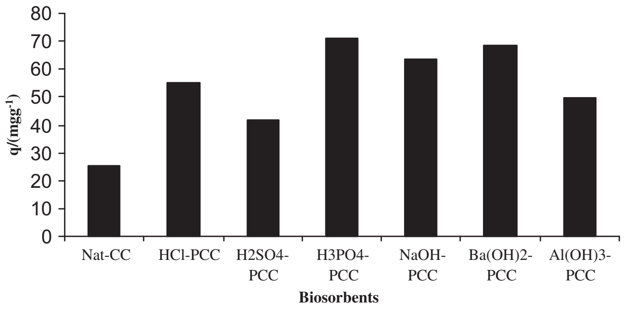

Fig. 1. Effect of pretreatments on biosorption of Zn(II).

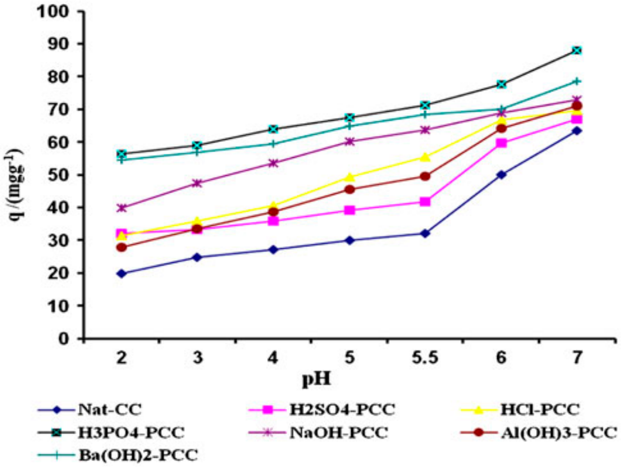

Fig. 2. Effect of pH on biosorption of Zn(II).

3.3. Effect of initial metal concentration

Different initial metal ion concentrations (25, 50, 100, 200, and 400 ppm) were taken with biomass of intact and pretreated corncob, and the sorption capacity of biomass was observed Fig. 3. Results of present investigation showed that as the initial metal ion concentration increased the sorption capacity q (mg g^{-1}) was also increased and the percentage removal decreased. As concentration increased from 25 to 400 mg L^{-1} sorption capacity q (mg g^{-1}) increased

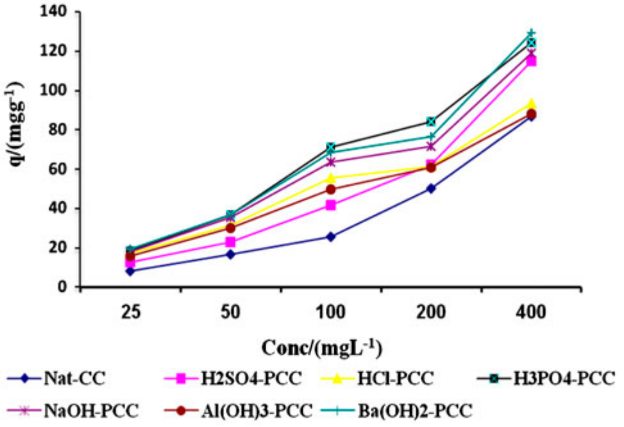

Fig. 3. Effect of initial metal concentration on biosorption of Zn(II).

Table 1
Comparison of Langmuir and Freundlich isotherm model for the biosorption of Zn(II) by native and pretreated corncob

Biosorbent	Langmuir model			Experimental value	Freundlich model			
	X_m (mg/g)	K_L (L/mg)	R^2	q (mg/g)	q_{max} (mg/g)	$1/n$	K_F (mg/g)	R^2
Nat–CC	161.29	0.0034	0.9518	86.74	89.8	0.753	1.184	0.9937
H_2SO_4–PCC	138.88	0.0391	0.992	114.8	112.07	0.68	2.396	0.9929
HCl–PCC	131.57	0.0336	0.993	93.41	58.57	0.428	8.3868	0.9328
H_3PO_4–PCC	136.98	0.0238	0.9733	124.07	136.95	0.462	10.216	0.8905
NaOH–PCC	131.57	0.0193	0.9306	118.737	120.87	0.455	9.264	0.4555
$Al(OH)_3$–PCC	4.79	0.0078	0.8846	87.9	94.2	0.459	6.7375	0.9506
$Ba(OH)_2$–PCC	140.84	0.021	0.9252	128.9	130.47	0.449	10.517	0.9161

from 8–86.74, 23–114.8, 17.2–93.41, 18.5–124.07, 18.1–118.74, 15.75–87.9 and 19.1–128.9 for Nat–CC, H_2SO_4–PCC, HCl–PCC, H_3PO_4–PCC, NaOH–PCC, $Al(OH)_3$–PCC, and $Ba(OH)_2$–PCC, respectively. The increase in sorption capacity may be elaborated in detail that at low metal ion concentration the available metal occupies adsorption sites more quickly. However at higher concentration, metal ions diffuse to the biomass surface by interparticle diffusion [19].

3.4. Equilibrium modeling

Adsorption isotherms of concentration of zinc from 25 to 400 $\mathrm{mg\,L^{-1}}$ with a fixed biosorbent dose (0.1 g/100 mL) at pH 5.5 were studied. The Freundlich and Langmuir isotherm models were applied to this study to test the better fit of data. The Freundlich and Langmuir isotherm models are the most extensively used models for studying the biosorption equilibrium between the solid biomass phase and the metal solution [20]. The empirical Freundlich isotherm governed by a heterogeneous surface is given below in Eq. (1) [21]:

$$\log q_e = \log K_f + (1/n) \log C_e \tag{1}$$

where C_e ($\mathrm{mg\,L^{-1}}$) is the equilibrium concentration, q_e is the amounts of metal ions adsorbed per specified amount of adsorbent at equilibrium. K_f and $1/n$ are constants obtained from regression equation called intercept and slope, respectively. The Langmuir isotherm model is applicable for monolayer biosorption onto surface and limited number of indistinguishable sites and agreed by the following Eq. (2) given below as:

$$C_e/q_e = 1/X_m K_L + C_e/X_m \tag{2}$$

where q_e is the amount of metal ions adsorbed at equilibrium, C_e is the equilibrium concentration, and X_m and K_L are the Langmuir constants [22]. Table 1 showed that Langmuir isotherm model had a better fitting model in contrast to Freundlich isotherm model. This was as a result of higher correlation coefficient exhibited by Langmuir.

3.5. Effect of contact time

Consequence of contact time for zinc was performed at optimum (pH = 5.5, biomass dose 0.1 g/100 mL) conditions. Fig. 4 indicated that as the contact time increased, metal uptake also increased sharply and then it became almost stable, denoting attainment of equilibrium. It showed that initially solute concentration was high and all adsorbent sites of biomass were vacant, but after approx. 120 min very low increase in metal uptake was observed due to the presence of few vacant active sites on the biomass [23]. The maximum zinc uptake was obtained by H_3PO_4–PCC was 71.2 $\mathrm{mg\,g^{-1}}$.

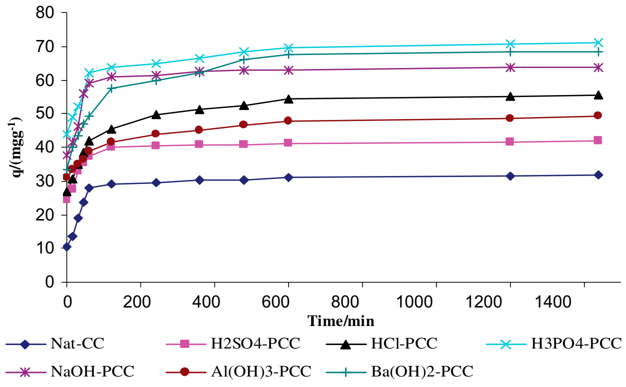

Fig. 4. Effect of contact time on biosorption of Zn(II).

Table 2
Comparison of pseudo-first-order and pseudo-second-order kinetic models

Biosorbent	Pseudo-first-order			q_{exp} (mg/g)	Pseudo-second-order		
	q_e (mg/g)	K_{1ad} (min^{-1})	R^2		q_e (mg/g)	K_{2ad} (mg/g min)	R^2
Nat–CC	8.69	0.00299	0.7777	32	32.15	0.00188	0.9997
H_2SO_4–PCC	6.77	0.00299	0.832	41.75	41.84	0.00318	1
HCl–PCC	18.91	0.00391	0.9411	55.4	55.86	0.0009	0.9996
H_3PO_4–PCC	15.96	0.00299	0.9134	70.6	71.42	0.00104	0.9997
NaOH–PCC	9.51	0.00391	0.8101	63.67	63.69	0.00232	1
$Al(OH)_3$–PCC	12.93	0.00253	0.9103	49.5	49.5	0.00111	0.9994
$Ba(OH)_2$–PCC	25.09	0.00437	0.9613	68.4	68.96	0.0007	0.9995

3.6. Kinetic modeling

In order to examine the kinetic mechanism of zinc biosorption and potential rate controlling step, two kinetic models pseudo-first-order and pseudo-second-order was fitted to the experimental data. The pseudo-first-order kinetic model for solid/liquid system of adsorption is expressed as in Eq. (3):

$$\log(q_e - q) = \log q_e - k_1 t/2.303 \tag{3}$$

where q_e and q (mg g^{-1}) are the amounts of Zn(II) adsorbed on the biosorbent at equilibrium and at any time t, respectively. k_1 is the rate constant of pseudo-first-order biosorption. The intercepts and slopes of plot of log ($q_e - q$) vs. t were used to calculate the first-order rate constant k_1 and equilibrium adsorption capacity q_e. Pseudo-second-order model is supported by the assumption that the rate of biosorption is proportional to the square of the number of unoccupied sites [24]. It is expressed in Eq. (4) as:

$$t/q = 1/k_2 q_e^2 + t/q_e \tag{4}$$

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 vs. t were used to calculate the pseudo-second-order rate constants k_2 and q_e. Table 2 indicated that pseudo-second-order kinetic model is best fitted into the data with higher value of correlation coefficient R^2 when compared with the pseudo-first-order kinetic model [25].

4. Conclusion

The present study on biosorption of Zn(II) from aqueous solution indicates that adsorption of the metal is appreciably governed by some parameters e.g. pH, initial metal concentration, pretreatment, and contact time. Chemical modifications significantly enhance the sorption capacity of biomass. The maximum biosorption is observed at pH 5.5. Among the two equilibrium isotherm models, Langmuir model describes the Zn(II) biosorption better. Pseudo-second-order kinetic model is best fitted to data when compared with pseudo-first-order model. Thus optimizations of parameters of biosorption, chemical pretreatments of biomass, and mechanism study are the main keys to shift the process of biosorption from laboratory to industry.

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