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Removal of Ni^{2+} from aqueous solution by adsorption onto maize tree-trunk polyaniline composite

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Abstract

Maize tree-trunk polyaniline composite was prepared by chemical polymerization method. Function groups belonging to materials were characterized by IR analysis and their morphological structure was examined by SEM image. The adsorption of Ni^{2+} was carried out onto composite in aqueous solution via varying pH, contact time and its initial concentration. The experimental adsorption data fitted into Freundlich adsorption isotherm model (r^2 = 0.9898) better than into Langmuir one (r^2 = 0.6764). The adsorption followed pseudo-second order kinetic model very well (r^2 = 0.9976). The maximum adsorption capacity of that composite was 66.67 mg/g which calculated from the pseudo-Langmuir equation.

Keywords. Maize tree-trunk polyaniline composite, removal of Ni^{2+}, isotherm and kinetic adsorptions.

1. INTRODUCTION

Removal of heavy metal ions from aqueous solution has been regarding mostly by scientists because of human health on the world which is damaged by strongly developing many industrial branches such as metallurgy, electroplating and trade village. All of them are resulting to critical environmental pollution in air or groundwater. Ni^{2+} ion is one of the most toxic chemical agents, therefore, many methods as well as adsorbents were regarded to find out for removing it from wastewater [1-4]. Among them the adsorption method is economic and efficient way because of inexpensive adsorbents and sample treatment process. Polyaniline (PANi) is one of the most promising polymer which is used widely to fabricate composites based on it and agriculture waste for removing heavy metal ions from wastewater [5-8] because of its stable environmental conductive property and easy regeneration.

The main objective of this work was to evaluate the adsorption isotherms for Ni^{2+} ion onto Maize tree-trunk polyaniline composite which prepared by chemical method.

2. EXPERIMENTAL

2.1. Synthesis procedure of Maize tree-trunk polyaniline composite

Carrying agent was prepared from maize tree-trunk (MTT) following procedure: it was firstly tried and then ground in micro size (< 100 μm). Continuously, it was ultrasonic for 20 minutes in acetone solution, then filtrated and washed by distilled water. Lastly, it was tried under vacuum at 50 ^oC until completely dry before use. Maize tree-trunk polyaniline (MTT-PANi) composite based on MTT and PANi was prepared by chemical method from acid medium containing aniline using ammonium persulfate as an oxidation agent. The reaction occurred in 18 h under continuous stirring at temperature of 1÷5 ^oC. After purification and changing it into emeraldine base (EB) by treatment with 0.5 M ammonia solution, it was dried in vacuum at 50-60 ^oC for 4-5 h and kept in a sealed bottle for adsorption of nickel ion.

2.2. Ni^{2+} adsorption

The pH effect was considered by varying pH from 1 to 7 when initial nickel concentration (C_0) was kept 1 mg/L with contact time of 40 min. The effect of contact time t (min) was investigated at C_0 = 1 mg/L and pH = 6 by t varied from 10 to 100 min. The effect of C_0 was studied at pH = 6 and t = 40 min due to changing C_0 from 0 to 2.235 mg/L.

Ni^{2+} concentrations in solution before and after adsorption onto adsorbent were analyzed by Atomic Absorption Spectroscopy (AAS) from which the adsorption amount could be calculated.

The adsorption capacity (q_t, mg/g) and the removal efficiency (H, %) were calculated from the following equations:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

$$H = \frac{(C_0 - C_t)}{C_0}.100\% \quad (2)$$

Where C_0 and C_t are the concentration of Ni^{2+} (mg/L) initially and at time t (min), respectively; V is the volume of the solution (mL), m is the mass of adsorbent (g).

The pseudo–first and second order kinetic models [8, 9] (equations 3 and 4, respectively) were used for analyzing kinetics and rate of Ni^{2+} adsorption onto MTT-PANi.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where q_e and q_t are the adsorption capacity of Ni^{2+}onto MTT-PANi at equilibrium and contact time t. The equilibrium rate constants of pseudo- first and second order adsorption are k_1 and k_2, respectively.

Based on the parameters of second - order adsorption kinetic model (equation 4), the equilibrium concentration of Ni^{2+} in solution can be calculated from the equation below:

$$C_e = C_0 - \frac{q_e m}{V} \quad (5)$$

Where q_e is the equilibrium adsorption capacity obtained from pseudo - second order rate law (mg/g), V is solution volume (L), m is mass of adsorbent (g), C_e and C_0 are the equilibrium and initial concentration in solution (mg/L), respectively.

The Langmuir (6) and Freundlich (7) adsorption isotherms [10, 11] were considered by following two equations below:

$$\frac{C}{q} = \frac{1}{q_m K_L} + \frac{C}{q_m} \quad (6)$$

$$\text{Log } q = \log K_F + \frac{1}{N_F}\log C \quad (7)$$

Where, C is Ni^{2+} concentration in solution after adsorption, q is adsorption capacity, K_L is Langmuir isotherm constant (L/mg), q_m is maximum adsorption capacity (mg/g), K_F (m/g) and N_F are Freundlich isotherm parameters.

3. RESULTS AND DISCUSSION

3.1. SEM image

The SEM image on figure 1 showed that MTT-PANi composite had morphology structure in short nanofibre form with diameter of 30÷50 nm, where PANi was continuous phase and MTT was dispersion one.

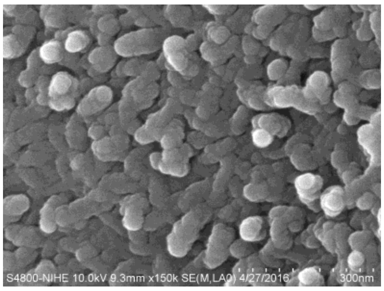

Figure 1: SEM image of MTT-PANi composite

3.2. IR-spectrum

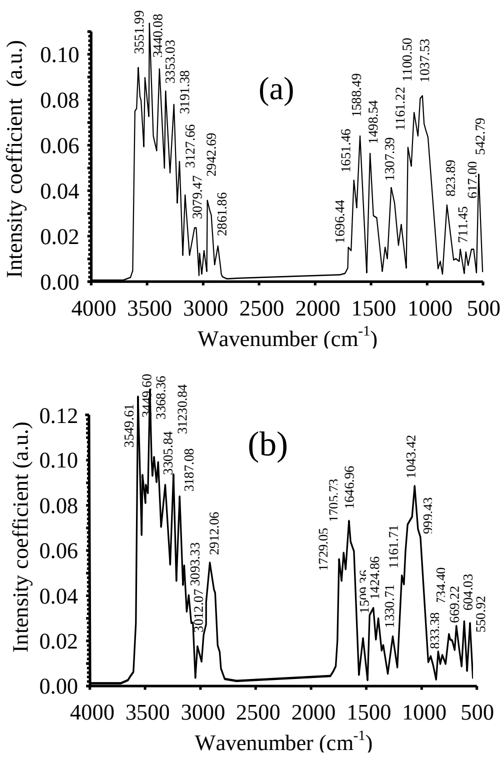

Figure 2: IR-spectrum of MTT-PANi composite (a) and MTT (b)

The data given in figure 2a showed that PANi coexisted in composite matrix because of the clear presence of benzenoid and quinoid ring vibrations at 1558 cm^{-1} and 1498 cm^{-1}, respectively. Additionally, other main groups simultaneously appear in the IR-spectrum such as the band from 3551 cm^{-1} to 3191 cm^{-1} assigning to the N-H stretching mode, from 3079 cm^{-1} to 2861 cm^{-1} (aromatic C-H), from 1307 cm^{-1} to 1037 cm^{-1} (-N=quinoid=N-). The signals at 1696 cm^{-1} and 1651 cm^{-1} assign to C=O belonging to carbonyl group due to MTT.

3.3. Effect of pH

The results presented in figure 3 showed that the adsorption of Ni^{2+} ion rose unlinear with increase of pH of solution. In strong acid medium (pH < 3) the removal efficiency of Ni^{2+} ion is very poor, but, it was better when pH over 4, among them the optimal pH of 6 could be used for continuous experiments.

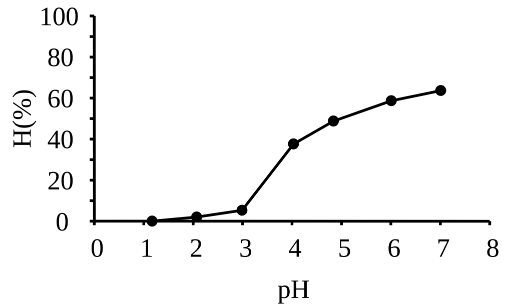

Figure 3: The effect of pH on the Ni^{2+} ion removal efficiency of MTT-PANi composite (C_0 = 1 mg/L; t = 40 min)

It can be explained that at low pH medium, PANi can not function as a ligand or chelating agent because of its acid doped state (-N groups are protonated), therefore, the metal uptake is not occurred [8]. Conversely, in high pH medium, it existed in undoped form, then its free amine or imine groups will be available for metal chelating resulting in significant increase of Ni^{2+} adsorption.

3.4. Effects of contact time and adsorption kinetics model

The figure 4 indicated that the adsorption capacity of Ni^{2+} ion onto MTT-PANi depended strongly on contact time t. It rose with increasing t during the first 40 initial minutes. After 40 min of contact time, the adsorption capacity changed insignificantly indicating that the equilibrium was obtained.

The adsorption rates and correlation coefficients (R^2) given in Table 1 resulted from figures 5 showed that the values of R^2 for the first order adsorption kinetic model (0.3997) are less than that for the second one (0.9976).

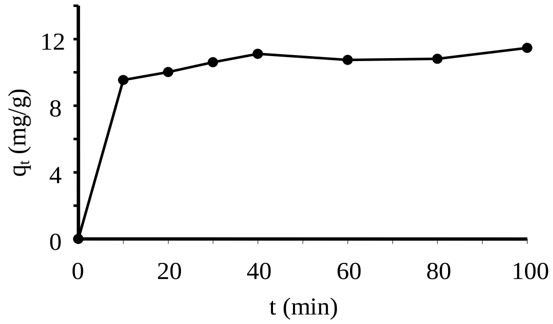

Figure 4: Plot of adsorption capacity versus time for initial Ni^{2+} concentration of 1 mg/L at pH = 6

There was a larger difference for q_e between the experimental (11.4666 mg/g) and calculated (1.5431 mg/g) values belonged to the first – order kinetic model. It explained that the adsorption process of Ni^{2+} onto regarded adsorbent did not follow the first-order kinetic model. Conversely, the calculated q_e value from the second-order equation (11.51 mg/g) agreed very well with the experimental one (11.4666 mg/g) indicated that the mechanism of the adsorption of Ni^{2+} ion onto MTT-PANi was followed by pseudo second – order kinetic.

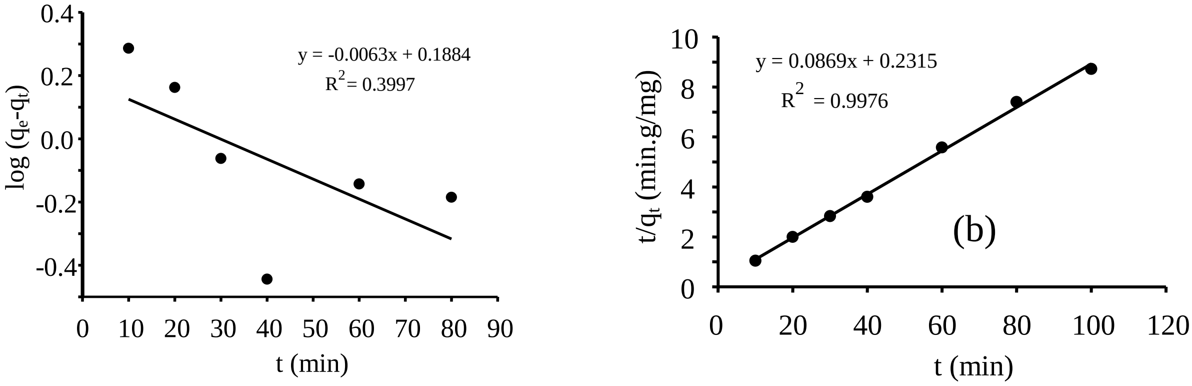

Figure 5: The first-order (a) and second-order (b) adsorption kinetic models of Ni^{2+} ion onto MTT-PANi composite (C_0 = 1 mg/L)

Table: Kinetic parameters for adsorption of Ni^{2+} onto MTT-PANi composite

C_0 (mg/L)	Experimental value q_e (mg/g)	First-order adsorption kinetic model			Second - order adsorption kinetic model		
		y = -0.0063x + 0.1884			y = 0.0869x + 0.2315		
		q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg.min)	R^2
1	11.4666	1.5431	0.0145	0.3997	11.51	0.033	0.9976

3.5. Effect of initial Ni^{2+} concentration

Figure 6 showed the effect of varying concentration on Ni^{2+} adsorption ability of MTT-PANi within 40 min contact time at pH of 6. It was found an efficiency of Ni^+ removal about near 60 % which was insignificantly different in research concentration of Ni^{2+} from 0.338 to 2.235 mg/L.

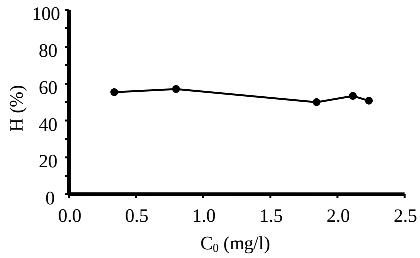

Figure 6: The influence of initial concentration on Ni^{2+} removal efficiency

3.6. Adsorption isotherms

The Langmuir dimensionless parameter can be calculated from equation (8):

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

Where K_L is Langmuir constant and C_0 is initial concentration of Ni^{2+}.

Table 2: Values of dimensionless Langmuir parameter R_L for Ni^{2+} ion adsorption

C_0 (mg/L)	0.338	0.798	1.845	2.115	2.235
R_L	0.9287	0.8466	0.7047	0.6755	0.6633

Table 3: Langmuir and Freundlich adsorption isotherm constants for Ni^{2+} onto MTT-PANi

Langmuir constants		Freundlich constants	
q_{max} (mg/g)	66.6700	q_{max} (mg/g)	66.6700
K_L (L/mg)	0.2271	K_L (L/mg)	0.2271
R^2	0.6764	R^2	0.6764

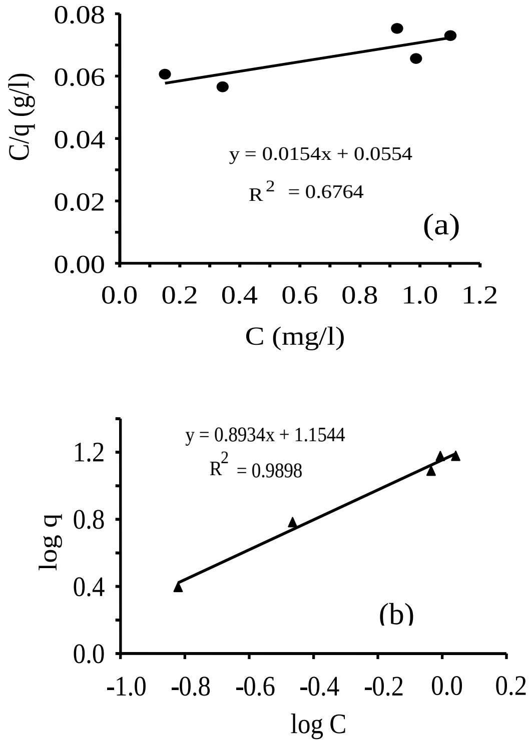

Figure 7: Langmuir plot (a) and Freundlich plot (b) for the adsorption of Ni^{2+} onto MTT-PANi

The obtained R_L (table 2) and N_F (table 3) values indicated that the adsorption process of Ni^{2+} ion was favorable because of $0 < R_L < 1$ and $1 < N_F < 10$ [5]. The data given on Table 3 obtained from figure 7 explained that this fitted into Freundlich isotherm model more suitable than into Langmuir one because of higher R^2 (0.9898). N_F The maximum adsorption capacity of Ni^{2+} ion was found 66.67 mg/g by Langmuir isotherm line, while K_F from Freundlich one was 14.269 mg/g.

4. CONCLUSION

Nanocomposite based on Maize tree-trunk and polyaniline was successfully synthesized by chemical method. It could be useful for the removal of Ni^{2+} ion from aqueous solution. The optimum conditions for Ni^{2+} removal were found at pH of 6 and equilibrium contact time of 40 min. The adsorption of Ni^{2+} onto MTT-PANi fitted into the pseudo-second order kinetic model and followed the Freundlich adsorption isotherm equation. The maximum adsorption capacity (q_{max}) and Langmuir constant (K_F) were 66.67 mg/g and 14.269 mg/g for Ni^{2+} adsorption onto MTT-PANi, respectively.

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