ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Removal of Heavy Metals from Wastewater Using Corn Cob.

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ABSTRACT

In this study, the adsorption behavior of a low-cost adsorbent, corn cob, with respect to Pb(II), Mn(II), Cd(II), Ni(II) and Co(II) ions, has been studied in order to consider its application to the purification of metal finishing processing industrial wastewater. The batch method was employed and parameters such as: biosorbent dose (0.5, 1, 2, 3, 4 and 5 g/L), influence of pH were carried out between (3 and 8) finding the optimal operating pH was (6), contact time to achieve the equilibrium is found to be (3 hours) for Pb(II), Cd(II), Ni(II) and Co(II) ions and (4 hours) for Mn(II) ions. Adsorption parameters were determined using both Langmuir and Freundlich isotherms, the experimental data were better fitted to the Langmuir equation than to Freundlich equation. Corn cob showed a real solution to remove heavy metals from real wastewaters.
Keywords: Biosorption, Removal, Heavy metal, Wastewater, Corn cob

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INTRODUCTION

According to the Environmental Protection Agency (EPA), heavy metal can be defined as; that metal has a higher density and can have a potential toxicity even if it has a lower concentration, such as: Pb(II), Mn(II), Cd(II), Ni(II) and Co(II) etc. Chemical precipitation, ion exchange, membrane filtration, reverse osmosis, adsorption and biosorption, all are technologies for heavy metals removal.

Activated carbon was the widely used adsorbent in wastewater treatment applications particularly for heavy metal removal; unfortunately, activated carbon remains an expensive and also requires complicated procedures to improve its removal performance for inorganic matters. Therefore, this situation makes it no longer attractive to be widely used because of cost inefficiency.

Due to those problems, alternative adsorbents to replace the costly activated carbon have investigated and illustrated in table (1). Because of their low cost and local availability, natural materials are classified as low-cost adsorbents.

Table 1: Biosorption capacities of different biosorbents for heavy metals

Metal	Biosorbent	Maximum Uptake (mg/g)	References
Ni^{2+}	Maize cob	18.4	[2]
	Saw dust	35	[3]
	Maize cob	10	[3]
Pb^{2+}	Cocosnucifera	19.4	[4]
	Maize cob	23	[4]
	Saw dust	20	[6]
	Coconut shell	75	[7]
	Coconut husk	75	[8]
	Myriophyllumspicatum	55.12	[9]
	Saccharomyces cerevisiae yeast	72.5	[10]
Zn^{2+}	Coconut shell	70	[7]
	Modified corn cob	70.2	[11]
	Leaves of dump palm	3	[12]
	Magnetically modified Peanut husk	3.6	[13]
	Cells of Streptomyces ciscaucasicus	42.75	[14]
	Cocoa pod husk	14.07	[15]
	Rapeseed waste	13.85	[16]
	Bacillus cereus	66.6	[17]
Cu^{2+}	Banana Peel	14.8	[6]
	Coconut shell	70	[7]
	Acer saccharum Leaves	14.9	[10]
	Saccharomyces cerevisiae yeast	42.5	[10]
	Leaves of dump palm	2.7	[12]
	Pomegranate peel	1.32	[17]
	Coconut husk	83	[18]
	Rice husk	44	[18]
	Groundnut shell	49	[18]
	Chestnut shell	12.56	[19]
Cr^{3+}	Maize cob	25	[3]
	Saw dust	42.5	[3]
	Corn cob powder	20	[5]
	Coconut husk	83	[8]
Mn^{2+}	Leaves of dump palm	3	[12]
	Maize Cobs	7	[20]
	Maize stalk	5.5	[20]
Fe^{3+}	Coconut shell	75	[7]
	Coconut husk	75	[8]
	Sugarcane bagasse	4.3	[22]
	Coconut coir	4.5	[22]

Biosorption is the removal of metals from solution by certain types of biomass which has an ability to bind and concentrate metals, many researchers in literature examples of some biosorbent heavy metals are shown in Table (1), it is concluded that, the adsorption capacities of the adsorbents vary, depending on the characteristics of the individual adsorbent, the extent of chemical modifications, and the concentration of adsorbate. [1] Thus, the use of low-cost adsorbents may contribute to the sustainability of the surrounding environment and offer a lot of promising benefits for commercial purpose in the future. [1]

In this research, corn cob used as a biosorbent to remove heavy metals from synthetic and real wastewaters.

MATERIALS AND METHODS

Preparation of the biosorbent

Corn cob was collected from a farm in Menoufia, Egypt, washed thoroughly to remove dust using tap water, followed by deionized water, dried in an oven at 80 °C for 12 h, grinded using a laboratory mill, sieved, then washed with deionized water followed by washing with diluted HCl and with diluted NaOH, last washing with deionized water, finally, dried to constant weight in convection oven at 80 °C for 24 hours.

Figure 1 (a & b) respectively showed the particle size and the distribution of porous structure along the surface of the corn cob particles.

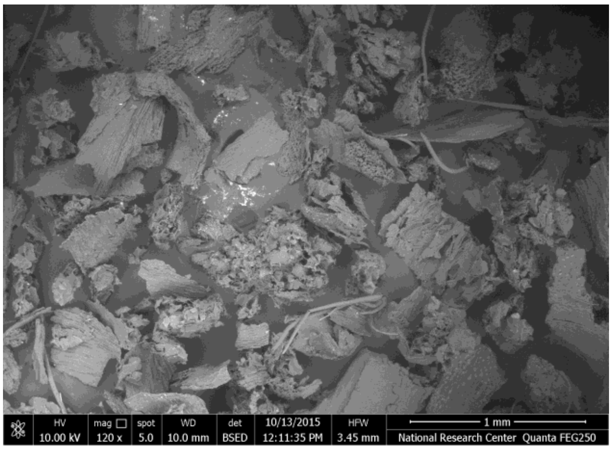

Figure 1a: SEM showing particle size for corn cob

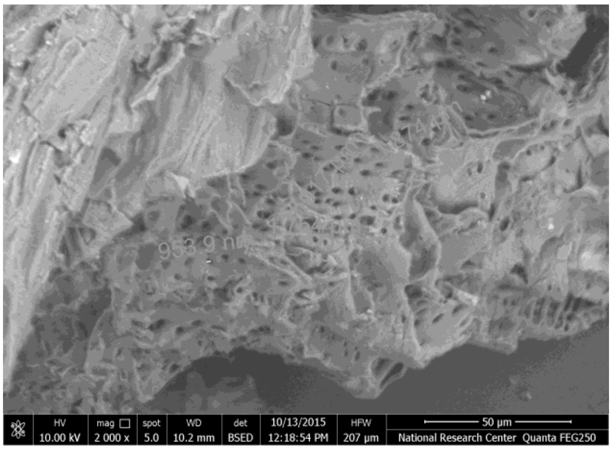

Figure 1b: SEM showing pore size for corn cob

The FTIR spectra showed in Figure (2), reveal bands characteristic to ν (C=O), ν(C=C), ν(OH) and ν(N-H) could be participated in the adsorption process for heavy metals.

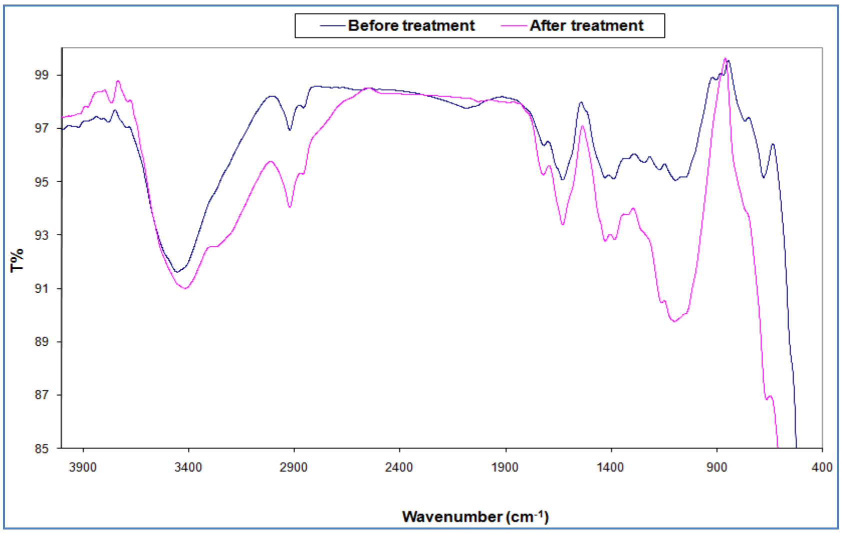

Figure 2: FTIR for corn cob

Chemicals and reagents

Freshly prepared solutions of $Pb(NO_3)_2$, $CdCl_2$, $CoCl_2{\cdot}6H_2O$, $MnSO_4{\cdot}H_2O$ and $NiCl_2{\cdot}6H_2O$ in different concentrations were used as heavy metal substrates.

Real sample of industrial wastewater collected from a metal industry at Sadat industrial city, Menoufia, Egypt.

Equipments

Lab shaker, Wiseshake, SHO-2D, South Korea, for stirring samples. pH-meter, WTW-inolab, Germany, for adjustment of pH of the solutions. Digital balance, Radwag AS 110/C/2, Poland. The concentrations of heavy metal ions are determined using atomic absorption spectrometer Varian Spectr-AA (220), USA. Scanning electron microscope (SEM) images at different magnifications were obtained using, Quanta-250 FEG, USA, used for evaluation of surface area, pore style and size of biosorbent. IR absorption spectra of the corn cob powder were recorded for the 350-4000 cm-1range using Jasco-FTIR-Spectroscopy, Japan.

Methodology

1. Freshly prepared solutions of Pb^{+2}, Cd^{+2},Co^{+2},Mn^{+2} and Ni^{+2}ions with known initial concentration and real industrial waste water were used as substrate for biosorption experiments.
2. pH is adjusted for solution before experiment.
3. Different Biosorbent doses added to 100 ml of prepared solution or to a real wastewater sample.
4. The mixtures have been shaken using lab shaker with speed 250 rpm for required time.
5. The biosorbents were separated by filtration through, Whatman qualitative No. 4, filter paper.
6. The concentration of residual heavy metal ions determined using the atomic absorption spectrometer.

RESULTS AND DISSCISSION

Effect of Sorbent dose

The effect of the amount of adsorbent on the removal of Pb^{+2}, Cd^{+2}, Co^{+2}, Mn^{+2} and Ni^{+2} ions by corn cob for varied adsorbent doses of 0.5, 1, 2, 3, 4 and 5 g/L at: pH (6), contact time (6) hours, initial heavy metal ions concentration (100 mg/L) and shaking speed (250 rpm).

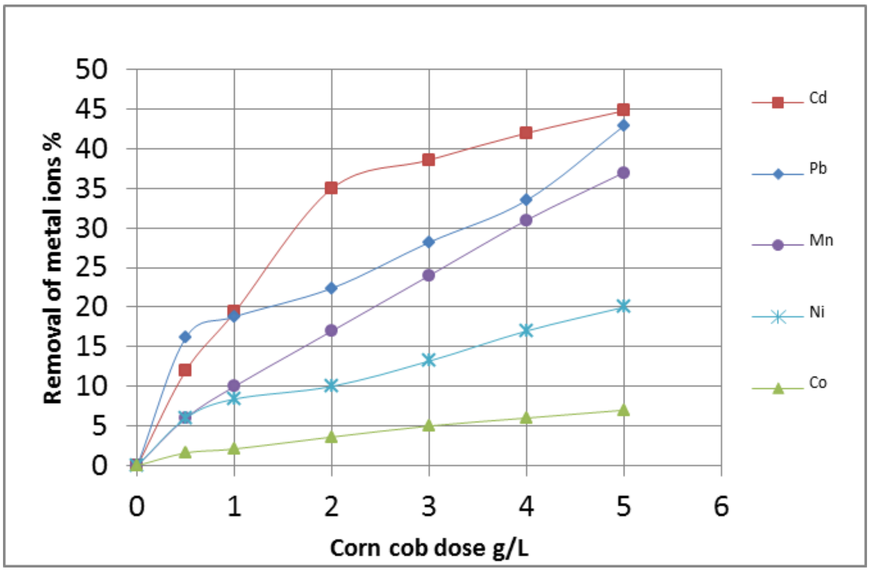

Figure 3a: Effect of corn cob dose on removal % of Pb^{+2}, Mn^{+2}, Cd^{+2}, Ni^{+2} and Co^{+2} ions

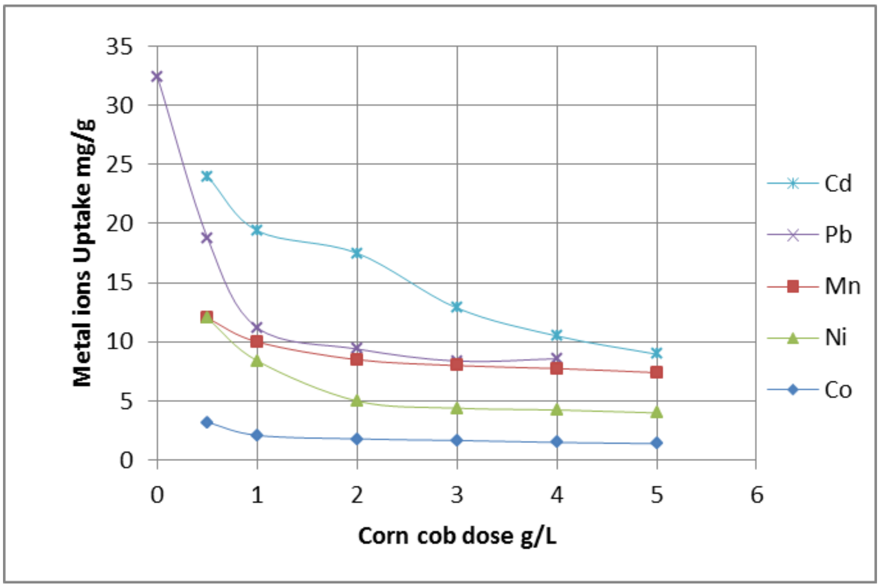

Figure 3b: Effect of corn cob dose on uptake of Pb^{+2}, Mn^{+2}, Cd^{+2}, Ni^{+2} and Co^{+2} ions

Figure (3a) showed metal ions removal% increased with increasing of corn cob dose. Figure (3b) showed metal ions uptake (adsorption capacity) decreased with increasing of corn cob dose that attributed to the saturation of the active sites.

Effect of pH

Studying effect of varying pH (3, 4, 5, 6, 7 and 8) on removal of metal ions at constant biosorbent dose (5g/L), Contact time (6 hour), initial heavy metal ions concentration (100 mg/L) and shaking speed (250 rpm).

The pH of the solution has a significant impact on the uptake of heavy metals is shown in Figure (4) , since it determines the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate [23]. Removal % of Pb^{+2}, Mn^{+2}, Cd^{+2}, Ni^{+2} and Co^{+2} ions increased rapidly as the pH value increased from (3 to 6) because of the competitive adsorption between hydrogen ion and the heavy metal cation at low pH [24]. At higher pH it appears a decrease in absorption, it may attributed to the abundance of OH^- ions that cause hindrance effect to the diffusion of metal ions to the organic matter [25].

Figure (4) shows maximum adsorption of Pb^{+2}, Mn^{+2}, Cd^{+2}, Ni^{+2} and Co^{+2} ions using corn cob at pH (6).

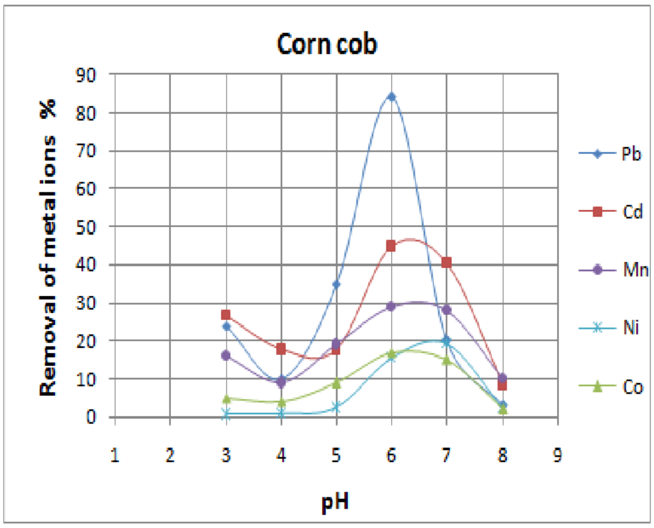

Figure 4: Effect of pH on metal ions removal

Effect of contact time

Studying effect of contact time (0.5, 1, 2, 3, 4, 5 and 6 hours) on the removal percentage of Pb^{+2}, Mn^{+2}, Cd^{+2}, Ni^{+2} and Co^{+2} ions by corn cob at constants: pH (6) , biosorbent dose(5 g/L), shaking speed (250rpm) and Initial heavy metal ion concentration (100 mg/L), the results are shown in Figure (5) The rate of uptake of metal ions was rapid in the first 30 min, then become slowly until reach equilibrium, at equilibrium, removal percentage was 43% for Pb^{+2}, 33% for Cd^{+2}, 12% for Co^{+2}, 37% for Mn^{+2} and 14% for Ni^{+2}. Equilibrium was reached for Pb^{+2}, Cd^{+2}, Ni^{+2} and Co^{+2}

removals within (3) hours but in case of Mn^{+2} reached after 4 hours using corn cob.

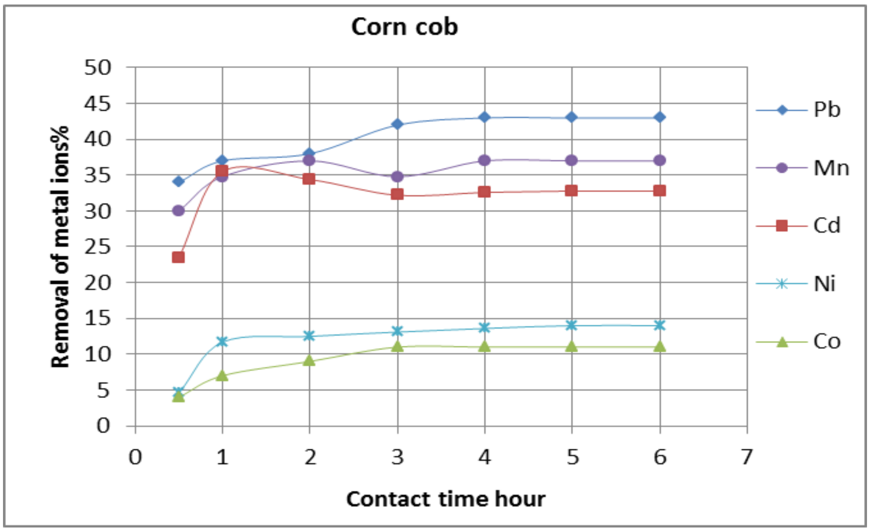

Figure 5: Effect of contact time on removal% of Pb^{+2}, Mn^{+2}, Cd^{+2}, Ni^{+2} and Co^{+2} ions

Effect of initial metal ion concentration (C_0):

The behavior of metal ion uptake by biosorbent were studied , which were carried out at 25 ± 2 °C using different initial metal ion concentrations (20, 40, 60, 90, 120 and 150 mg/L) at optimum pH (6), Contact time (6 hours), biosorbent dose (5 g/L) and shaking speed (250 rpm). The results are shown in Figure (6) which indicate that the percentage removal decreases with the increase in initial metal ion concentration. While with increasing Pb^{+2} concentrations the binding sites become more quickly saturated as the amount of biosorbent concentration remained constant [11]. The maximum removal% was 100% for Pb^{+2}, 85% for Cd^{+2}, 70% for Mn^{+2}, 35% for Ni^{+2} and Co^{+2} at metal ions concentration (20 mg/L).

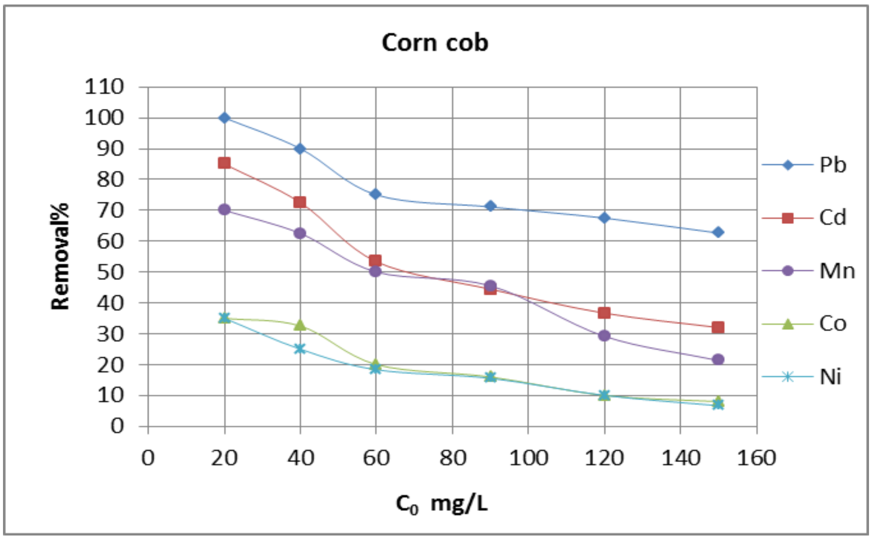

Figure 6: Effect of initial metal ion concentration on removal of Pb^{+2}, Co^{+2}, Cd^{+2}, Ni^{+2}, Mn^{+2} ions

Adsorption isotherm

An adsorption isotherm equation is an expression of the relation between the amount of solute adsorbed and the concentration of the solute in the fluid phase, since the adsorption isotherms are important to describe how adsorbates will interact with the adsorbents and so are critical for design purposes; therefore, the correlation of equilibrium data using an equation is essential for practical adsorption operation. Two isotherm equations were adopted in this study, as follows:

Langmuir isotherm equation:

The Langmuir equation is based on the assumptions that maximum adsorption corresponds to a saturated mono-layer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface [26].

The Langmuir isotherm is defined as:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (1)$$

and in linearized form is:

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

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} \times C_e \quad (3)$$

Where q_m and K_L are Langmuir constants related to the sorption capacity, and sorption energy, respectively, Ce is the equilibrium concentration in mg/L, and qe is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g).

The essential characteristics of Langmuir dimensionless constant separation factor or equilibrium parameter, R_L, which is defined by the following equation [26]:

$$R_L = \frac{1}{1 + K_L \times C_0} \quad (4)$$

From the value of RL calculated from above expression, the nature of the adsorption process to be either unfavorable (R_L>1), linear when (R_L=1), favorable when (0<R_L< 1) and irreversible when (R_L=0).

The RL-values for the adsorption process of Pb^{+2}, Cd^{+2}, Co^{+2}, Mn^{+2}, and Ni^{+2} with corn cob have values between 0 and 1, indicating the adsorption process is favorable [28].

The plots of Ce/qe against Ce are shown in Figure (7); the adsorption of Pb^{+2}, Mn^{+2}, Cd^{+2}, Ni^{+2} and Co^{+2} ions on corn cob gave a straight line. The Langmuir isotherm constants and their correlation coefficients R^2 are shown in Table (2).

Table 2: Langmuir constants for the sorption of Pb^{+2}, Mn^{+2}, Cd^{+2}, Ni^{+2} and Co^{+2}ions onto corn cob.

Metal ions	Slope	intercept	q_{max}(mg/gm)	K_L	R_L	R^2
Pb^{+2}	0.05	0.003	20.00	16.67	(0.000-0.003)	0.909
Cd^{+2}	0.097	1.066	10.31	0.09	(0.068-0.355)	0.986
Co^{+2}	0.397	0.748	2.52	0.53	(0.01 - 0.06)	0.974
Mn^{+2}	0.143	0.537	6.99	0.27	(0.01 - 0.05)	0.977
Ni^{+2}	0.453	0.002	2.21	226.50	(000002 - 0.00022)	0.950

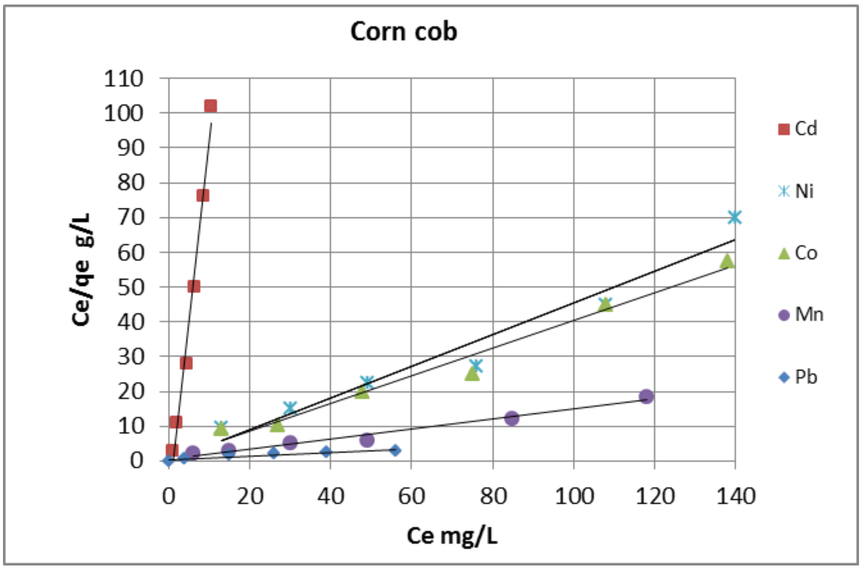

Figure 7: Langmuir plot of corn cob as adsorbent for Pb^{+2}, Mn^{+2}, Cd^{+2},Ni^{+2} and Co^{+2} ions removal

Freundlich isotherm equation

The Freundlich sorption isotherm, one of the most widely used mathematical descriptions, gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies.

The Freundlich isotherm is defined as:

$$q_e = C_e^{1/n} \quad (5)$$

and in linearized form is:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (6)$$

where Ce is the equilibrium concentration in mg/L, qe = amount of adsorbate adsorbed per unit weight of adsorbent (mg/g). "K_F" is a parameter related to the temperature and "n" is a characteristic constant for the adsorption system under study, The plots of (ln qe) against (ln Ce) are shown in Figure (8); the adsorption of Pb^{+2}, Mn^{+2}, Cd^{+2}, Ni^{+2} and Co^{+2} ions onto the different adsorbents gave a straight line; values of "n" between 2 and 10 show good adsorption [29]. The Freundlich isotherm constants and their correlation coefficients R^2 are shown in table (3).

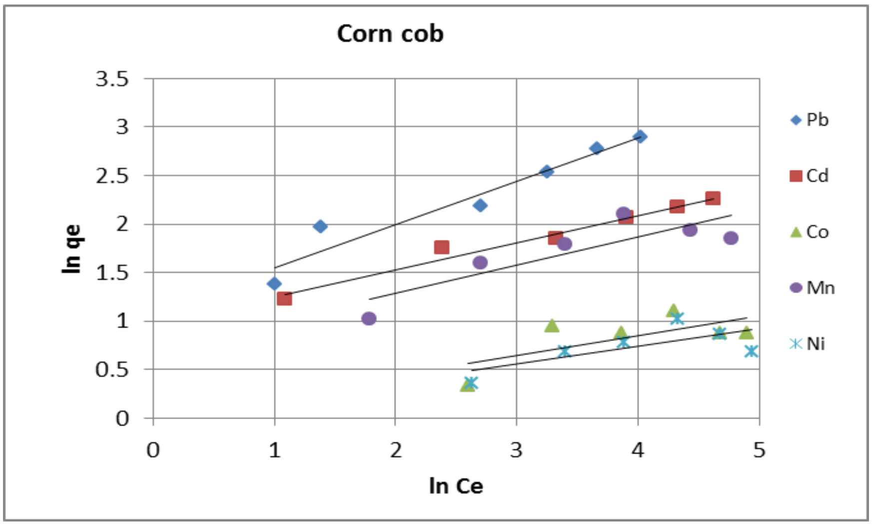

Figure 8: Freundlich plot of corn cob for Pb^{+2}, Mn^{+2}, Cd^{+2}, Ni^{+2} and Co^{+2} ions removal

Table 3: Freundlich constants for the sorption of Pb^{+2}, Mn^{+2}, Cd^{+2}, Ni^{+2} and Co^{+2} ions onto corn cob.

Metal ions	Slope	Intercept	Ln K_F	K_F	1/n	n	R^2
Pb^{+2}	0.445	1.1	1.1	3.0	0.4	2.2	0.933
Cd^{+2}	0.28	0.97	0.97	2.6	0.28	3.6	0.974
Co^{+2}	0.202	0.04	0.04	1.0	0.202	5.0	0.454
Mn^{+2}	0.29	0.70	0.7	2.0	0.29	3.4	0.729
Ni^{+2}	0.183	0.004	0.004	1.004	0.183	5.5	0.506

Case Study

Application for the treatment method to real industrial wastewater collected from a metal industry at Sadat industrial city, Menoufia, Egypt. From FTIR spectra shown in figure (2) illustrated that the difference between the free corn cob before treatment of wastewater and after, it subjected to the treatment process of real wastewater and illustrate stretch effect to the spectra which may attributed to the function groups at the surface of corn cob that bonded to metal ions.

Results in Table (4) represented the industrial wastewater characterization before and after treatment using corn cob. The treated wastewater has a higher organic load than the raw wastewater due to the low organic content in raw wastewater and the partial solubility of organic matter found in corn cob in water. A complete removal of Lead ions, removal of Cyanide, Zinc, Copper, Iron, Nickel and Chromium ions were 38%, 29%, 24%, 99%, 16%, and 17% respectively.

Table 4: Industrial wastewater characterization before and after treatment using Corn cob

Parameter	Unit	Raw wastewater	Treated wastewater
pH	--	6.6	6.2
COD	mg/L	95	215
BOD	mg/L	30	95
Phenol	mg/L	0.1	<0.1
Oil	mg/L	16.5	18
Sett. S	mg/L	N.D.	N.D.
TSS	mg/L	75	8
TDS	mg/L	818	1480
s.H_2S	mg/L	N.D.	N.D.
PO4	mg/L	1.7	0.52
TKN	mg/L	33	51
NO_3	mg/L	0.16	0.2
Heavy Metals.			
CN	mg/L	11	6.8
Pb	mg/L	0.26	N.D.
Zn	mg/L	11.61	8.3
Cu	mg/L	11.55	8.8
Fe	mg/L	2.13	0.2
Ni	mg/L	30.76	26
Cr	mg/L	44.69	37

CONCLUSION

Low-cost adsorbents as corn cob for the removal of Pb^{+2}, Mn^{+2}, Cd^{+2},Ni^{+2} and Co^{+2} ions from aqueous solutions. The batch method was employed; parameters such as pH, contact time, adsorbent dose and initial metal concentration were studied at temperature 25 ± 2 °C.

The adsorption increase with increasing of adsorbent dose, while the adsorption capacity (qe) decrease with increasing of sorbent dose.

The optimum pH corresponding to the maximum adsorption ions removal was at pH 6. Pb^{+2}, Mn^{+2}, Cd^{+2},Ni^{+2} and Co^{+2} ions were adsorbed onto the adsorbents very rapidly within the first 30 minutes, while equilibrium was attained within 3 hour for Pb^{+2}, Cd^{+2},Ni^{+2} and Co^{+2} ions, But for Mn^{+2} is 4 hours.

The essential characteristics of Langmuir dimensionless constant separation factor or equilibrium parameter, ($0<R_L<1$), that means the adsorptions is Favorable.

The Langmuir isotherm better fitted the experimental data since the correlation coefficient (R^2) for the Langmuir isotherm was higher than that of the Freundlich isotherm for five metals.

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