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SORPTION KINETICS OF ZINC AND NICKEL IONS ON MAIZE COB♦

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Abstract: The removal of zinc and nickel ions from aqueous solutions by adsorption on maize cobs was investigated. The amount of the metal ions increased with time. The highest sorption rates of the metal ions were obtained in the first ten minutes, in the next fifty minutes the uptake rate gradually decreases progressive and practically is zero after sixty minutes. The sorption rates were 72% for Zn^{2+}, and 82% for Ni^{2+}. This study showed that the sorption of zinc and nickel ions on maize cobs is particle diffusion controlled. The rate coefficients for particle diffusion were 0.053 min^{-1} for Zn^{2+} and 0.076 min^{-1} for Ni^{2+}.

Keywords: *heavy metal, maize cob, adsorption, kinetics*

INTRODUCTION

The removal of heavy metal from wastewater represents an important problem for public health. Heavy metals are the most important noxious elements from the environment owing to their toxicity and nonbiodegradability. The most important heavy metal contamination exists in wastewater from metal plating facilities, mining operations and tanneries. Many methods can be used for the removal of heavy metals:

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solvent extraction, evaporation, ion exchange, chemical precipitation, biological treatment and membrane processing [6]. Recently were developed new adsorbents and improved existing adsorbents like granular activated carbon, other adsorbents such as iron oxide coated sand, porous cellulose carrier modified with polyethyleneimine, iron coated granular activated carbon, chitosan and modified chitosan, etc. One of the exploitation is the use of natural wastes.

Natural wastes are low cost material, are abundant in nature, or are by-products or wastes material from another industry [4]. Rice straw, maize cobs, walnut expeller meal, peanut skins, wool, peanut hulls, sugar cane bagasse, waste tea leaves, exhausted coffee, coconut husks are some of the examples of the agricultural products and by-products used for removal of heavy metals from wastewater [1-2, 7-10].

Romania is an important maize producer, the surface cultivated being about 34% from arable surface of the country (the surface cultivated with maize in Romania is up to 74% from the surface cultivated with this cereal in EU). Maize cobs contain 38% cellulose, 46.5% hemicellulose, 9.65% lignin, 3% proteins and has been identified as new sorbent for removal of heavy metals in aqueous solutions.

The studies showed that the metal ions adsorption on the agricultural wastes and by-products is possible as a result of the interactions or coordination to functional groups present in natural protein, lipids and carbohydrates positioned on cell wall. The sorption rate of metal ions on the sorbent is affected by the factors such as the number of reactive sites on the substrate, the particle size of the sorbent, the report metal ions – sorbent, experimental conditions [4].

The sorption of metal ions on the sorbent is particle diffusion controlled and this could be affected by the following processes: diffusion of the metal ions from the solution to the film surrounding the particle, diffusion from the film to the particle surface, diffusion from the surface to the internal sites, and uptake the metal ions [5]. The fractional attainment of equilibrium is a function of $D^+/D \cdot r_0^2$, where D^+ is the distribution coefficient of the metal ions, r_0 is the particle radius, D is the diffusion coefficient of the counter ions in the solution [1]. In these conditions the sorption of the metal ion in solution is facilitated by a reduction in the size of the metal ion.

In this study the rate of adsorption of zinc and nickel on maize cobs was investigated.

MATERIALS AND METHODS

Preparation of sorbent

The maize cobs were washed with de-ionized water, cut in the small pieces, air-dried and powdered in a grinder. The meal was sieved through a 500 μm mesh and then through 400 μm. The meal retained on the 400 μm was soaked in dilute nitric acid solution (2% v/v) overnight, rinsed with de-ionized water and air-dried.

2 g maize cob into a 100 mL solution of the metal ion was used in the experiments.

Preparation of test solutions

Initial concentration of 100 mg/L of both two metal ions test solutions was prepared. The investigation was realized at pH of 5.0 and 7.5 and a temperature of 30ºC.

Adsorption studies

The sorbent was added in the test solutions, pH and temperature were fixed. Different samples were left to stand for 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 and 120 minutes. The samples were filtered rapidly and the metal ions concentration in the filtrate was measured with a HACH DR/2010 spectrophotometer using the Standard Methods for the Examination of Water and Wastewater. All experiments were duplicated and showed differences of less than 5.0%.

RESULTS AND DISCUSSION

The results obtained showed that the sorption rates for both two metal ions on the maize cobs increase between zero to one hundred minutes. From Figure 1 was observed that the best sorption rates were obtained for zinc ions after ten minutes, in the next fifty minutes the uptake rate gradually decreases progressive and practically is zero after sixty minutes.

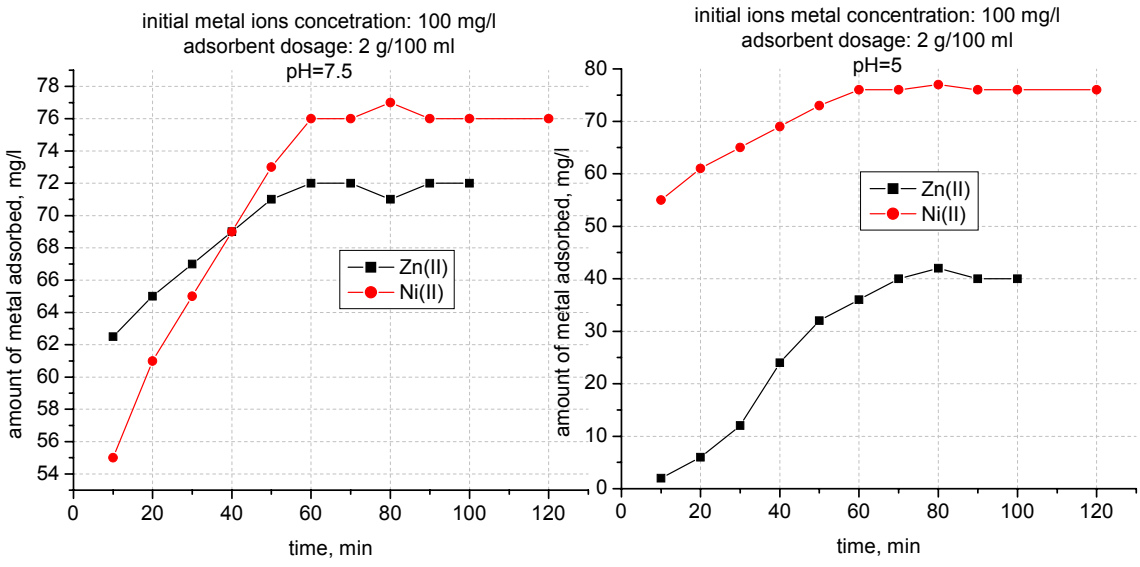

Figure 1. *Amount of adsorbed metal ions (mg/L) against time*

Table 1 show the percentage of metal ions adsorbed and the amount of metal ions adsorbed on the maize cobs at *p*H 5 and 7.5 (mg/g) against time.
It has been found that for zinc ions the sorption rates after sixty minutes at lower *p*H were 40%, while at *p*H of 7.5 the sorption rate was 72%. The investigation showed that

for nickel ions the sorption rate on the maize cobs was greater both at acidic pH (sorption rate 76 %) and alkaline pH (sorption rate 82 %) than for zinc ions.

The major components of maize cobs are cellulose and hemicellulose and these contains free carboxyl groups that coordinate ions metal. Also, both compounds contain hydroxyl groups that may bind ions metal but to a lesser extent than carboxyl group on the other hand the maize cobs may contain higher proteine levels that will supply sulfhydryl, amino, and carboxyl groups. The sorption rates of the ions metal reduced at lower *p*H suggest that the bound metals could be removed by lowering the *p*H of solution; the protons displace the adsorbed ions metal.
The results showed that maximum adsorption occurred at 36 mg/g for Zn(II), respectively 41 mg/g for Ni(II), at *p*H of 7.5.

Table 1. *The adsorption of metal ions by maize cobs as a function of contact time*

Time, min	% adsorption of metal ions				mg metal ions /g sorbent			
	*p*H = 5.0		*p*H = 7.5		*p*H = 5.0		*p*H = 7.5	
	Ni^{2+}	Zn^{2+}	Ni^{2+}	Zn^{2+}	Ni^{2+}	Zn^{2+}	Ni^{2+}	Zn^{2+}
10	55	2	61	62.5	27.5	1	30.5	31.3
20	61	6	68	65.0	30.5	3	34.0	32.5
30	65	12	75	67.0	32.5	6	37.5	33.5
40	69	24	80	69.0	34.5	12	40.0	34.5
50	73	32	82	71.0	36.5	16	41.0	35.5
60	76	36	81	72.0	38.0	18	40.5	36.0
70	76	40	82	72.0	38.0	20	41.0	36.0
80	77	42	81	71.0	37.5	21	40.5	35.5
90	76	40	81	72.0	38.0	20	40.5	36.0
100	76	40	82	72.0	38.0	20	41.0	36.0
120	76	nd	82	nd	38.0	nd	41.0	nd

Differential adsorption of metal ions from solutions by an adsorbent depends [1] on the following:

- differences in ionic radii of the metal ions – 0.74 Å for Zn^{2+} and 0.69 Å for Ni^{2+}, in accordance to Pauling,
- differences in the affinity of the metal ions for the active groups of the adsorbent,
- nature of the anions of the metal ion salt.

The intraparticulate diffusivity and the fractional attainment of equilibrium were calculated. The equation [1] used is:

$$ln(1-\alpha) = - K_P \cdot t \qquad (1)$$

where:

- α is the fractional attainment of equilibrium, representing the report between the concentration of metal ions at t time and the concentration at $t = \infty$,
- K_P is the rate coefficient for particle diffusion controlled process corresponding to particle size of the sorbent,
- $ln(1-\alpha)$ is a measure of the intraparticle diffusivity.

From Figure 2 is observed the plot of the fractional attainment of equilibrium against time. The values of α increase to 50 minute, thereupon these values converge to one. The sorption rate was faster for Ni^{2+} than for Zn^{2+}.

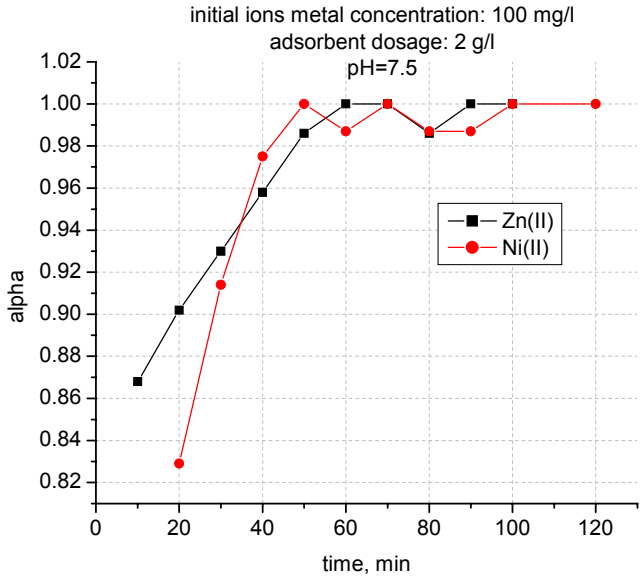

Figure 2. *Plot of the fractional attainment of equilibrium (α) against time*

For both metal ions the plot of ln(1-α) against time is a straight line (Figure 3). The rate coefficients for particle diffusion controlled sorption are shown in Table 2. The results obtained, 0.053 min^{-1} for Zn^{2+} and 0.076 for Ni^{2+} showed that it is possible to consider that diffusion rate affects adsorption rate.

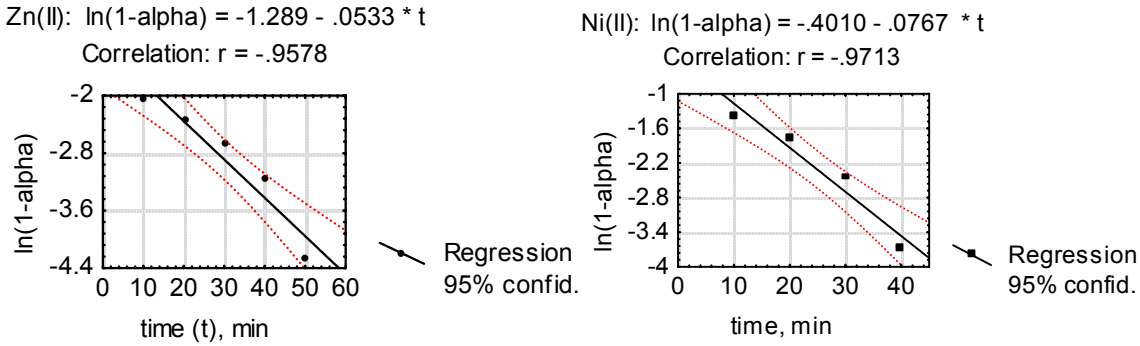

Figure 3. *Plot of particle diffusivity [ln(1-α)] against time*

Table 2. *Rate coefficient for particle diffusion controlled sorption for the analyzed metal ions on maize cobs*

Metal ions	Zn^{2+}	Ni^{2+}
K_P, **min^{-1}**	0.053	0.076

CONCLUSIONS

The amount of the ions metal adsorbed increased with time. The sorption rates were 72% for Zn^{2+}, after 60 minutes, and 82% for Ni^{2+}, after 50 minutes. This study showed that the sorption of zinc and nickel ions on maize cobs is particle diffusion controlled. The rate coefficients for particle diffusion were 0.053 min^{-1} for Zn^{2+} and 0.076 min^{-1} for Ni^{2+}.

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