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Removal of Cu (II), Ni (II), and Co (II) ions from aqueous solution using low cost adsorbent: Isotherms, kinetics and equilibrium aspects

Nagwa A. Badawy[1], Amina A. El-Bayaa[1] and Enas Amdeha[2*]

[1]*Chemistry Department, Faculty of Science, Al-Azhar University (Girls), Nasr City, Cairo, Egypt*
[2]*Process Design and Development Department, Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt*

ABSTRACT

Environmental protection becomes a difficult task as many industries produce wastes that cause serious pollution. An industrial solid waste of sugarcane had been converted into an inexpensive and effective adsorbent to be used for the removal of some metal from aqueous solution. Effect of various parameters e.g., metal ion concentration, adsorbent dose, solution pH, and contacting time on the removal of Cu (II), Ni (II), and Co (II) ions had been studied. Maximum adsorption of Cu (II), Ni (II), and Co (II) ions were 78 %, 72%, and 69 %, occurred at metal ion concentration 70 ppm and at pH value of 6.5, 6.0 and 6.0, respectively. A dose of 14 g/l of adsorbent was sufficient for the optimum removal of metal ions. The material exhibits good adsorption capacity and the adsorption data follow the Langmuir model better than the Freundlich model. Kinetic parameters of adsorbent for the removal of each metal ion from wastewater were studied.

Keywords: Adsorption isotherm, Kinetic, waste of sugarcane, metal ions, Environmental protection.

INTRODUCTION

Environmental pollution, as a consequence of the industrialization process, is one of the major problems that have to be solved and controlled. The presence of metal ions in municipal or industrial wastewater and their potential impact have been a subject of scientific environmental research for a long time because of their extreme toxicity even at low concentrations, and their tendency to accumulate in the food chain, causing various disorders for living organisms [1].

Heavy metals are released into the environment from a number of industries such as mining, plating, dyeing, automobile manufacturing and metal processing. The presence of heavy metals in the environment has led to a number of environmental problems. Heavy metals are not biodegradable and have become an eco-toxicological hazard of prime interest and increasing significance owing to their harmful effect on human physiology and other biological systems when they exceed the tolerance levels. The removal of toxic metals from wastewater is a matter of great interest in the field of water pollution, which is a serious cause of environmental degradation. Heavy metals such as copper, nickel and cobalt are among the most common pollutants found in industrial effluents [2].

As a consequence, methods to remove metal species from wastewaters have been the subject of different researches, in order to improve the water quality. A number of methods for metal ions removal from wastewaters have been used, but most have disadvantages, such as continuous input of chemicals, high cost and even incomplete metal removal. These methods are based on physical or chemical replacement, generating yet another problem in the form of a toxic sludge [3].

Adsorption is a very effective process for a variety of applications, and now it is considered an economical and efficient method for metal ions removal from wastewaters. The adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substance. The need of alternative low-cost sorbents has encouraged the search for new and cheap sorption processes for aqueous effluent treatment, as these materials could reduce significantly the wastewater-treatment cost. With the increase in environmental awareness and governmental policies there has also been an emphasis on the development of new environmentally friendly ways to decontaminate waters using low-cost methods and materials. Several alternative materials from natural sources have been proposed [4].

Agricultural by-products are considered to be low value products, which are arbitrarily discarded or burned, resulting in resource loss and environmental pollution. Utilization of agriculture waste residues for the wastewater treatment at least has the following advantages: 1) there are available abundantly at no or low cost, 2) disposal of the wastes is a serious environmental problem in the area which has extensive agricultural activities. A number of agricultural waste and by-products of cellulosic origin have been studied in the literature for their capacity to remove adsorbate from aqueous solutions,such as fly ash, coal, biosorbents [5], barley husks, sugarcane bagasse, wheat straw [6], corncobs, barley husks, tree ferns [7], wood chips, and corn-cob shreds [8]. Some researchers studied the natural materials including by-products and wastes from agricultural and forest industries. These materials could be assumed as low-cost since they require little processing and are abundant in nature. Also, they can be used either directly or after an activation treatment. Bailey et al. reviewed a wide variety of low-cost sorbents for the removal of heavy metals from wastewaters [3, 9].

An industrial solid waste of sugarcane is the residual cane pulp remaining after the sugar has been extracted. It is basically built by macromolecules with humic and fulvic substances, lignin, cellulose, hemicelluloses and proteins that have adsorptive sites such as carbonyl, carboxylic, amine and hydroxyl groups, able to adsorb the adsorbate by the ion exchange phenomena or by complexation [9]. Egypt generates a lot of the industrial solid waste of sugarcane each year therefore it is important to highlight that the use of agricultural wastes for the treatment of aqueous effluents, primarily as alternative adsorbent materials, may be an advantage, since they remove inert pollutants from the wastewaters and may contribute to minimize the environmental impacts caused by inadequate disposal of these wastes.

This study aimed to assess the capacity of industrial solid waste of sugarcane to remove Cu (II), Ni (II) and Co (II) ions by using the adsorption process. Optimum parameters affecting the adsorption, e.g., adsorbent doses, pH, contact time, initial metal ion concentration was investigated. The experimental results were analyzed in terms of three adsorption isotherm equations: The Langmuir, Freundlich and Dubinin-Radushkevich. A detailed analysis of two kinetic models equations, pseudo-first-order and pseudo-second-order was studied to investigate the removal of Cu (II), Ni (II) and Co (II) ions from wastewater.

EXPERIMENTAL SECTION

2.1. Materials

All chemicals used were of analytical reagent grade. Aqueous metal solutions were prepared by dissolving appropriate quantities of metal chloride salts (Aldrich Chemical Company, USA). Doubly distilled water was used throughout. The adsorption behavior was studied at the solution pH after 48-h period. Stock solutions of 500 ppm metal were prepared by dissolving appropriate amount of $CuCl_2.2H_2O$, $CoCl_2.6H_2O$ and $NiCl_2.6H_2O$ in 1000 ml double distilled water. Other concentrations varying between 20 – 120 ppm were prepared from stock solution by dilution; all reagents used are Analytical-grade (Aldrich Chemical Company, USA).

2.2. Adsorbent and its characterisation

Low cost adsorbent industrial solid waste of sugarcane (ISWS) is a waste byproduct from sugar industry, were obtained from Abou-Korkas Sugar Factory, El-Minia, Egypt. (ISWS) was used as such without any pretreatment except for sieving of very fine particles. The point zero charge (pH_{pzc}) of (ISWS) was determined by the solid addition method [10]. The Boehm titration procedure was used to calculate the amount of surface acidic and basic functional groups [10].

2.3. Apparatus

The metal ions concentrations were determined by UV-Visible Spectrophotometer, Perkin Elimer-Iamda spectrophotometer model 201. This is a double-beam digital reading and recording instrument whose wavelength range is 190– 1200 nm, quartz cell of 1.00 and 0.10 cm standard path-length were used for measurements. The pH values of all prepared solutions were measured using pH meter model OP-02/2 (Germany) with a combined electrode reading to +0.05 pH value. Water bath connected with thermostat and 100 ml double jacket cell (UKT-

Germany).

2.4. Batch adsorption studies

Adsorption experiments were carried out by adding 0.35 g of adsorbent in 25 ml of desired concentration of adsorbate solution to be in contact for 48 h at room temperature. All of the batch experiments were conducted in duplicate and the results are the means. Metal ions concentrations in the supernatant solutions were analyzed using a UV-visible Spectrophotometer. The absorbance was measured at the maximum wavelengths, λ_{max} = 777 nm, 510 nm and 392 nm for Cu (II), Co (II) and Ni (II) ions respectively. The adsorbate solutions were diluted when measurements of the absorbance exceeded the linearity of the calibration curve.

The effects of various parameters were determined during batch experiments. The effect of the pH on adsorption was studied by shaking 0.35 g of the adsorbent in 25 ml of adsorbate solutions for 48 h. A series of [70 ppm] of Cu (II), Co (II) and Ni (II) ions were adjusted to an initial pH range of 1.5 – 12.0 by adding dilute HCl or NaOH. To study the effect of contact time, the samples were withdrawn at increasing contact time intervals ranging from 5 min. to 2 h for each metal ion. The kinetics of adsorption was determined. The effect of the adsorbent dosage was investigated by varying the amount of adsorbent from 4 to 20 g/l. Blank runs, with only (ISWS) in 25 ml of double distilled water, were conducted simultaneously at similar conditions to account for any color leached by the (ISWS) and adsorbed by glass containers.

The removal (%) of each metal ion by (ISWS)wascalculated using the following equations: Removal (%) = 100 $(C_o-C_e)/C_o$ (1)

Where C_o and C_e are the concentrations of the adsorbate in initial and final solutions, respectively[11].

1.5. Equilibrium adsorption isotherm

The most commonly used isotherm theories have been adopted in this work, namely, the Langmuir, Freundlich and Dubnin–Radushkevich equilibrium isotherm theories.

1.5.1.Langmuir isotherm model

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface[12]. The Langmuirequation can be described by the linearized form [13]:

$$C_e/q_e = (1/q_m\, b) + (C_e/q_m) \qquad (2)$$

The linear plot of specific sorption (C_e/q_e) against the equilibrium concentration (C_e) shows that the adsorption obeys the Langmuir model. The adsorption capacity q_m and energy of adsorption b were determined from the slope and intercept of the plot.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by equation:

$$R_L = 1/\,(1 + bC_o) \qquad (3)$$

R_L values between 0 and 1 indicate favorable adsorption of metal ion on resin at the concentration studied.

R_L value	Nature of adsorption process
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

1.5.2.Freundlich isotherm model

The Freundlich adsorption isotherm represents the relationship between the amount of metal adsorbed per unitmass of the adsorbent q_e and the concentration of the metal in solution at equilibrium. The Freundlich adsorption isotherm [13] is:

$$q_e = K_F\, C_e^{1/n} \qquad (4)$$

The equation can be linearized by taking logarithms to find the parameters K_F and n:

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (5)$$

The logarithmic plot of the Freundlich expression for the amount of metal ion adsorbed per unit mass of the adsorbent (q_e) and the concentration of metal ion at equilibrium (C_e). The values of K_F and n were calculated from the slope and intercept of the plot.

1.5.3.Dubinin–Radushkevich (D–R) isotherm model

Langmuir and Freundlich isotherms do not give any idea about adsorption mechanism. D-R isotherm describes adsorption on a single type of uniform pores. In this respect the D-R isotherm is an analogue of Langmuir type but it is more general because it does not assume a homogeneous surface or constant sorption potential [14]. In order to understand the adsorption type, D-R isotherms were obtained. The D-R isotherm which is given with the following equation:

$$q_e = q_m \exp (- \beta\varepsilon^2) \qquad (6)$$

And linearized form of the equation is given as:

$$\ln q_e = \ln q_m – \beta\varepsilon^2 \qquad (7)$$

Where ε (Polanyi potential) is:

$$\varepsilon = RT \ln (1+ (1/C_e)) \qquad (8)$$

, q_e is the amount of solute adsorbed per unit weight of adsorbent (mol/g), β is a constant related to the adsorption energy (mol^2/kJ^2) and q_s is the adsorption capacity (mol/g).

The values of q_m and β were calculated from the intercept and slope of the ln q_e versus ε^2 plots.

1.6. Adsorption kinetic models

1.6.1.Pseudo-first order (Lagergren's kinetics):

Lagergren-first-order equation [15] is the most popular kinetics equation. The form is:

$$dq_t/dt= k_1(q_e − q_t) \qquad (9)$$

After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (9) becomes the following:

$$\text{Log} (q_e − q_t) = \log q_e − (k_1/2.303) t \qquad (10)$$

Where q_t is the amount of adsorption at time t (min) (mg/g); k_1 the rate constant of the equation (l/min); q_e is the amount of adsorption at equilibrium (mg/g) [16–18]. The adsorption rate constant, k_1, can be determined experimentally by plotting of log (q_e −q_t) against t.

1.6.2.Pseudo-second order

The pseudo-second-order model is represented as:

$$dq_t/dt = k_2(q_e-q_t)^2 \qquad (11)$$

where k_2 is the pseudo-second-order rate constant (g/mg min). Integrating Eq. (11) and noting that ($q_t = 0$) at ($t = 0$), the following equation is obtained:

$$q_t = tk_2q^2{}_e / (1+t\, k_2q_e) \qquad (12)$$

The initial sorption rate, h (mg/g min), at t→0 is defined as:

$$h = k_2q^2{}_e \qquad (13)$$

The q_e is obtained from the slope of the t/q_t versus t and h is obtained from the intercept. Since q_e is known from the slope, the k_2 can be determined from the value of h [19].

RESULTS AND DISCUSSION

3.1.Adsorbent characterization

Industrial solid waste of sugarcane (ISWS) consists of cellulose (50%), hemicellulose (27%) and lignin (23%). The presence of these three biological polymers causes adsorbent to be rich in hydroxyl and phenolic groups [20]. The mechanism of adsorption for (ISWS) is linked to the role played by the essential stretching functional groups like Hydroxyl (–OH), Carboxylic acid (–COOH), carbonyl (C=O), C-H, and other aromatic and phenolic groups existing in the sorbents.

3.1.1.Determination of the point of zero charge

It is well known that aqueous phase distribution of solute species is dependent on the pH of the solution. The data on the adsorption of solute species onto the surface of adsorbents at different pH values should give a fairly good idea about the pH range favorable for the adsorption process. The point zero charge of (ISWS) was determined and the results are shown in Fig. (1). Since KNO_3 solution was used, it is desirable to have a fixed background electrolyte concentration that is high enough to minimize the total salt concentration changes during the titration and no clear effect of KNO_3 was found on the mobility. The pH_{pzc} values were known by determining the position where the resulting curves cut through the pH_0 axis as shown in Fig. (1). The pH_{pzc} was found to be 5.25, for (ISWS) sample .This is a convenient index of a surface when the latter becomes either positively charged or negatively charged as a function of pH. When the pH of the aqueous solution is below the pH_{pzc}, the surface of the adsorbent will become positively charged. Meanwhile, the surface of the adsorbent will become negatively charged when the solution pH is greater than pH_{pzc}.

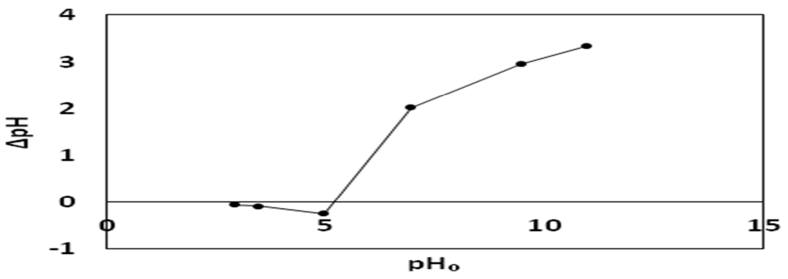

Fig.(1) Determination of Point Zero Charge (pH_{pzc})of ISWS

*3.1.2.*Characterization of the surface functional groups

The Boehm's technique was used to characterize the surface chemical property of the adsorbent. Several assumptions were made before the surface acidity and basicity could however be calculated. It was assumed that acidic group generally, could only be neutralized by NaOH, Na_2CO_3 and $NaHCO_3$while all basic groups would be neutralized by HCl.

The properties of the surface functional groups were investigated through the Boehm titration. The titrations results confirmed the presence of –OH (0.15 mmol/g), –COOH (0.192 mmol/g), Lactone (0.013 mmol/g), acidity (0.355mmol/g),basicity (0.037mmol/g) functional groups in the lignocelluloses moiety of the adsorbent, and probably these groups are the major binding groups responsible for adsorption.

3.2.Determination of optimum conditions

3.2.1. Effect of initial metal concentration

The initial metal ion concentration provides an important driving force to overcome all mass transfer resistance of metal between the aqueous and solid phases. The effect of initial metal concentration on removal efficiency of Cu (II), Ni (II) and Co (II) adsorption by (ISWS) was studied by batch adsorption experiments, which were carried out at 25^0C and adsorbent dose (14g/l), using different initial metal ion concentrations (20 – 120 ppm) at fixed pH. The results are shown in Fig. (2) which indicate that the percentage removal decreases with the increase in initial metal ion concentration. This is because there were no more adsorption sites on the adsorption surface of the adsorbent material [21–22]. While the initial Cu(II), Ni(II) and Co(II) ion concentration increased from 20 to 120 ppm, the adsorption % decreased from 98% to 49.2%, 96% to 39% and 95% to 35% for Cu(II), Ni(II) and Co(II) respectively.

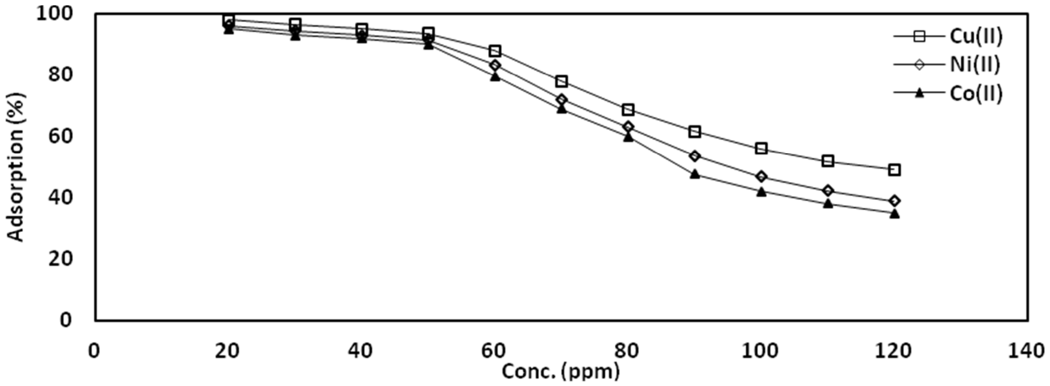

Fig. (2): Effect of initial Cu (II), Ni (II) and Co (II) ions Conc. on the adsorption (%) by (ISWS) [dose = 14g/l] in aqueous media at 25°C

3.2.2. Effect of adsorbent dose of ISWS on removal efficiency Cu (II), Ni (II) and Co (II)

The effect of the adsorbent dose on removal of Cu (II), Ni (II) and Co (II) was studied by varying the dose of the adsorbent from 4 to 20 g/l at fixed pH, temperature and adsorbate concentration. The results are presented in Fig. (3). The adsorption increases from 20.14 % to 78 %, 15.29 % to 72 % and 12.43 % to 68.57 % with increase in adsorbent dose from 4 to 14 g/l in case of Cu (II), Ni (II) and Co (II) respectively, and then became almost constant in all cases, indicating that a dose of 14 g/l of adsorbent is sufficient for the optimum removal of copper, nickel and cobalt [23– 24]. An increase in the adsorption with the adsorbent dosage can be attributed to greater surface area and the availability of more adsorption sites. The adsorbent dose of adsorbent material to be used is of great importance, not only to have an efficient removal of the metal ions, but also to project the area required to stock the adsorbent material resulting from the treatment process.

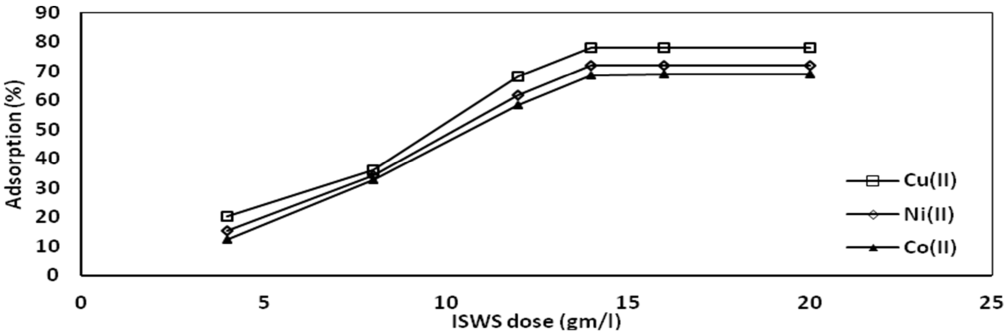

Fig. (3): Effect of (ISWS) dose on the adsorption (%) of Cu (II), Ni (II) and Co (II) ions [70 ppm] in aqueous media at 25°C

3.2.3. Effect of contact time on removal efficiency of Cu (II), Ni (II) and Co (II)

The effect of contact time on the removal efficiency of Cu (II), Ni (II) and Co (II) by (ISWS) was studied. The results are shown in Fig. (4) illustrated that the rate of uptake of metal ions was quite rapid; in the first 30 min **.** The removal efficiencywas 38.5 % for Cu (II), 31.0 % for Ni (II) and 34.7 % for Co (II), due to larger surface area available of adsorbent. At equilibrium, 78.0 % of Cu (II) ions, 71.86 % of Ni (II) ions and 68.6 % of Co (II) ions were removed. The curves in Fig. (4)present a double nature, consisting of a linear curve followed by leveling of the curve at equilibrium time beyond which there is no further increase in amount of adsorption. The linear portion of the curve reflects surface layer diffusion and its plateau portion represents pore diffusion [25–26]. Equilibrium was reached for Cu (II), Ni (II) and Co (II) removal within 60, 70 and 80 min, respectively. This is in agreement with the results obtained by Sharma et al. for remediation of chromium rich waters and wastewaters by fly ash [21].

In physical adsorption most of the adsorbate species are adsorbed within a short interval of contact time. However, strong chemical binding of the adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption studies in literature reveal that the uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between those two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases [27].

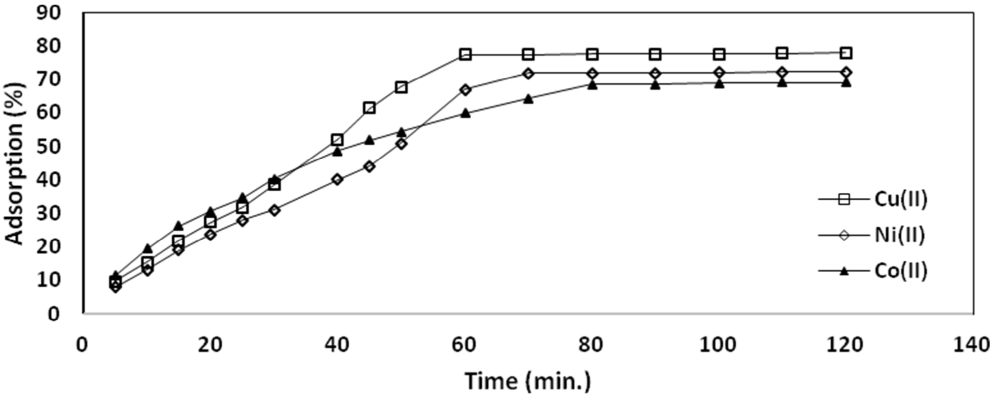

Fig. (4): Effect of contact time on the removal (%) of Cu (II), Ni (II) and Co (II) ions concentration [70 ppm] by (ISWS) [dose = 14 g/l] in aqueous media at 25ºC

3.2.4. Effect of pH on removal efficiency of Cu (II), Ni (II) and Co (II)

One of the most important factors affecting adsorption of metal ions is acidity of solution. The metal ion adsorption is affected by the pH of the solution thereby changing the surface charge of the adsorbent and metal speciation. Fig. (5)shows the effect of pH on removal of Cu (II), Ni (II) and Co (II) ions by (ISWS).In pH range of 1.5 – 2.1, there is littleor no adsorption and with the increase of pH, the amount of metal ions uptake tended to increase and a sharp increase in removal (%) wasobserved in the pH ranging from 3.0 to 6.0. At about pH 6.0 a plateau wasreached, e.g., there was no significant difference between pH 6.0 and7.0 in the maximum Ni(II) adsorption capacity. These seemed toindicate that the optimum pH value for Ni(II) adsorption would be around 6.0. This is agreeing with the previously explained in other papers [22]. Maximum removal percentages were 69 % at pH 6.0 for Co (II) and 78 % at pH 6.5 for Cu (II)

The two main factors influencing the variation in adsorption trend at different solution pH for the system under study may be due to the pH_{pzc} of adsorbent and metal ions speciation in solution as a function of pHs. The pH_{pzc} of (ISWS) is 5.25 (i.e. the surface charge density at pH 5.25 is zero) and it clearly shows that the surface is carrying positive charge below pH 5.25 and negative charge above pH 5.25. This observation is in line with the experimental data indicating low amount of adsorption below pH 5.25 due to the repulsion of metal ions species by positively charged adsorbent surface, whereas there is substantial increase in the amount of adsorption above pH 5.25 when the surface is negatively charged and metal ions species get easily adsorbed due to inter ionic attractions. At higher pHvalues, especially after 6.8, the amount of adsorption is almost constant or slightly decreaseddue to the formation of $M(OH)_2$, which tends to precipitateat higher pH values.

The surface of adsorbent generally displays ISWS –OH and ISWS –O surface entities. Thus the mechanism behind the adsorption of M (II) onto (ISWS) can be illustrated by the following expressions:

2 ISWS –OH + M(II) ↔ $(ISWS–O)_2M + 2H^+$
Or
2 ISWS –O+ M(II) ↔ $(ISWS–O)_2M$

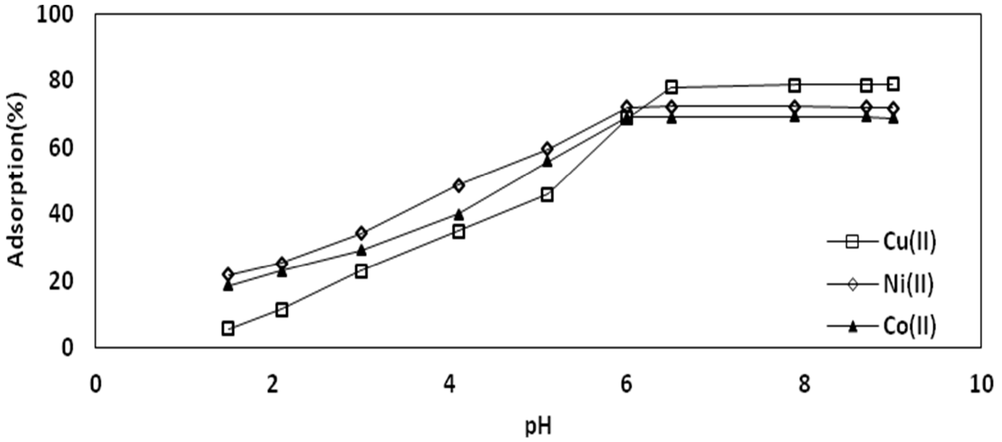

Fig. (5): Effect of pH on the removal (%) of Cu (II), Ni (II) and Co (II) ions concentration [70 ppm] by (ISWS) [dose = 14 g/l] in aqueous media at 25ºC

The optimum pH for the adsorption of Ni (II) onto (ISWS) was found to be 6.0 and thereby the adsorption mechanism involves the exchange between H^+ on the surface of adsorbent and the Ni (II) in the aqueous phase. This may lead to the formation of an ion exchanged complex and was confirmed by the lowering of pH after the Ni (II) adsorption process [26]. The decreasing affinity of (ISWS) for binding to the Cu (II) and Co (II) metal ions can be arranged based on their uptake values according to the following order: Cu(II) > Co(II).

3.3.Adsorption Isotherms

In order to optimize the design of an adsorption system to remove metal ions, it is important to establish the most appropriate correlations for the equilibrium data for each system. Three isotherm models have been tested in the present study; Langmuir, Freundlich and Dubnin models. The applicability of the isotherm equations is compared by judging the correlation coefficient, R^2.

3.3.1.Langmuir model

The Langmuir adsorption constants evaluated from the equation (2) with correlation coefficients are presented in (Table 1) **.**The shape of the Langmuir isotherm was investigated by the dimensionless constant separation term (R_L) to determine high affinity adsorption. In the present study, the values of R_L were observed to be in the range 0.0006 – 0.0790, indicating that the adsorption processwere favorable [28].

Table (1): Langmuir isotherm constants of Cu (II), Ni (II) and Co (II) ions [70 ppm] by (ISWS) [dose = 14 g/l] in aqueous media at 25°C

Adsorbate	Regression equations	q_m(mg/g)	b (l/mg)	R^2
Cu(II)	y = 0.2390x + 0.2662	4.180	0.899	0.999
Ni(II)	y = 0.2962x + 0.0197	3.380	15.020	0.999
Co(II)	y = 0.3314x - 0.1561	3.020	2.120	0.997

3.3.2.Freundlich model

The Freundlich adsorption model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with an exponential distribution of active centers, characteristic of heterogeneous surfaces. The slope 1/*n*, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for 1/*n* below one indicates a normal Freundlich isotherm while 1/*n* above one is an indicative of cooperative adsorption [28]. The values of K_F and 1/*n* are determined from the equation (5) with correlation coefficients are presented in (Table 2).

Table (2): Freundlich isotherm constants of Cu (II), Ni (II) and Co (II) ions [70 ppm] adsorption by (ISWS) [dose = 14 g/l] in aqueous media at 25°C

Adsorbate	Regression equations	1/n	n	K_F	R^2
Cu (II)	y = 0.3341x + 0.3211	0.334	2.990	2.095	0.993
Ni (II)	y = 0.6152x + 0.1608	0.615	1.630	1.448	0.991
Co (II)	y = -0.1356x + 0.7224	0.136	7.370	5.277	0.985

3.3.3.Dubinin and Radushkevich isotherm

Another equation used in the analysis of isotherms was proposed by Dubinin and Radushkevich. Calculated Dubinin–Radushkevich constants for the adsorption for Cu (II), Ni (II) and Co (II) were determined from the equation (6-8) with correlation coefficients are presented in Table (3).

Table (3): Dubinin isotherm constants of Cu (II), Ni (II) and Co (II) ions [70 ppm] adsorption by (ISWS) [dose = 14 g/l] in aqueous media at 25ºC

Adsorbate	Regression Eq.	R^2	β (mol^2/kJ^2)	q_m (mol/g)	ε(kJ/mol)
Cu(II)	y = -0.3831x + 1.3799	0.992	0.383	3.975	1.142
Ni(II)	y = -0.4039x + 1.2674	0.978	0.404	3.552	1.113
Co(II)	y = -0.3068x + 1.1945	0.981	0.307	3.302	1.277

3.4.Adsorption kinetic study

In order to investigate the adsorption processes of Cu (II), Ni (II) and Co (II) by (ISWS)in aqueous media at different temperatures, pseudo-first-order and pseudo-second-order kinetic models were used.

3.4.1.Pseudo-first-order model

The pseudo-first order rate constant, k_1 and the adsorption capacity, q_e of Cu (II), Ni (II) and Co (II) ions adsorption on (ISWS)at 25^0C, 40 ^{0}C and 50^0C were evaluated from the equation (10)and presented in Table (4). It can be seen that the adsorption rate of each metal ions increased with increasing temperature. This may be attributed to increase in the rate of pore diffusion.

Table (4): The pseudo-first-order equation parameters for Cu (II), Ni (II) and Co (II) ions [70 ppm] adsorbed by (ISWS), in aqueous media at different temperatures

Kinetic parameters	Adsorption capacity, q_e			pseudo-first-order rate constant, k_1			R^2		
	25 ^{0}C	40 ^{0}C	50 ^{0}C	25 ^{0}C	40 ^{0}C	50 ^{0}C	25 ^{0}C	40 ^{0}C	50 ^{0}C
Cu(II)	**3.88**	**4.00**	**4.07**	**0.0115**	**0.0177**	**0.0244**	**0.993**	**0.992**	**0.991**
Ni(II)	**3.60**	**3.66**	**3.76**	**0.0212**	**0.0210**	**0.0237**	**0.992**	**0.994**	**0.991**
Co(II)	**3.44**	**3.54**	**3.62**	**0.0210**	**0.0212**	**0.0306**	**0.992**	**0.994**	**0.991**

3.4.2.Pseudo-second-order model

The pseudo-second-order, $k_2$and the sorption capacity, q_e of Cu (II), Ni (II) and Co (II) ions adsorption on (ISWS)at25^{0}C, 40 ^{0}C and 50^{0}C were evaluated from the equations (12and 13)and presented in Table (5). It can be concluded from Tables (4 and 5) that pseudo-first order equation provides the best correlation coefficient, whereas the pseudo-second order do not give a good fit to the experimental data for the adsorption of Cu (II), Ni (II) and Co (II) ions.

Table (5): The pseudo-second-order equation parameters for Cu (II), Ni (II) and Co (II) ions [70 ppm] adsorbed by (ISWS), in aqueous media at different temperatures

Kinetic parameters	Adsorption capacity, q_e			pseudo-second-order rate constant, k_2			R^2		
	25 ^{0}C	40 ^{0}C	50 ^{0}C	25 ^{0}C	40 ^{0}C	50 ^{0}C	25 ^{0}C	40 ^{0}C	50 ^{0}C
Cu(II)	**7.5760**	**7.0420**	**9.1160**	**0.0015**	**0.0020**	**0.0012**	**0.978**	**0.973**	**0.984**
Ni(II)	**6.0060**	**6.7890**	**8.1170**	**0.0021**	**0.0016**	**0.0012**	**0.984**	**0.976**	**0.987**
Co(II)	**5.6180**	**3.6860**	**4.8500**	**0.0024**	**0.0088**	**0.0051**	**0.970**	**0.971**	**0.979**

3.5. Mechanism of metal ion adsorption

Mechanisms involved in the biosorption process by agro-based biomasses include ion exchange, chelation, precipitation, adsorption by physical forces and ion entrapment in inter and intra-fibrillar capillaries and spaces of the structural lignin and polysaccharide networks as a result of diffusion through cell wall and membrane. Some information about the surface chemistry characterization of the (ISWS functional groups, can be used as evidences in proposing the adsorption mechanism. Also adsorption kinetics and equilibrium can be used to explain the adsorption mechanism.

In this studied chemisorptions controlled mechanism can be postulated as the mechanism governing the adsorption process. It was also possible that metal ions were bound into carboxylate groups in the lignocellulosic structure of (ISWS) by creating ionic forces with carboxylic oxygen atoms. These oxygen atoms exhibited negative charge in their structure as a result of the dissociation of carboxylic groups. The negatively charged oxygen atom in carboxylate anions will coordinate with metal cations, resulting in the formation of metal–carboxylate complexes (COO–M) on the adsorbent surface. These conclusions support the mechanism previously explained in other papersbased on the interaction of metal ions with acidic functional groups in the biomass surface [22, 29].

CONCLUSION

The Boehm titration results confirmed the presence of –OH and –COOH functional groups in the lignocelluloses moiety of the industrial solid waste of sugarcane (ISWS), and probably these groups are the major binding groups responsible for adsorbent adsorption. The pH_{pzc} was found to be 5.25.

The removal (%) for metals ions under investigation decreases with increasing metal ions concentrations in aqueous solutions. The highest Cu (II), Ni (II) and Co (II) ions removal efficiency was 98%, 96% and 95% respectively, for 20 ppm concentration and (ISWS) dose 14 g/l. The adsorption increases with time and attains equilibrium in 60, 70 and 80 min for Cu (II), Ni (II) and Co (II) respectively, at 25˚C for initial metal ions concentrations of (70 ppm). The maximum adsorption for Cu (II) 78% at pH = 6.5, Ni (II) 72% at pH = 6.0 and Co (II) 69% at pH = 6.0. The material exhibits good adsorption capacity and the adsorption data follow the Langmuir model better than the Freundlich model. The pseudo-first order equation provides the best correlation coefficient.

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