

Studies on Removal of Hexavalent Chromium Ion from Aqueous Solution Using Polyaniline Composite

Emad .M. Al-kinani

Department of Chemistry, College of Science, Al-Mustansiriya University, Baghdad-Iraq.

E-mail: Emadmalek2001@yahoo.com.

Abstract

Polyaniline (PANI) composites were prepared by polymerization of aniline in acidic medium using ammonium persulphate as initiator in the presence of Kaoline (PANK) and Bentonite (PANP). The pure PANI and their polyaniline composites were characterized by FTIR and Scanning Electron Microscope respectively. The SEM images have clearly shown the formation of polyaniline composites. The composites were used to removal of Cr(VI) ion pollutants from aqueous solutions. The equilibrium time increases with initial Cr(VI) concentration. experimental data are in good coincidence with Langmuir and Freundlich adsorption isotherm models, and have shown a good fitting to the experimental data. Adsorption of Cr(VI) obeys pseudo-second order equation with good correlation.

Keywords: adsorption kinetic; polyaniline composite, Cr(VI).

Introduction

Heavy metal pollution is one of the most important environmental problems to today. Among the various heavy metals Heavy metal pollution is characterized by its strong concealing ability and accumulative damage, and it cannot be biodegraded thus hazardous to the ecological environment and, more seriously, can cause various diseases, e.g., headaches, nausea, vomiting, abdominal pain, insomnia, forgetfulness, neurological disorders and liver damage [1–3]. Thus, the removal and recovery of heavy metals has become one of the most predominant aspects of environment a research, chromium (Cr) is a cause of great concern because of the serious problems it generates in ecosystems [4] this element chromium in aqueous solutions exists in two stable oxidation states, referred to as Cr(III) and Cr(VI) [5] Although trivalent chromium is an essential micronutrient associated with the metabolism of lipids and carbohydrates, and whose absence is related to diabetes and cardiovascular disease, Cr(VI) is considered dangerous to public health due to its mutagenic and carcinogenic properties [6] In human, it is known that chromium(VI) is also capable of causing lung, liver and kidney cancer, severe gastric damage and other health problems [7]

Many methods and materials have been developed for environmental cleanup and

remediation of chromium from polluted water, including adsorption [8] electrochemical precipitation, [9] ion exchange, reverse osmosis, membrane filtration [10] and biomaterials [11]

Clay minerals are added to polymers to improve their thermal and mechanical properties. The challenge in the synthesis of this kind of composites is combining a hydrophilic layered material with a hydrophobic organic part. Frequently, in aim to ensure the contact between the components a surfactant is added (e.g. quaternary alkylammonium salts). Its functional groups interact electrostatically with clay layers and a hydrocarbon chain facilitates polymer introduction. In the case of the macromolecules containing carboxylic groups ion exchange between them and the cations balancing the negative charge of clay layers can occur – this eliminates the necessity of surfactant using [12].

Polyaniline was originally known in 1835 as “aniline black”, a term used for any product obtained by the oxidation of aniline. [13] This conducting polymer is well-known for its ease of synthesis, environmental stability, and unique acid/ base doping/dedoping and oxidation/reduction chemistry, Polyaniline can be readily synthesized by either chemical oxidation or electrochemical polymerization of aniline under mild condition [13-15].

Experimental

2.1- Materials

Materials used in this study included ammonium persulfate (Aldrich), Anilin 99% (Merck) was distilled under vacuum and nitrogen atmosphere before use, Acetone, Aldrich. Ethanol (BDH) and potassium dichromate of analar grade from (BDH). All other reagents were used without purification.

2.2- Instrumentation

UV-Visible spectrometer, CARY 100 con. Water bath shaker type lab companion BS-11, digital scale KERN-ABBS, SEM (Holand, SEM TYPE(Phillips XL Series 30), pH meter type trans BP 300 and shimadzu 8400 FTIR were employed in this work.

2.3. Preparation of polyaniline composites

The polyaniline composites were prepared by in situ polymerization of aniline in the presence of Kaoline and Na-Bentonite in hydrochloric acid solution by rapid addition of a specified amount of ammonium persulfate (APS) in 1M HCl to the mixture then was moderately stirred for 3 hours The product was filtered and washed with distilled water then ethanol and acetone to remove unreacted aniline, oligomers and impurities then dried in an oven at 80 C° for 6 h and stored in a sealed container [16].

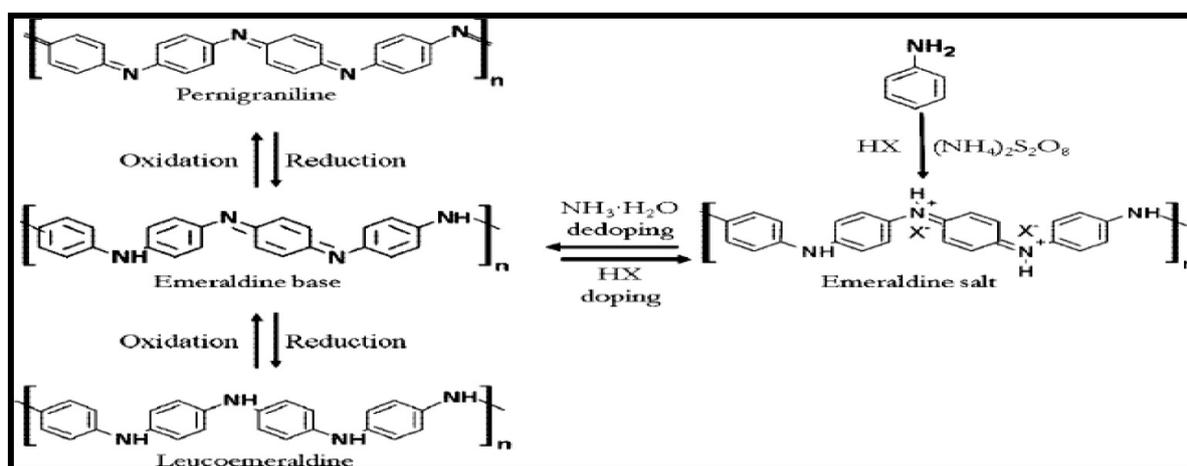


Fig.(1): Schematic diagram showing the chemical structure, synthesis, reversible acid/base doping/dedoping, and redox chemistry of PANI [17].

2.4 Adsorption experiments

Preparation of potassium dichromate solution

The stock solutions of Cr(VI) of concentration 1 g/L was prepared by dissolving 2.8 grams of analytical grade of $\text{K}_2\text{Cr}_2\text{O}_7$ in 1 L of distilled water. The stock solution was further diluted with distilled water to desired concentration to obtain the standard solutions. The initial pH of the test solutions was adjusted to the desired value by using dilute solutions of HCl and NaOH. The required lower concentrations were prepared by dilution of the stock solution. All precautions were taken to minimize the loss due to evaporation during the preparation of solutions and subsequent measurements. The stock solutions were prepared fresh for each experiment as the concentration of the stock

solution may change on long standing. The linear regression curve was drawn between the absorption and concentration for each sample, Fig.(2). For calibrating the UV-Visible spectrophotometer standard sample of dichromate was prepared and corresponding adsorption for each concentration was measured at λ_{max} 372nm. The removal percentage R% of Cr(VI) was calculated using the following equation

$$\text{R\%} = \frac{(C_i - C_e)}{C_i} \times 100 \dots\dots\dots (1)$$

Were, C_i and C_e are the initial and final concentration (mg/L) of Cr(VI).

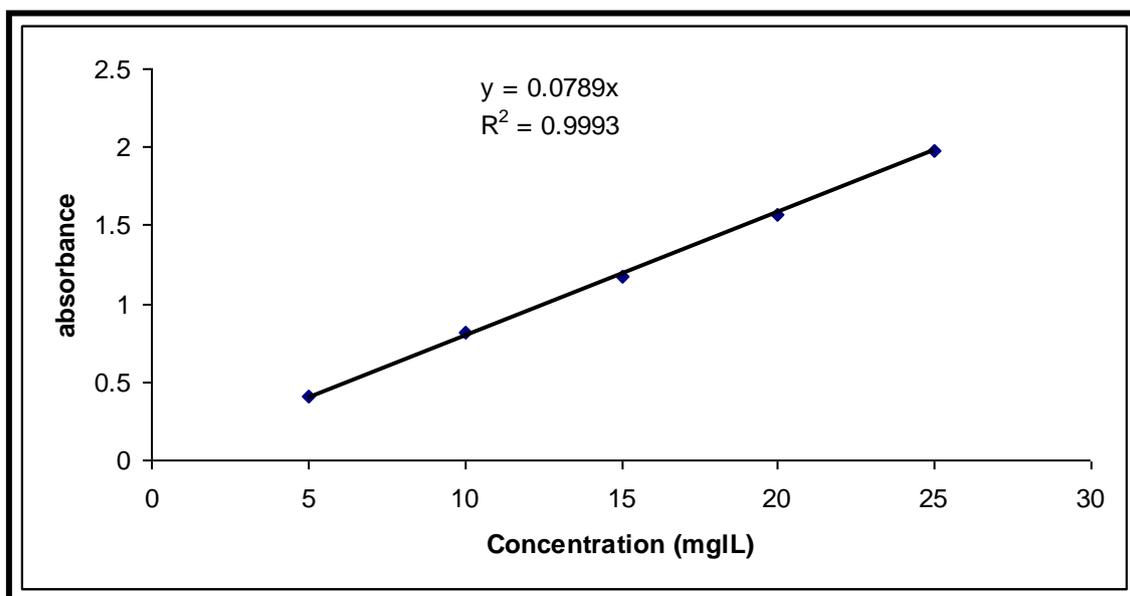


Fig.(2): Calibration curve of Cr(VI) using UV Spectrometer at 372 nm.

Adsorption kinetics

In this study, 0.2g of PANP and PANK were added to a 50 mL Cr(VI) solutions of 50 ppm at pH 2.0. The system was stirred at 25 °C. Each sample was removed at a determined time, in the order of 5, 10, 60, 90 and 120 min. The concentration of Cr(VI) in the supernatant was determined by U.V Spectrometer at 372 nm.

Isotherms and the effect of temperature

This study is also performed in batch using Cr(VI) solutions with concentrations between 10 - 60 ppm and pH 2.0. Solution volumes of 50 mL were added to 0.2g of PANP and PANK the system maintained under constant stirring in a temperature controlled system for a period of 60 min. This procedure was performed at temperatures of 25, 35 and 45 °C. The concentration of Cr(VI) was then determined by U.V Spectrometer at 372 nm.

Effect of dosage and initial metal ion concentration

The effect of dosages on metal ion uptake was investigated through a series of dosages from 0.05 g to 0.4 g at a temperature of 30°C. As for the test works on the effect of the initial metal ion concentration, the concentration used was varied from 10 to 40 ppm. This initial metal ion concentration was chosen so that it is within the range used by other researchers who carried out 'related studies'.

Effect of pH

The effect of pH was studied from initial pH of 1.0 to 5.0. This was done to minimize the possibility of precipitation of the metal ions at higher pH. Metal ion test solutions were adjusted to different pH values by using 0.1 M H₂SO₄ and/or 0.1 M NaOH accordingly. Some experiments were carried out without using PANP and PANK as adsorbent.

Results and Discussion

FT-IR

The presence of the characteristic absorption peaks of PANI in the FTIR spectrum indicates the successful polymerization of aniline via interfacial or rapid mixing methods and composites, as shown in Fig.(3). FTIR spectrum PANI showed characteristic bands at 1543 cm⁻¹ and 1426 cm⁻¹ (stretching vibration of quinoid ring and benzenoid ring), 3400 cm⁻¹ (N-H str), and 1291 cm⁻¹ (C-N) [18].

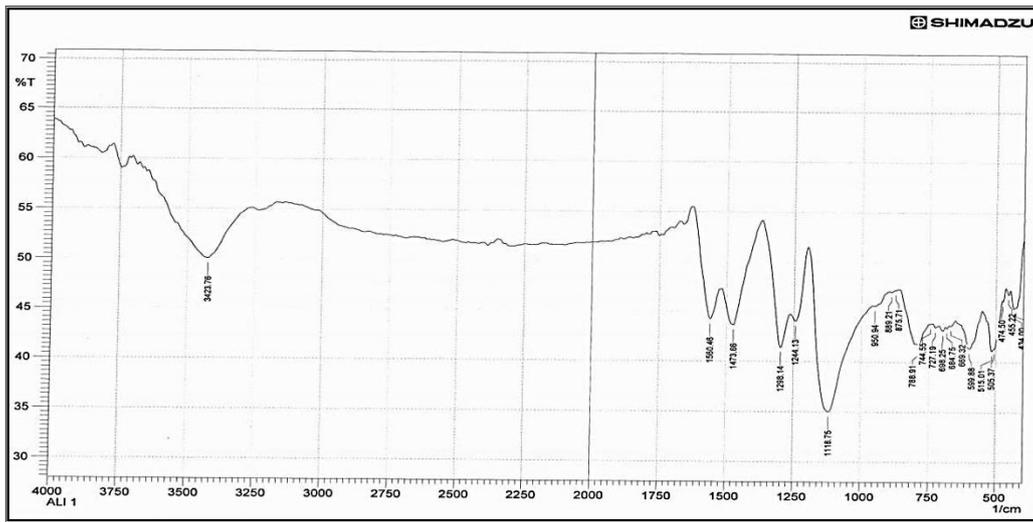


Fig.(3): FTIR Spectram of PANI.

Scanning Electron Microscope SEM.

SEM image in Fig.(4) and (5). analysis provided information about the size and the surface morphology of PANP and PANK respectively.

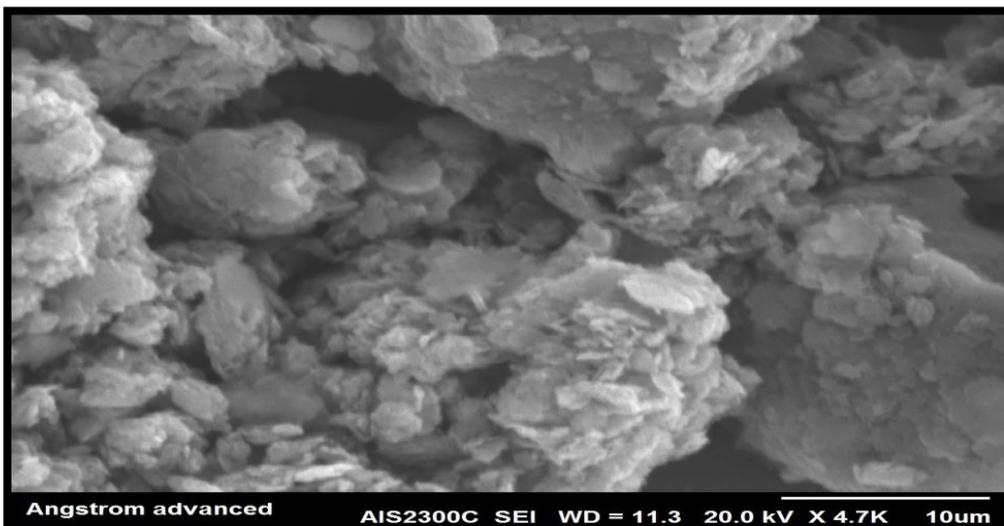


Fig.(4): SEM image of polyaniline composite PANK.



Fig.(5): SEM image of polyaniline composite PANP.

Effect of contact time

Efficient removal of the Chromium ion with the effect of contact time by the PANP and PANK were studied and the results are shown in Fig.(6). The efficiency increases with increase in time of contact, this result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

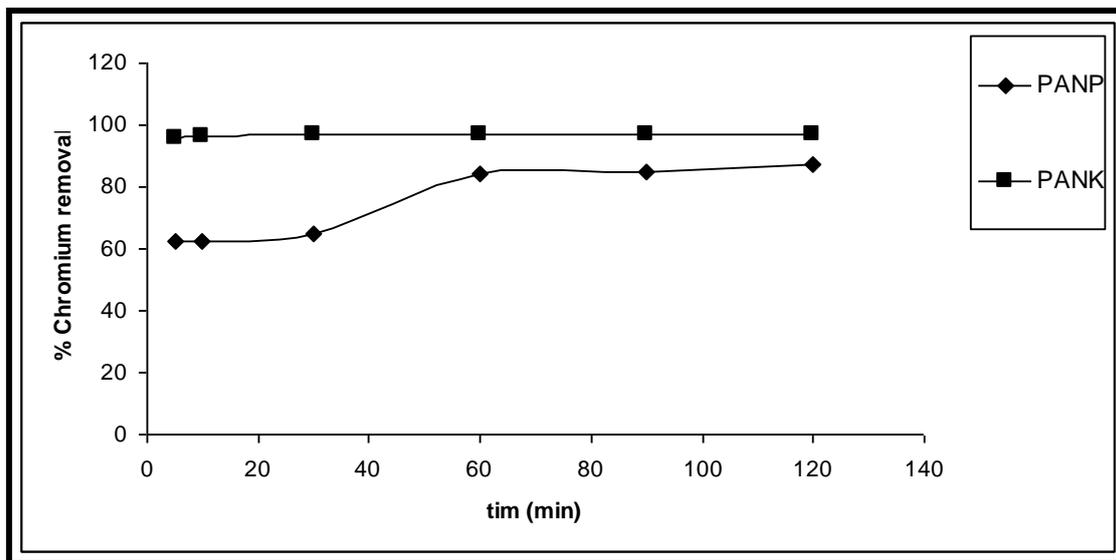


Fig.(6): Effect of contact time on the adsorption of Cr(VI).

Effect of Adsorbent Dose

The effect of the adsorbent dosage on the chromium adsorption on PANP and PANK is shown in Fig.(7). The percentage removal of chromium increased with increase of the adsorbent dosage. The increase in adsorption with the increase in amount of adsorbent PANP and PANK dose may be attributed to the fact that more surface area is available for adsorption to occur. The number of available

adsorption sites increases by increasing the sorbent and it results an increase in removal efficiency.

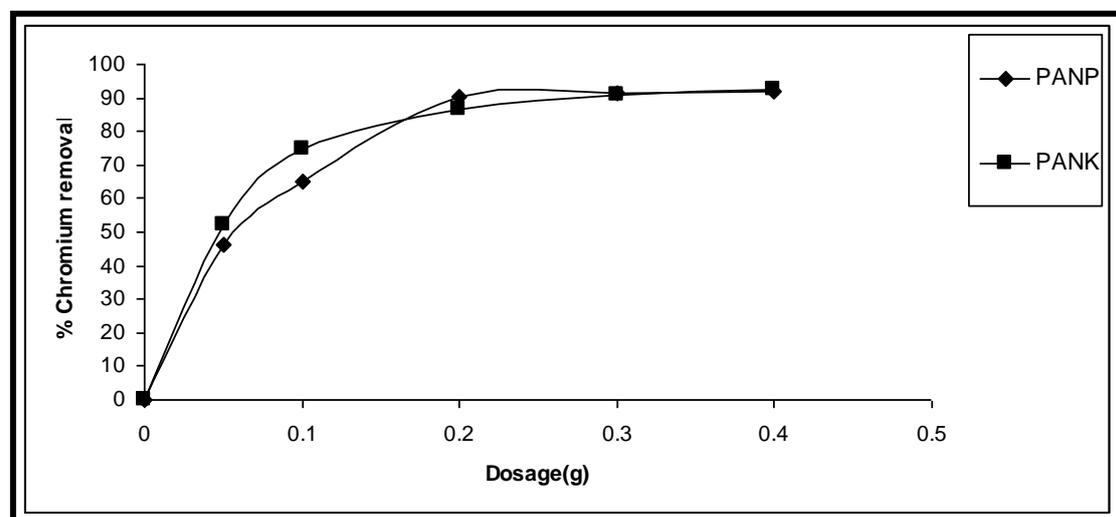


Fig.(7): Effect of Dosage on equilibrium concentration of Cr(VI).

Effect of pH

The effect of pH is an important parameter affecting adsorption of heavy metals. Cr(VI) removal was studied in the pH range of 1.0 – 5.0 for PANP and PANK and results are shown in Fig.(8). It is clear from the figure that the percentage of adsorption of Cr(VI) decreases with increase in pH from 1.0 to 5.0. The role of hydrogen ion concentration was examined in solutions at different pH [19]. The pH of the solution affects the surface charge of the adsorbents [20]. The hydrogen and hydroxyl ions are adsorbed quite strongly, and therefore the adsorption of other ions is affected by the pH of the solution [21]. It was observed that with the increase in the pH of

the solution, the extent of metal ions removal increased for the adsorbent. The maximum adsorption was obtained at pH 2. The concept of increasing metal removal with increasing pH can be explained on the basis of a decrease in competition between proton and metal cations for same functional groups and by the decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions. Decrease in adsorption at higher pH is due to formation of soluble hydroxyl complexes.

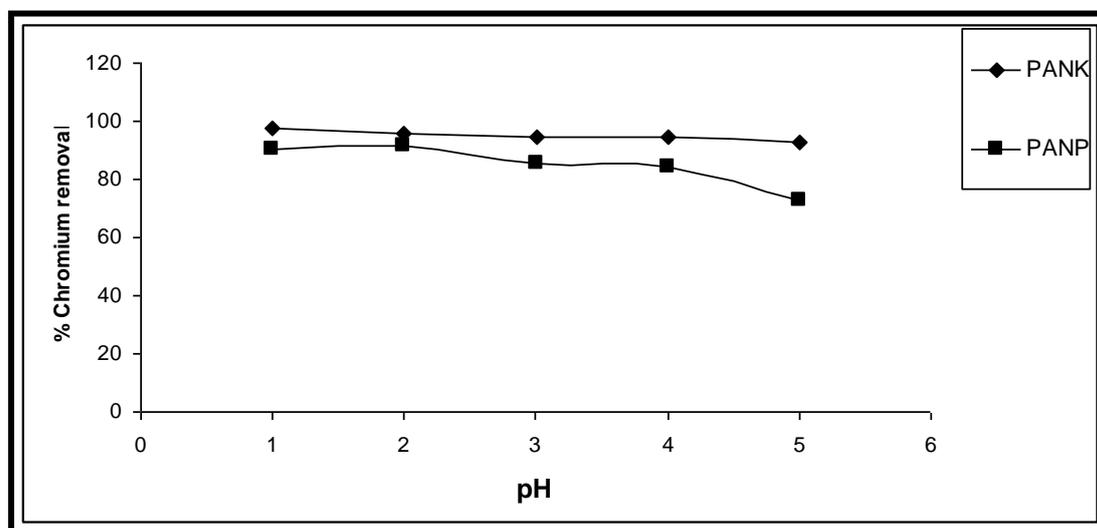


Fig.(8): Effect of pH on equilibrium concentration of Cr(VI).

Adsorption Isotherms.

The experimental data were fitted to the Langmuir [22], and Freundlich [23] isotherm model. Although the Langmuir and Freundlich isotherms were firstly introduced about 90 years ago, they still remain the two most commonly used adsorption isotherm equations. Their success undoubtedly reflects their ability to fit a wide variety of sorption data quite well. The Langmuir model represents chemisorption on a set of well defined localized adsorption sites, having the same adsorption energies independent of surface coverage and no interaction between adsorbed molecules. Langmuir isotherm assumes monolayer coverage of adsorbate onto adsorbent. Freundlich isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. This isotherm

does not predict any saturation of the adsorbent surface; thus, infinite surface coverage is predicted, indicating physisorption on the surface. Figs. (9,10,11 and 12) presents the isotherms resulted from the adsorption of Cr(VI) onto PANP and PANK. Furthermore, Table (I) reports the maximum adsorption capacities (Qmax) and the other isothermal parameters resulted from the fitting. The linear form of Langmuir isotherm equation is given as.

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

The linear form of Freundlich isotherm is represented by the equation.

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \dots\dots\dots (3)$$

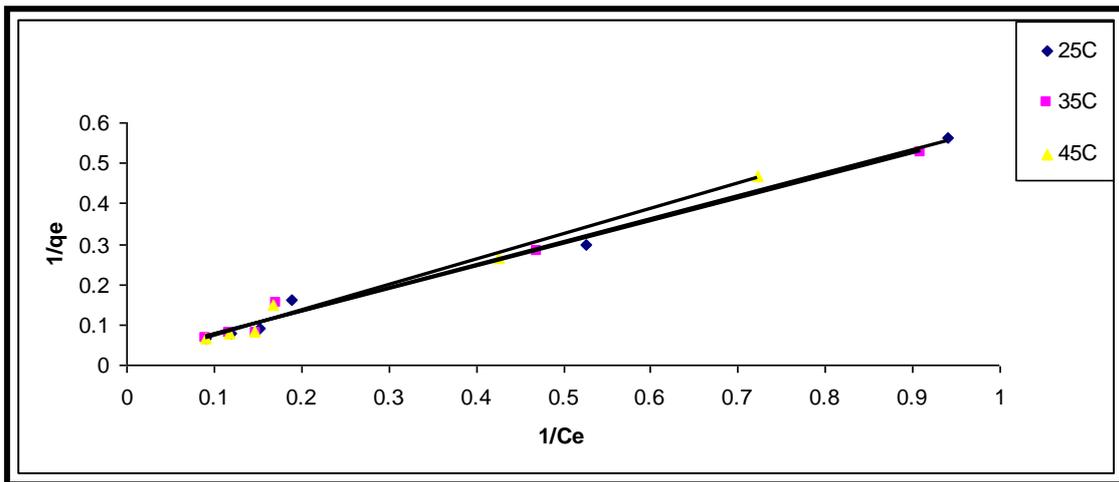


Fig.(9): Langmuir adsorption isotherm for adsorption of Cr(VI) PANK.

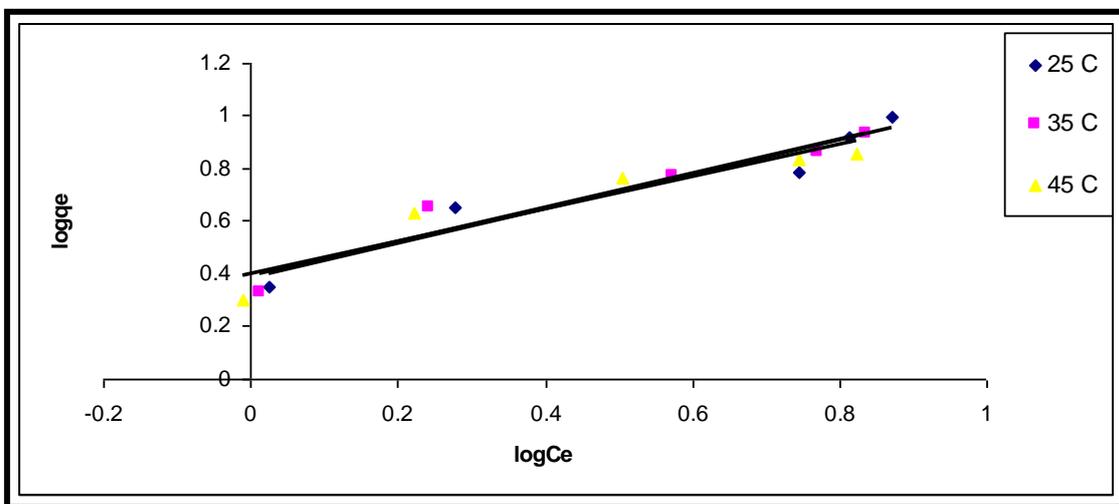


Fig.(10): Langmuir adsorption isotherm for adsorption of Cr(VI) PANP.

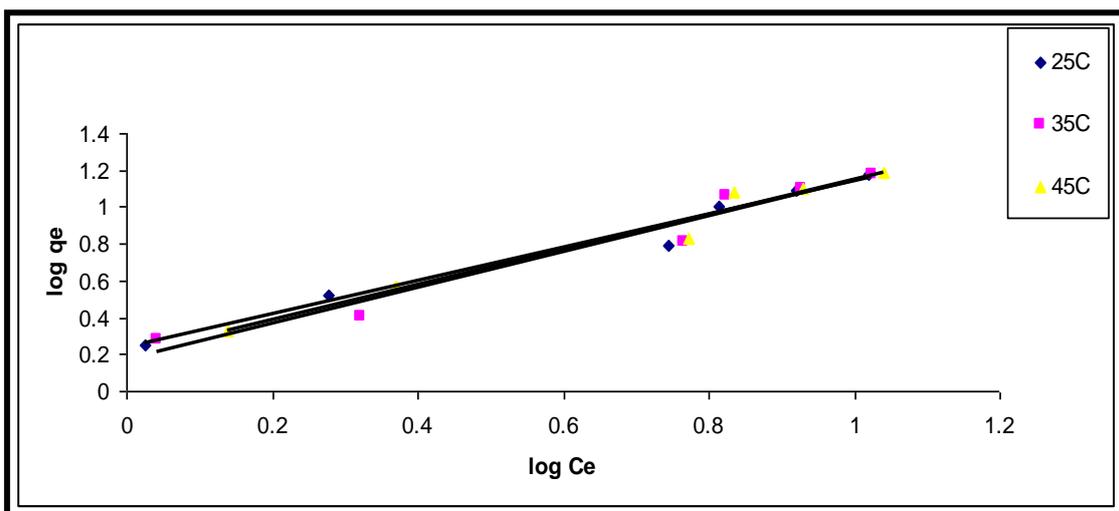


Fig.(11): Freundlich adsorption isotherm for adsorption of Cr(VI) PANK.

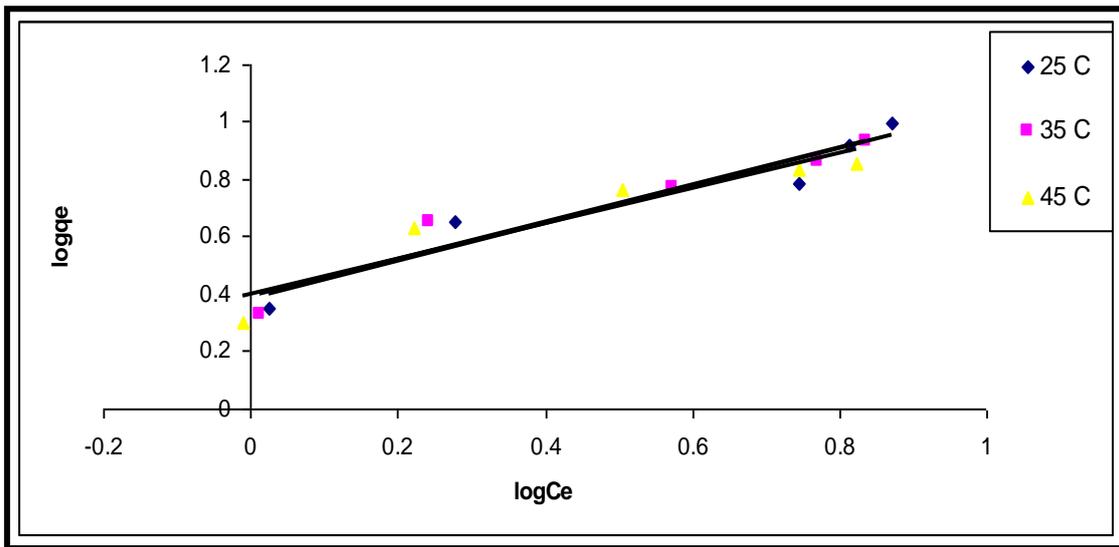


Fig.(12): Freundlich adsorption isotherm for adsorption of Cr(VI) PANP.

Table (I)
Values of the Langmuir and Freundlich constants for the adsorption of Cr(VI) onto PANP and PANK.

Absorbent	langmiur		freundlich			
	$Q_m \text{ mg/g}^{-1}$	$k_L \text{ Lmg}^{-1}$	R^2	K_f	$\text{g}^{-1} \text{ L}^n \text{ mg}^{1-n}$	n
PANP	7.56	0.02	0.9642	4.161	1.3	0.9461
PANK	7.87	0.031	0.9438	4.820	0.76	0.9298

Kinetics studies

Kinetic models are used to examine the rate of the adsorption process in the present work; the kinetic data obtained from this study have been analyzed by using pseudo-first-order and pseudo-second-order models.

The kinetics adsorption of chromium on PANK and PANP were analyzed using pseudo first- order [24] and pseudo-second-order [25] kinetics models. The linearized form of pseudo-first-order Lagergren equation is given as Eq. (4).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \dots\dots\dots (4)$$

The pseudo-second-order rate equation is given as Eq. (5).

$$\left(\frac{t}{q_t} \right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} (t) \dots\dots\dots (5)$$

where q_e and q_t are the amounts of metal adsorbed (mg/g) at equilibrium and at time t (min), k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the adsorption rate constant of pseudo-first-order, pseudosecond-order adsorption rate, respectively. The linear plots of $\log (q_e - q_t)$

versus t and (t/q_t) versus t are drawn for the pseudo-first-order and the pseudo-second-order models, respectively. The rate constants k_1 and k_2 can be obtained from the plot of experimental data. The rate constant k_1 , k_2 and q_e calculated from the slopes and intercepts of the linear plot of $\ln (q_e - q_t)$ or (t/q_t) against t respectively (Figures 13 and 14). It is seen that Cr(VI) adsorption is well described by the pseudo second order reaction kinetic. Moreover, the correlation coefficient (R^2), of second order reaction kinetic for PANP and PANK (0.9997 and 0.9999) is higher than that of the first order reaction kinetic (0.8818 and 0.9207) and greater value of rate. Table (II) shows the rate constants, q_e (experimental and calculated) and correlation coefficient (R^2) for pseudo first and second order reaction kinetic.

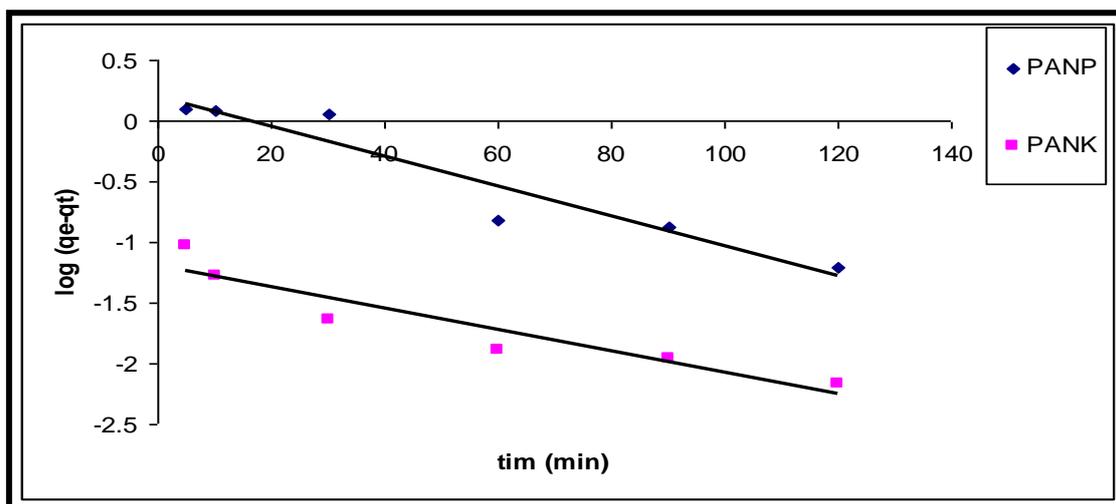


Fig.(13): The pseudo-first-order kinetic models for the adsorption of Cr(VI) by PANP and PANK.

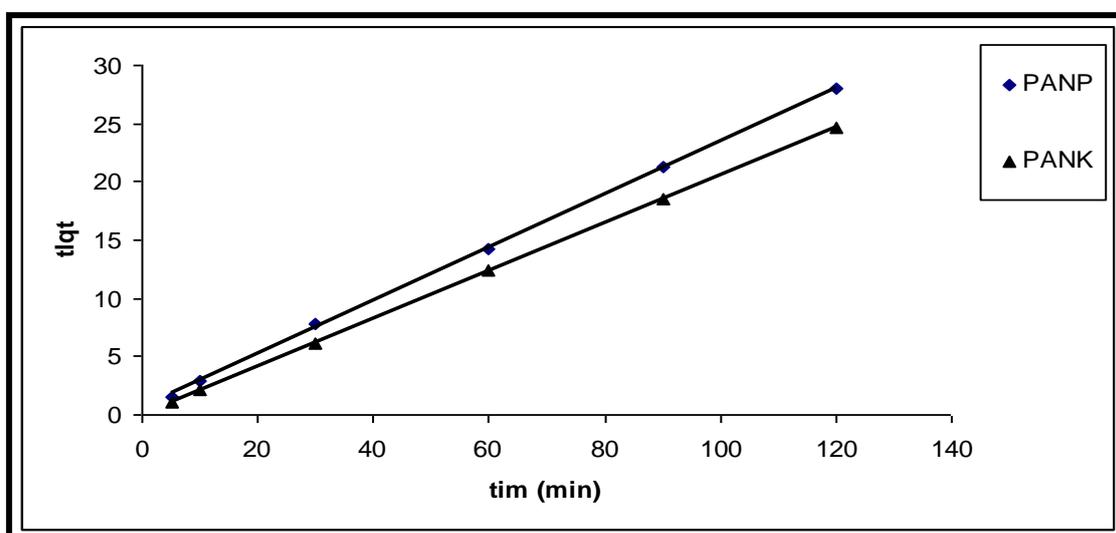


Fig.(14): The pseudo-second-order kinetic models for the adsorption of Cr(VI) by PANP and PANK.

Table (II)

Kinetic parameters for the adsorption of Cr(VI) onto PANP and PANK.

Adsorbent	PANP	PANK
Pseudo-first-order model		
$k_1 / 10^{-2} \text{ min}^{-1}$	0.026	0.020
R^2	0.920	0.881
q_e (experimental), mg g^{-1}	7.083	9.391
q_e (kinetic plot), mg g^{-1}	4.932	5.618
Pseudo-second-order model		
$k_2 / 10^{-4} \text{ g mg}^{-1} \text{ min}^{-1}$	0.08	1.50
R^2	0.999	1
q_e (experimental), mg g^{-1}	4.875	4.290
q_e (kinetic plot), mg g^{-1}	4.870	4.301

Conclusion

The removal of Cr (VI) from aqueous solution depend on the pH of solution with maximum adsorption obtained at pH 2.0 The removal percentage of Cr(VI) onto PANK was reduced from 97% at pH 2 to 92% at pH 5, from 90% at pH 2 to 72% at pH 6 onto PANP, The adsorption data have been explained in terms of Langmuir and Freundlich equations. The sorption kinetics was tested for the pseudo-first order and pseudo-second order reaction. The results revealed that the adsorptions of Cr(VI) onto PANP and PANK, were found to fit well with the Freundlich isotherm. The rate constants of adsorption for kinetic models were calculated and good correlation coefficients obtained for the pseudo-second-order kinetic model.

References

- [1] Jain C.K., Singhal D.C., Sharma M.K., "Adsorption of zinc on bed sediment of River Hindon Adsorption models and kinetics". *J. Hazard. Mater*, 114, 231–239, 2004.
- [2] Sekar M., Sakthi V., Rengaraj S., "Kinetics equilibrium adsorption study of lead(II) onto activated carbon prepared from coconut shell", *J. Colloid Interface Sci*, 79, 307–313, 2004.
- [3] Iqbal M., Saeed A., Zafar S.I., "Hybrid biosorbent: an innovative matrix to enhance the biosorption of Cd(II) from aqueous solution" , *J. Hazard. Mater*, 148, 47–55, 2007.
- [4] Anirudhan T. S., Nima J., Divya P. L., *Appl. Surf. Sci*, 279, 441, 2013.
- [5] Bhaumik A., Maity V. V., Srinivasu M. S., "Onyango, Enhanced removal of Cr(VI) from aqueous solution using polypyrrole/ Fe₃O₄ magnetic nanocomposite", *Journal of Hazardous Materials*, 190, 381-390, 2011.
- [6] Toledo T. V., Bellato C. R., Pessoa K. D., Fontes M. P. F., "Removal of chromium (VI) from aqueous solutions using the calcined magntic composite hydrotalcite-iron oxide: kinetic and thermodynamic equilibrium", *Quim*, 36, 419,2013.
- [7] Nguyen V.N., Lee J.C., Jeong J., Pandey B.D., "Enhancing The Adsorption of Chromium (VI) From The Acidic Chloride Media Using Solvent Impregnated Resin (SIR)". *Chemical Engineering Journal*, 219, 174–182, 2013.
- [8] Amuda O. S., Giwa A. A., Bello I. A., "Removal of heavy metal from industrial Waste water using modified activated coconut shell carbon", *Biochemical Engineering Journal*, 36, 174–181, 2007.
- [9] Kongsricharoern N., Polprasert. C., "Electrochemical precipitation of chromium (Cr⁶) from an electroplating waste water", *Water Sci Technol*, 31, 109–117, 1995.
- [10] Zhang D., Wei. S., Kaila. C., Su. X., Karki. A. B, Young., D. P , "Carbon-stabilized Iron Nanoparticles for Environmental Remediation", *Nanoscale*, 2, 917–919, 2010.
- [11] Park. D., Yun. Y. S., Lee H. W., Park. J. M., "Advanced kinetic model of the Cr(VI) removal by biomaterials at various pHs and temperatures", *Bioresour. Technol.*, 99, 1141–1147, 2008.
- [12] Tran N.H., Dennis G.R., Milev A.S., Kamali Kannangara G.S., Wilson M.A., Lamb R.N, "Interactions of sodium montmorillonite with poly(acrylic acid)", *Journal of Colloid and Interface Science*, 290, 392–396, 2005.
- [13] Genies E. M., Boyle A., Lapkowski M., Tsintavis C, "Polyaniline - A historical Survey", *Synth. Met*, 36, 139–182, 1990.
- [14] MacDiarmid A. G., Chiang J. C., Richter A. F., Epstein A. J., "Polyaniline - A new concept in conducting polymers", *Synth. Met*, 18, 285–290, 1987.
- [15] Chandrasekhar P., "Conducting Polymers Fundamentals and Applications: A Practical Approach", Kluwer Academic Publishers: Boston, MA, 1999.
- [16] Ansari R., "Application of polyaniline and its composites for adsorption/recovery of chromium(VI) from aqueous solutions", *Acta Chim. Slov*, 53, 88–94, 2006.
- [17] Li D., Huang J., Kaner R.B., "Polyaniline nanofibers: a unique polymer nanostructure for versatile applications", *Acc. Chem. Res*, 42, 135–145, 2009.
- [18] Sudha J.D., Sivakala S., Chandrakanth C.K., Neethu K.S., Rohini K.N., Ramakrishnan R, "Percolated conductive polyaniline-clay nanocomposite in polyvinyl chloride through the combined

approach porous template and self-assembly” , Express Polym. Lett, 8(2), 107–115, 2014.

- [19] Chattopadhyay. D. P., Milind S., “International Journal of Polymer Science” Volume, Article ID 939536, 7, 2010,
- [20] Elliott., H. A. Huang., “Adsorption characteristic of some Cu(II) complexes on alumina silicates” Water Research, 15(7), 849-854, 1981.
- [21] Yu H., Covey G.H., O'Connor A.J., “Silvichemicals from pulp mill wastes: biosorption of metal ions on ellagic acid” Appita Journal , 54,511–517. 2001.
- [22] Langmuir I., “The adsorption of gases on plane surfaces of glass, mica and platinum”, J. Am. Chem. Am. Chem. Soc, 40 (9), 1361–1403, 1918.
- [23] Freundlich H., “Over the adsorption in solution.” Z. Phys. Chem., 57, 385–470, 1906.
- [24] Ho Y.S., “Citation review of Lagergren kinetic rate equation on adsorption reactions” Scientometrics, 59,171–177, 2004.
- [25] Ho Y. S., “Review of second-order models for adsorption systems”, J. Hazard Mater, 136 (3), 681-689. 2006.

الخلاصة

في هذا البحث تم تحضير متراكبات البولي انيلين عن طريق البلمرة بالاكسدة بوجود الحامض. ان طريقة المزج السريع استخدمت لتحضير متراكبات البولي انيلين مع الكاولين وسميت PANK ومع البنثونايت, PANP. شخّصت المتراكبات البوليمرية بوساطة المجهر الالكتروني الماسح SEM وطيف الاشعة تحت الحمراء FT-IR. كذلك تم استخدام هذه المتراكبات في ازالة ايون الكروم السداسي من المحاليل المائية. تضمن البحث دراسة العوامل المؤثرة على عملية الامتزاز: الدالة الحمضية, زمن التفاعل, كمية المادة المازة وتركيز ايون الكروم السداسي. كذلك تم دراسة حركية امتزاز ايون الكروم السداسي باستخدام: المعادلة الحركية من الدرجة الاولى الكاذبة و المعادلة الحركية من الدرجة الثانية الكاذبة حيث وجد ان الدراسة تخضع للمعادلة الحركية الكاذبة من الدرجة الثانية. كذلك تم دراسة ايزوثيرمات الامتزاز باستخدام معادلة فريندليش ولانكماير وتبين ان الامتزاز لا يتبع كلا المعادلتين.