



Removal of copper ions from electroplating effluent solutions with native corn cob and corn stalk and chemically modified corn stalk

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ABSTRACT

Rapid industrialization throughout the world has generated huge volumes of wastes containing toxic materials such as metal ions. The presence of heavy metals in wastewater and surface water is the major concern of the public health and the environment. The aim of this research was to remove the Cu ions from electroplating effluent solutions using biosorbents: corn cob and corn stalk. In addition to use the natural biosorbent, modification of corn stalk by nitric acid was also studied. The surface morphology of adsorbents was observed using a scanning electron microscope. The porous and tubular structure of the corncob and corn stalk indicated their capability in adsorption of metal ions from the solution. In order to study the equilibrium adsorption extent, Langmuir & Freundlich models were used. It was found that the maximum sorption capacity of corn cob was higher than the corn stalk. On the other hand, the modified corn stalk showed higher capacity than both corncob and corn stalk without modification.

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Introduction

Most heavy metal ions are dangerous in excessive concentrations. Heavy metal ions and their toxic effects have become a major world problem, causing harm to human life and the environment. This pollution is introduced to soil and water by industrial human activities and has considerable effects by joining the food chain. Wastewaters containing heavy metal ion pollutants come from different industrial activities such as electroplating, mining, power plants and electrical equipment manufacturing. Organic pollutants and heavy metal ions limit the agricultural application of sewage sludge, however, they tend to accumulate along the food chain and bring potential risks to animals and humans [1]. Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders; therefore they must be removed before discharge [2].

The recommendation of the World Health Organization for the safe amount of Cu (II) ion is 2 mg/l in drinking water and 0.05–1.5 mg/l in industrial effluent discharge. Long term exposure of Cu (II) causes stomachache, irritation of nose, mouth, eyes and headache [2]. There are various methods for the removal of heavy metals, such as chemical precipitation, reverse osmosis, ion exchange, coagulation and adsorption [3,4]. Among different physicochemical processes, sorption can be the best prospects

for overall treatment owing to its economical feasibility and environmental friendly behavior [5]. The process of adsorption implies the presence of an “adsorbent” solid that binds molecules by physical attractive forces, ion exchange, and chemical binding. It is advisable that the adsorbent is available in large quantities, easily regenerable, and cheap. Adsorbent materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from wastewater streams. Agricultural by-products usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups. These groups have the ability to bind heavy metal ions by donation of an electron pair from these groups to form complexes with the metal ions in solution [6]. In several papers, it has been reported that some of these by-products have a natural capacity for the ion exchange of divalent cations [7,8]. It has been found that by modifying agricultural by-products, their ion exchange capacity can be increased.

Corn is one of the largest production crops in the world. Corn cob, corn husk, corn leaf and corn stalk are abundant agriculture residues from corn, but most are burnt without utilization [9]. However, these residues have been studied recently for adsorption [9–11].

The main objective of this research was to study the raw natural corn cob and corn stalk to determine their adsorption capacity in removing Cu (II) ions from simulated contaminated samples. The adsorption of Cu (II) from aqueous solution using modified corn stalk with nitric acid was also investigated. Finally, the adsorption

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equilibrium was expressed using Langmuir and Freundlich models and the surface morphology of adsorbents was observed using a scanning electron microscope.

Materials and methods

Adsorbent preparation

Raw corn stalk (RCS) and raw corn cob (RCC) were obtained from a farm near Shiraz, Iran. After removing the grains from the cob and removing the leaves from the stalk, the biomasses were cut into small slices. The samples were then ground through a 70-mesh sieve to achieve a uniform particle size. Then the powder was washed three times with distilled water and was dried in an oven at 50 °C until constant weight. Leyva-Ramos [7] method was used for oxidation of the corn stalk. The corn stalk was oxidized with nitric acid solutions by adding 40 g corn stalk to 200 ml of the acid solution in a flask. The concentration of the acid solutions was 1 M. The solution containing the corn stalk was heated for 2 h keeping the temperature at 50 °C. Afterward, the solution containing the corn stalk was allowed to cool and drained to separate the solution. The corn stalk was oxidized with nitric acid and was washed several times with distilled water until the pH of the distilled water ceased to change while washing. It was finally dried in an oven at 50 °C for 24 h.

Characterization of adsorbents

The adsorbent was characterized using a S-360 Cambridge Scanning Electron Microscope (SEM).

The pH at point zero charge (pHpzc) of the modified corn stalk (MCS) was determined by the pH drift method used by Yang et al. [5], with the modification that sodium chloride was used as an inert electrolyte. Prior to measurement of pH drift, the MCS was thoroughly washed with water followed by dilute sodium hydroxide (0.01 M) to neutralize any free nitric acid that may have remained and finally soaked in HCl for 24 h. After filtration, it was washed with distilled water and the “enriched” MCS was then air-dried. This was done to ensure the removal of any potential effects on pH drift due to dissolution of salts in MCS. The pH of test solutions was adjusted in 0.005 M NaCl using 0.5 M HCl or 0.5 M NaOH. A 0.06 g of Modified corn stalk was added into 20 mL of the pH-adjusted solution in a plastic capped vial and equilibrated for 24 h [5]. The final pH was measured using a pH meter (model 827-metrohm) and plotted against the initial pH. The pH at which the curve crosses the $\text{pH}_{\text{initial}} = \text{pH}_{\text{final}}$ line was taken as pH_{pzc} . In order to find optimum range of pH, the experiment was carried out by adding specific amounts of corncob to 100 ml of CuSO_4 solution in a pH range between 1.5 and 4.5.

The functional groups of RCS and MCS were characterized by a Fourier transform infrared (FTIR) spectrophotometer (model Bruker Vector 22 Instrument), using KBr discs to prepare RCS and MCS.

Batch experiment and analysis

The aqueous solution of heavy metal was prepared with dissolving CuSO_4 in distilled water. The adsorption isotherm experiments were performed at 220 rpm on the magnetic stirrer with 1 g of adsorbent in Erlenmeyer flask containing 100 ml of CuSO_4 solution with the initial concentration of 3, 5 and 6 mmol/l at 298 K and pH = 4.5. In order to determine the amount of Cu ions in the solution, an AA-800 atomic absorption spectrophotometer made by Perkin-Elmer Company was used with limit of detection (LOD) equal to 1 ppb (the detection limit (according to IUPAC) is the smallest concentration or absolute amount of analyte that has a

signal significantly larger than the signal arising from a reagent blank).

Sorption experiments

To determine the amount of Cu (II) ion sorbed on the adsorbents used in this study, Eq. (1) [1,3] was used:

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (1)$$

where C_0 is the initial concentration of the metal ion (mmol/l) and C_e is the concentration of the metal ions after equilibrium, V and M are volume of the solution (l) and mass of adsorbent (g), respectively, whereas q_e is the adsorption capacity per unit mass of the adsorbents (mmol/g).

Equilibrium isotherms

There are several models that express a relation between the amounts of sorption and the residual solute concentration. The most frequent models are the Langmuir and Freundlich adsorption isotherms.

Langmuir isotherm is the most important model of monolayer adsorption, based on the assumption of a fixed number of adsorption sites, and each site can hold only one adsorbate molecule (the adsorbed layer is one molecule in thickness). All sites are equivalent and there is no interaction between the adsorbed molecules [1,12,13].

The prepared solutions were left in contact with adsorbents until equilibrium was reached. While the experiment was performed, a sample was taken to determine the final Cu (II) concentration in different times to evaluate the equilibrium time. After 2 h, the adsorbent was separated from the solution with a filter and the solution was analyzed using an atomic absorption spectrophotometer to determine the equilibrium concentration of the Cu (II) ion.

The Langmuir equation is as follows (Eq. (2)) [3,14]:

$$\left(\frac{C_e}{q_e}\right) = \frac{1}{q_m \times b} + \frac{C_e}{q_m} \quad (2)$$

where q_m is the maximum adsorption capacity (mmol/g) and b is the Langmuir isotherm constant, according to Langmuir equation.

The degree of suitability was estimated from the value of separation factor, which can be obtained by Eq. (3) [1,3,15]:

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

The values less than unity show that the sorption of metal ions to the adsorbents particles under investigation is optimum and the sorption process is favorable. Table 1 the optimum range of R_L .

Freundlich isotherm model is an experimental model, usually expressed by Eq. (4) [1,3]:

$$q_e = K_f \times (C_e)^{1/n} \quad (4)$$

It can also be expressed in a logarithmic form as Eq. (5) [1,3]:

$$\ln q_e = b_f \times \ln C_e + \ln K_f \quad (5)$$

where K_f is the Freundlich constant and b_f is the Freundlich exponent.

Table 1
Ranges of R_L [1,3].

Type of isotherm	Values of R_L
Unfavorable	$R_L > 1$
Linear	$R_L = 1$
Favorable	$0 < R_L < 1$
Irreversible	$R_L < 0$

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