Mahmood M. Barbooti
Department of Applied Science, University of Technology, P.O. Box 35045, Baghdad, Iraq.

Raghad H. Hilal
Department of Production Engineering and Metallurgy, University of Technology, Baghdad, Iraq.

Balkees D. Al-Dabbagh
Department of Applied Science, University of Technology, Baghdad, Iraq.

Preparation, Characterization and Utilization of Polyacrylamid-Kaolin Composite in the Removal of Nickel Ions From Water

Abstract-*A composite material of polymeric matrix Polyacrylamid (PAM) that is reinforced by a certified clay mineral of the Iraqi kaolinite at several weight ratios (10, 20, 30, 40 and 50%) was prepared by mixing the polymer water solution with the clay followed by hand molding method. Some of the mechanical properties of the prepared composite such as tensile strength, impact and hardness Shore A were studied to improve the mechanical capability to be as a sorbent for the removal of heavy metals from water. The results showed an improvement in the mechanical properties as the kaolin content was increased. The powdered material was evaluated as a sorbent for nickel ions from aqueous solution using batch conditions. Experimental design (Box- Wilson) system was applied to determine the optimum working conditions such as composite amount, pH and contact time. Results proved reasonable adsorption efficiency and relatively high adsorption capacity of the composite towards the Ni ions removal of from water. The optimum conditions were sorbent amount of 10.0 g/l, pH = 7, and contact time of 100 min.*

Keywords- *Kaolin-polyacrylamide composite, Nickel adsorption, experimental design; optimization, adsorption (efficiency and capacity).*

1. Introduction

Environmental pollution by heavy metals, HMs, has accelerated dramatically during the last few decades because of the link of minerals with industrial developments like mining, metallurgical, electronic, electroplating and metal finishing processes [1]. The HM are associated with some harmful effects on living organisms causing, among other things, disorders of the nervous system due to the tendency to accumulate in the brain, bone, or liver [2, 3]. The metal ion can support the generation of ultra-oxide and hydroxyl radical, which, consequently may lead to deterioration of lipids, nucleic acids and proteins [4]. Therefore, it is necessary to treat metal contaminated wastewater prior to its discharge to the environment. Adsorption is one of the promising alternatives to remove heavy metal and organic pollutants from water. As early as 1990, Wehrli et al. [5] reported that heavy metals could be adsorbed on aluminum oxide as a surface complex formation model.

The search for low-cost adsorbents with reliable metal-binding capacities has intensified [6].

The adsorption power of Iraqi clay minerals was utilized by some investigators for the removal of heavy metals from water [7]. Membranes were used to remove dissolved species like organic compound [8]. Recently, polymer inclusive membranes are gaining more and more popularity because of their improved mechanical properties and chemical resistance in comparison with support liquid membranes. The addition of plasticizer to the polymer membrane helps in blending the carrier with a polymer matrix and causes an increase of membranes elasticity [9]. Modification of the membrane surface led to change the physical and chemical properties of membranes without affecting other properties. Therefore, the separation properties of membranes depends on the surface characteristics [10]. Tashauoei, et al. [11] succeeded in the removal of Cr (VI) via adsorption by surface modified nano-zeolite and reported a sorption capacity of 14.16 mg $Cr(VI).g^{-1}$ at pH = 3.0 at room temperature. Moslehi and Nahid [12] used raw and modified diatomite for the removal of HM from water. The diatomite was impregnated with $MnO2$ to give an increase in adsorption capacity which was 40, 34and 33 mg/g for Pb, Ni and Cu ions respectively.

Polyacrylamide is a widely used material in many industrial and water treatment applications such as the ion of solids in water, paper making processes and screen-printing [13]. The linear soil conditioning utilizes linear, water-soluble, anionic polyacrylamide. It is used for erosion

control in order to protect the water quality of nearby rivers and streams. Similarly, the absorbent properties of one of its copolymers can be utilized as an additive in body-powder. The ionic form of polyacrylamide was found as important role in the potable water treatment industry. Trivalent metal salts, like ferric chloride and aluminum chloride, are bridged by the long polymer chains of polyacrylamide. This has resulted in significant enhancement of the flocculation rate to improve the removal of total organic content (TOC) from raw water. Polyacrylamide is also often used in molecular biology applications as a medium for electrophoresis of proteins and nucleic acids in a technique known as PAGE [13].

Jeong et al. [14] reported the synthesis of hydroxyapatite/polyacrylamide composite hydrogels with various contents and their removal capability of Pb ions in aqueous solutions. A hydrogel made with hydroxypropyl cellulose (HPC) and polyacrylamide (PAAm) was utilized for the removal of Pb, Ni and Cu ions. The hydrogel successfully removed these metals, as shown by the results of atomic absorption spectroscopy where the polymer has removed 53% of Pb, 52% of Ni and 51% of Cu [15].

The aim of the present work is at the incorporation of Iraqi white Kaolin into polyamide to improve its mechanical properties such as tensile and impact strength, hardness and permeability and utilizing the produced composite for the removal of nickel by adsorption from water solution.

2. Materials and Methods

I. Apparatus

The tensile strength test was carried out on a Jianqiao tensile testing device. Charpy Impact Test was performed on a TMI 0-30 Ft-Lb Charpy Tension Impact Testing Machine, S/N A22775. The hardness of the materials was measured for the thin sheets of the materials with digital hardness tester represented as Shore A. The nickel concentration was measured using Shimadzu flame atomic absorption spectrophotometer. The operating conditions were as specified by the manufacturer.

II. Materials and chemicals

A certified kaolinite clay mineral was supplied by the Iraqi Geological Survey with and composed of SiO_2, 56.98 %, Fe_2O_3, 5.69%, Al_2O_3, 14.96%, CaO, 4.64%, MgO, 1.47%, and loss on ignition of 11.90 wt%. Polyacrylamid was a product of the Interchimiques, SA France in the form of white

color powder. Nickel standard solution (2000 mg.L^{-1}) was prepared by dissolving analytical grade nickel powder (Hopkin& Williams) in analytical grade nitric acid and proper dilution in a calibrated flask. Five buffer solutions were prepared to fulfill the experimental requirements using analytical grade chemicals. Potassium chloride (KCl), and buffers of various pH values were Reidel de Haene products. All dilutions and standard solution preparations were done with deionized water.

III. Experimental Design

For the determination of optimum operating conditions of the adsorption, we utilized the central composite design (CCD) [16]. This allows the investigation of the effects of the parameters at the working ranges of time: 20 - 180 min, composite weight, (2.5 – 12.5 g.L^{-1}, and the pH 3.0-8.5 as the three main parameters. The method is often useful in response surface that allows building a second-order model for the response variable without the need to use a complete three level factorial design. The CCD consists of a 2factorial with center points and axial points, where k is the number of factors in the experiment. The 2kdesign with the addition of the center points and axial points allows estimations of linear, linear by linear interaction and quadratic terms in the model. The determination of experimental range is required to connect both of coded level and the corresponding real variables, where the variables coded value between (-1.73 and +1.73):

$$X \text{ coded} = \frac{X \text{ actual} - X \text{ center}}{(X \text{ center} - X \text{ min})/\sqrt{k}} \quad \ldots\ldots (1)$$

According to eq. 1, the expression of coded variable level for the system is shown in Table 1, where X_1= time (min), X_2= pH and X_3= sorbent content (g.L^{-1}). For Ni adsorption on PAM-Kaolin five levels of each factor were used, including two levels of the factor. Five levels of each parameter were used:

composite dose, 5-12.5 g.L^{-1}; pH, 3.0-8.5; and contact time, 20-180 min.

The adsorption efficiency values, Ads%, were calculated from the residual nickel concentration values and fed to the system to estimate the coefficients of the quadratic polynomial equation which relates the response with the operating variables.

Table 1: Experiments sequence according to control composite design

Run No.	Coded Variables	Real Variables		
	X_3, X_2, X_1	wt. (g.L^{-1})	pH	Time(min)

1	-1, -1, -1	60	5	4.4
2	-1, -1, 1	60	5	7.1
3	1, -1, -1	60	10	4.4
4	1, -1, 1	60	10	7.1
5	-1, 1, -1	140	5	4.4
6	-1, 1, 1	140	5	7.1
7	1, 1, -1	140	10	4.4
8	1, 1, 1	140	10	7.1
9	0, 0, -1.732	20	7.5	5.75
10	0, 0, 1.732	180	7.5	5.75
11	0, 0, -1.732	100	2.5	5.75
12	0 0, 1.732	100	12.5	3
13	0, -1.732, 0	100	7.5	8.5
14	0, 1.732, 0	100	7.5	5.75
15	0, 0, 0	100	7.5	5.75
16	0, 0, 0	100	7.5	5.75
17	0, 0, 0	100	7.5	5.75
18	0, 0, 0	60	7.5	5.75

IV. Procedures

IV.1 Preparation (PAM- White Kaolin) composites

Hand molding method was applied for the preparation of the composite material at various weight ratios ranging from10 to 50%.PAM water solution was stirred and the calculated amount of the clay was added gradually with certain heating. The output of the mixing process was a homogeneous mixture of dense composite material. It was then poured into molds specially configured for this purpose and left to dry for more than 24 hours to end up with the composite as a thin film. Part of the material was ground in a ball mill.

IV.2 Nickel Adsorption on composite powder

Box-Wilson system was applied to study the adsorption of Ni^{+2} from aqueous solution under various experimental conditions such as weight of composite material (2.5, 5, 7.5, 10 and 12.5g/l), experimental time (20, 60, 100,140 and 180min) and buffers (pH= 3, 4.4, 5.75, 7.1 and 8.5). The calculated composite amount was placed in plastic transparent vessels with tight cap and 60 mL capacity together with 4 mL of 1.0 M KCl solution and 1 mL of 2000 ug.mL-1 solution. The volume was completed to a total of 40 mL with the specific buffer solution. The samples containers were placed on the top of a rotating shaker and run at a speed of 250 rpm for specified time intervals. The containers were removed from the shaker, and centrifuged at 3000 rpm for 15 min. The decanted supernatant liquid was filtered using syringe filter with 0.2 μm filter. The filtrates were kept at 4° C until the analysis time. The samples were analyzed for the Ni concentration by atomic absorption spectrophotometry.

2. Results and Discussion

I. Preparation (PAM – kaolin) composite

The PAM-Kaolin composite was prepared by adding the polymer gradually to the clay water suspension with continuous mixing. The mixing was continued with some heating. The resultant solution was left at room temperature to dry. Hand molding was employed to prepare the membrane specimen with no pressure application. The particle size of kaolin is important factor in establishing efficient diffusion into the liquid phase. Further, the mechanical properties will be improved. For this reason smaller grain size less than 0.045 mm has been chosen for PAM-kaolin preparation.

II. Mechanical Tests of (PAM – kaolin) composite

The following mechanical tests were carried out on PAM - kaolin composites prepared at various weight ratios of polymeric to reach the best composition of composite. Figure 1 shows the effect of clay content on the tensile strength of the composite. The tensile strength of the composite was increased almost linearly with the increasing of kaolin content (correlation coefficient, R^2= 0.956). The highest value (2.29 N.mm^{-2}) was recorded at 50% clay content. The increase in the filler (kaolin) contact surface with the polymer matrix acts as an efficient stress transfer agent in the composites and the good dispersion of clay that lead to the higher tensile strength [17].

Fig. 2 shows the effect of clay content on the impact strength of the PAM-Kaoline composite. The purpose of the impact strength test was to select the composite with a high impact resistance to bear momentum of the fluid flowing through it. It was clear that the addition of clay has significantly improved the impact strength of the composite. A linear relationship could be obtained between the impact strength and the clay mineral content (R^2 = 0.947). The highest value of impact strength (3.39 J.m^{-2}) was obtained at the highest clay content used (50%).This behavior is due to the good penetration of clay particles and the polymer during the polymerization process. In addition, the good interface between them.

Figure 3 shows the effect of clay content on the hardness of the composite. The measured hardness Shore A of PAM alone was 73.93, and a linear increase could be obtained for the composite material (membrane) with increase of the clay content (R^2 = 0.905). The highest value of hardness 95.05 at clay rate (50%).
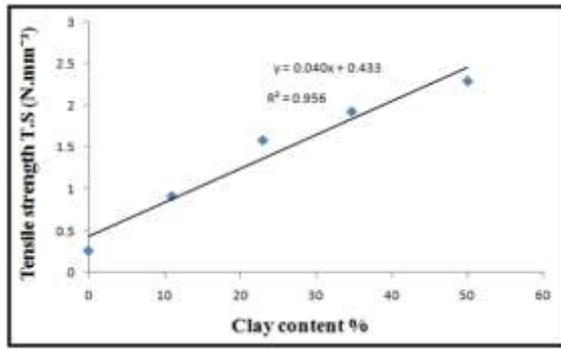
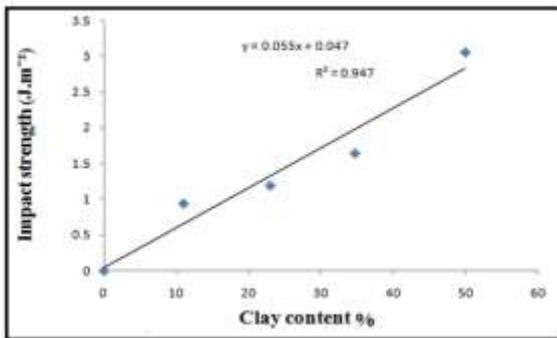**Figure 1: The effect of clay content on the tensile strength of the PAM – kaolin composite**.

Figure 2: Effect of clay content on the impact strength of the PAM-Kaoline composite.
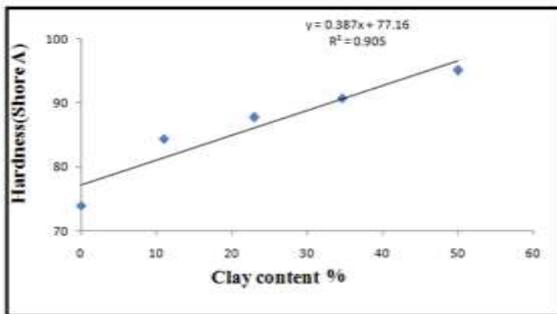

Figure 3: Effect of clay content on the hardness of the composite.

III. Adsorption study

The prepared composite was tested for its adsorption behavior towards Ni ions from aqueous solution. The program has specified the experimental conditions covering the five levels to furnish the requirements of 18 runs. The last five experiments were identical in their conditions and run at the center values of the parameters to allow the estimation of the precision of the work. The residual Ni^{2+} concentrations were used to calculate the adsorption efficiency, Ads %, as follows:

The adsorption efficiency, Ads%, and the adsorption capacity ($\mu g/g$) were calculated for the samples.

$$Ads \% = [(C_i - C_f)/C_i] *100\% \qquad (2)$$
$$\text{Adsorption capacity } (\mu g/g) = [(C_i - C_f)/m].V \qquad (3)$$

Where C_i, C_f are the initial and actualconcentration of Ni^{+2} respectively and V= volume (ml), m= mass (g/l).

The model equation which describes the process can be described by equation 4:

$$(Y=a_0+a_1x_1+a_2x_2+a_3x_3+a_4x_1^2 +a_5x_2^2 +a_6x_3^2 +a_7x_1x_2 +a_8x_1x_3 +a_9x_2x_3) \qquad (4)$$

The residual nickel concentration and the calculated adsorption efficiency are listed for the corresponding experimental parameters in Table 2. The applicability of the model was tested by the correlation of the experimental Ads% values with the calculated. The program was designed to calculate the coefficients of the quadratic polynomial equation (4) which relates the adsorption efficiency to the operating parameters. The calculated coefficients were substituted in the equation to result in the relation of the adsorption efficiency with the three parameters and their interactions. The resulted relation equation was as follows:

$$\textbf{Ads.\%} = 103.385 - 0.068*t - 0.990*pH - 41.495*wt. + 0.0004*t^2 + 0.085*pH^2 + 10.67*wt.^2 - 0.0069t*pH + 0.123t*wt. + 3.63pH*wt. \qquad (5)$$

The significance of the parameters effects on the Ads.% was reflected by the value of the coefficient related to that paeameter. The a_4 attained avalue (0.0004) which is very close to zero as in equation (5). Thus the 5th term of the equation can be omitted from the equation and so on. The final form of the equation can be:

$$\textbf{Ads.\%} = 103.385 - 0.0677*t - 0.9904*pH - 41.4951*wt. + 0.0853*pH^2 + 10.6739*wt.^2 + 0.1228t*wt. + 3.6285pH*wt. \qquad (6)$$

Equation 6 was used to calculate the Ads% values for all the levels of the parameters using the excel facility. The output of the program also contained the predicted (calculated) values of the Ads% for the combinations of the parameter values of the 18 experiments in Table 1. The predicted values were plotted against the experimentally observed values to check the fitness of the selected model. The plot is shown in Figure 4. Accordingly, the fitness of the model to experimental data was acceptable and the correlation coefficient, R^2, was 0.846.
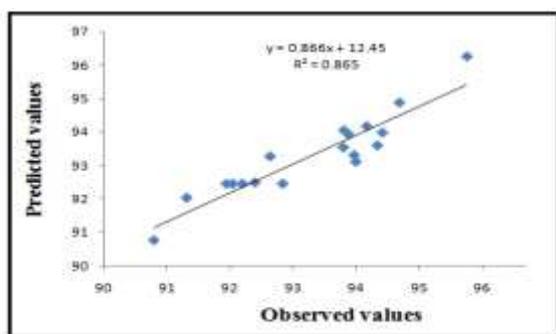
Figure 4: Correlation of observed and predicted values to the Ads%.

The expected normal values of $Y_{obs.}$-$Y_{calc.}$ were plotted against absolute residual values as shown in Figure 5. The evidence on the validity of the selected model was apparent from the linearity of the correlation.

IV. Effect of operating parameters on Ads%

The optimization of adsorption process necessitates the evaluation of the best experimental conditions that result in the highest efficiency. The optimal conditions have also taken into consideration the economy of the process.

IV.1. Effect of sorbent amount:

Fig. 6 shows the relation of Ads% with the amount of composite at various pH values and fixed contact time (100 min). At low pH value (3.0), the ads.% was decreased dramatically as the amount of composite increased in the solution. The rate of decrease got lower as the pH value moved upward. Under neutral condition (pH=7), the ads.% appeared independent on the amount of the composite. Furthermore, the ads% showed a slight increase with composite amount increased at the slightly alkaline medium (pH=8.5).
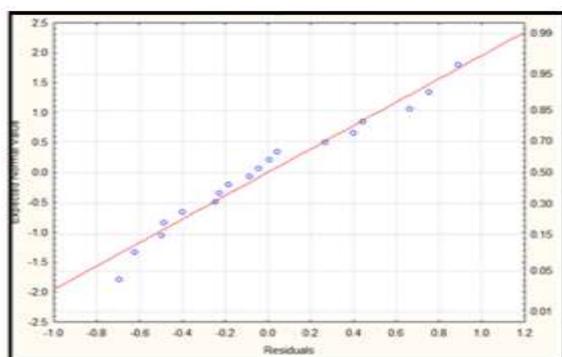

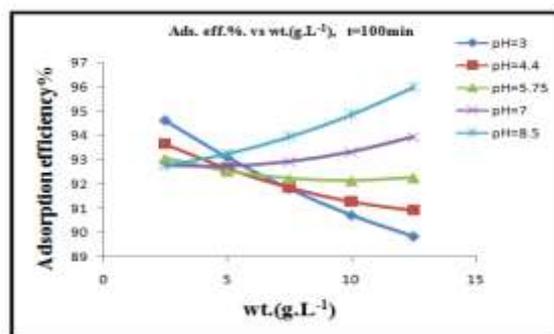**Figure 5: Convergence range of the observed and predicted to the Ads% values.**

Figure 6: The relation of adsorption efficiency with the amount of composite at various pH values and fixed contact time (100min).

Figure 7, shows the dependence of adsorption efficiency on composite amount at various contact times and fixed pH value of 7. At 2.5 g.L^{-1} of the adsorbent, the ads.% had a maximum value of 98.18% at 180 min. For all the contact time values, the ads.% gave minimum values over the composite amount of 5-7g.L^{-1}. Beyond 7 g.L^{-1} significant increase in the ads.% was observed and reached a max. value at the (12.5 g.L^{-1}).

IV.2. Effect of the pH

Fig. 8 shows the relation of adsorption efficiency with pH at various times and fixed amount of adsorbent of 10 g.L^{-1}. It is clear that the change of ads.% of Ni^{+2} with pH exhibited similar trend, where the increase in pH values were in favor of the Ads%. However, rate of Ads% increase with pH decreases as the equilibration time increases. In acid environment (pH = 3), the Ads% was changes from 90.02 up to 96.53% for the contact time values of 20 to 180 min.. With the increase of contact time, the rate of increase was lower and only a slight increase could be observed in the Ads% at 180min. Thus, after a contact time of 180min, neutral solution resulted in a high ads% regardless of the pH solution.
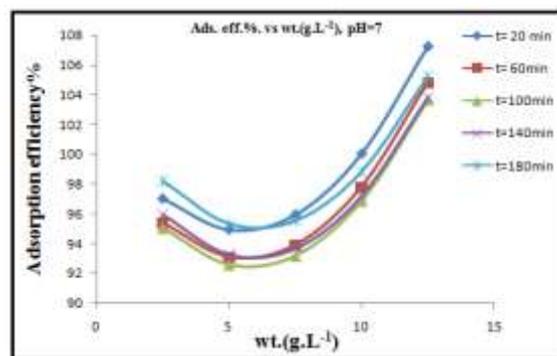

Figure 7: The dependence of adsorption efficiency on composite amount at various contact times and fixed pH value of 7.
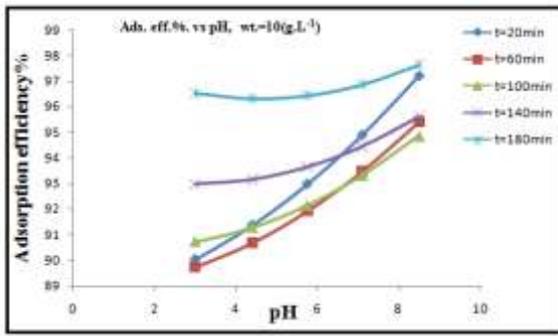
Figure 8: Relation of adsorption efficiency with pH at various times and fixed amount of adsorbent (10 g.L^{-1})

IV.3. Effect of the time

Figure 9 shows the relation of adsorption efficiency of Ni^{+2} with the contact time at various amounts of composite material and pH=7. The Ads% has a paraboloic relation with the contact time at such a neutral medium. The minimum values were obtained at higher contact time for lower composite content. The ads% showed a decrease as the contact time increases and attained minimum values that were dependent on the amount of the composite, being shifted to longer time as the composite content decreased. Afterwards, the ads% showed an increase up to a maximum value of 98.5% at 12.5g.L^{-1} and 180min.

V. Effect of operation parameters on adsorption capacity

The calculated adsorption capacity, Cap%, values were fed to the experimental design program to check the applicability of the model. The program was designed to calculate the coefficients of the quadratic polynomial equation (4) which relates the response to the operating parameters. The calculated coefficients were substituted in the equation to result in the relation of the Cap% with three parameters and their interactions. The resulted net relation equation was as follows:

Cap%=21141-217*pH-82933*wt+23*(wt)^2+2*(pH)^2+98951*(t*wt)-73.8*pH*

(7)

Equation 7 was used to calculate the Cap% values for all the levels of the parameters using the excel facility. The output of the program also contained the predicted or calculated values of the adsorption capacity. The predicted values were plotted against the experimentally observed values to check the fitness of the selected model. The fitness was acceptable and the correlation coefficient, R^2, was 0.825. The expected normal (Y$_{obs.}$-Y$_{calc.}$) values were plotted against the residual values as shown in Figure 10.

Reasonable correlation could be observed to stand, as evidence on the validity of the selected model is apparent from the linearity of the correlation.

V.1.Effect of the amount of adsorbent material

Figure 11 shows the relation of adsorption capacity, ads cap, with the amount of adsorbent material at various pH values and fixed contact time (100min).It can be noted that at all pH values, the behavior of the system was the same, where there was a decrease of (ads cap) values with the increase of composite content. The ads. cap showed a minimum value at about 7.5 g.L^{-1}. Beyond a composite content of 8 g.L^{-1}, the adsorption capacity values were increased significantly. The highest value was 20853.8 µg Ni.g^{-1} which obtained at 12.5 g.L^{-1} and pH=3.
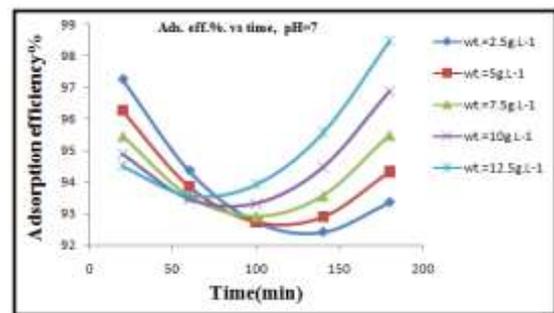

Figure 9: Relation of adsorption efficiency with time at various amounts of adsorbent material and pH = 7
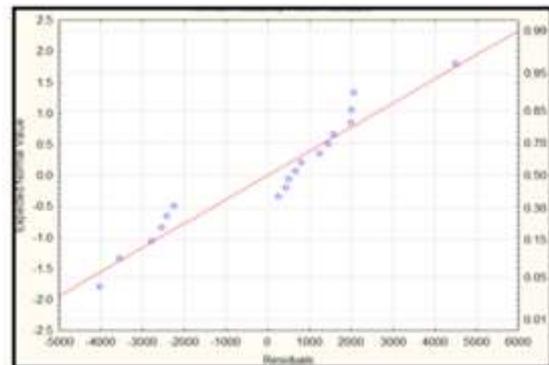

Figure 10: Convergence range of the observed and predicted to the adsorption capacity values of the (PAM - kaolin) composite.
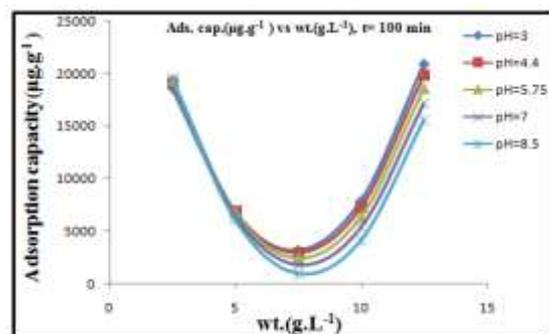
V.2 Effect of the contact time

Figure 12 shows the relation of the adsorption capacity with time at various pH values and fixed amount of adsorbent of 10 g.L^{-1}. For the acidic medium (pH=3), the capacity values differ slightly (7500 to 8000 μg.g^{-1}) over a wide range of contact time. The adsorption capacity were decreased with increasing of time at a rate that was dependent on the pH value. For the slightly acidic media (4 and 5.75), there was a slow decrease of the capacity with time. Neutral and slightly alkaline solution (pH=7 and 8.5) exhibited significant decrease in capacity with contact time.

V.3. Effect of the pH

Figure 13 shows the dependence of Ads cap values on the pH at various contact times and fixed composite amount (10.0 g.L^{-1}). It is clear that the increase of pH has a negative effect on nickel adsorption capacity especially for the long time duration. In the acid solution (pH = 3), the nickel adsorption capacity was almost identicaland the rather the highest (8213.6 μg.g^{-1}) regardless of the contact time elapsed. On further increase of contact time, there was a sharp decrease in the adsorption capacity value as the pH value was increased. At a pH value of 8.5, the variation of the capacity values was the highest among the range being above 8000 μg.g^{-1} for the 20 min time and less than 1000 μg.g^{-1} for 180 minutes.
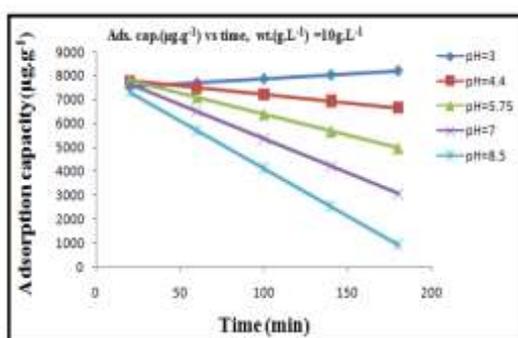

Figure 12: The relation of the adsorption capacity with time at various pH values and fixed amount of adsorbent at10 g.L^{-1}
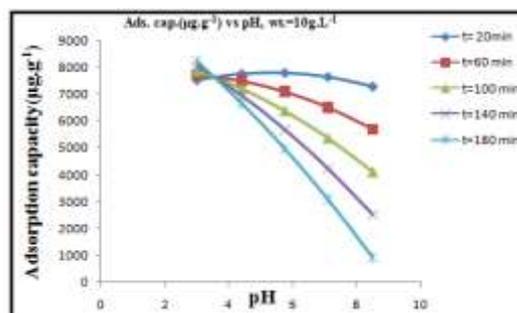

Figure 13: The relation of adsorption capacity with pH at various contact times and fixed clay amount (10 g.L^{-1}).

4. Conclusions

The study has proved that it is possible to prepare effective composite in the extraction of nickel ions from water solutions with more than 97% efficiency from polymers containing functional groups (PAM) with clay minerals. The 1:1 (polymer: kaolin) composition of the composite is most reliable giving good mechanical properties.

The composite ha reduced the dependency of the process on the operating conditions especially the pH of the solution. The most effective factor in the sorption was the amount of the sorbent composite.

Because the study is required many variables, statistical programs such as Statistica and Nova could be used to provide material possibilities by shortening the number of laboratory experiments and producing computer feeding results to obtain optimal extraction conditions.

5. References

[1] U.U. Jadhav, H. Hocheng, "A review of recovery of metals from industrial waste," J. Achiev. Mater. Manuf. Eng., 54, 2, 2012.

[2] P. Szyczewski, P. Niedzielski, T. Sobczyński and J. Siepak, "Heavymetals in Poland," Pol. J. Environ. Stud., 18, 5, 755, 2009.

[3] V. Angelova, R. Ivanova, K. Ivanov, "Heavy metal accumulation and distribution in oil crops," Common Soil. Sci. Plan, 35, 2551, 2005.

[4] A.D. Marias, and D.M. Blackhurst, "Do Heavy Metal Counter the Potential Health Benefits of Wine?," J. Endocrinol., Metabolism and Diabetes of South Africa,14,77-79, 2009.

[5] B. Wehrli, S. Ibric and W. Stumm, "Adsorption kinetics of vanadium (IV) and chromium (III) to aluminum oxide: Evidence for a two-step mechanism," Colloids and Surfaces, 51, 77-88, 1990.

[6] M.A. Barakat, "New trends in removing heavy metals from industrial wastewater," Arab. J. Chemistry 4, 361–377, 2011.

[7] M.M. Barbooti, "Simultaneous Removal of Chromium and Lead from Water by Sorption on Iraqi Montmorillonite," J. Environ. Protection, 6, 237-249, 2015.

[8] P.A. Shivajirao, "Treatment of distillery waste water using membrane technologies", Internat. J. Adv. Eng. Res. Stud., III (1) 275- 283, 2012.

[9] B. Kwankhao, Microfiltration Membranes via Electro spinning of Polyethersulfone Solution, Thesis, Univ. Duisburg- Essen Lehrstuhl Rur Technische Chemie II, 2013.

[10] L. Zarybnicka, E. Stranska, J. Machotova and G. Lencova, "Preparation of Two-Layer Anion-Exchange Poly (ethersulfone) Based Membrane: Effect of Surface Modification," Lucie Z Internat. J. Polymer Sci., 2016, Article ID 8213694, 8 pages, 2016.

[11] H. Tashauoei, R. Movahedian H. Attar, M. Kamali, M.M. Amin, and M. Nikaeen, "Removal of Hexavalent Chromium (VI) from Aqueous Solutions using Surface Modified Nanozeolite A," Int. J. Environ. Res., 4, 3, 491-500, 2010.

[12] P. Moslehi and P. Nahid, "Heavy metal removal from water and wastewater using raw and modified diatomite," Inter. J. Engineer, 20, 2 2007, 141-146, 2007.

[13] Wikipedia, 2016, https://en.wikipedia.org/wiki/Polyacrylamide.

[14] Y.G. Jeong, B.G. Min, WS. Lyoo, SC. Lee, "Preparation and lead ion removal property of hydroxyapatite/polyacrylamide composite hydrogels," J. Hazardous Mater., 159, 2-3, 294-29, 2008.

[15] J.L. Zamarripa–Cerón, J.C. García-Cruz, A.C. Martínez–Arellano, C.F. Castro–Guerrero, M.E. Ángeles–San Martín, A.B Morales–Cepeda, "Heavy Metal Removal Using Hydroxypropyl Cellulose and Poly-acrylamide Gels, Kinetical Study," Appl. Polym. Sci., 133, 43285, 2016.

[16] J. Lawson, "Design and analysis of experiments with SAS," CRC Press, Boca Rato, Fl, 2009.

[17] A.G. Supri H. Salmah, K. Hazwan, "Low density polyethylene-nanoclay composites: the effect of poly(acrylic acid) on mechanical properties, XRD, morphology properties and water absorption," Malaysian Polym J 3, 2, 39-53, 2008.