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Adsorption Features of Uranium ions from Aqueous Solutions by Poly Vinyl Alcohol / Poly Aniline Composite

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Abstract

Polyvinyl alcohol / Poly-aniline composite (PVA/PANI) has been prepared by oxidative polymerization of aniline to test its applicability for uranium ions adsorption. The prepared composite is characterized by BET, FT-IR and SEM. Different controlling factors have been tested namely; pH, contact time, temperature, S/ L ratio and initial uranium ions concentration. The adsorption dependence on pH gives supportive indication for the effect of complex formation on the adsorption process. The kinetics investigation fit to pseudo second order model. Negative values for enthalpy and entropy changes have been obtained. Uranium ions adsorption from waste effluents assured the high adsorption affinity of the prepared composite.

Keywords: Uranium, polyvinyl alcohol, poly-aniline, composite

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1-Introduction

The increasing range of contaminants in water has become a significant matter all over the world, due to the large population increase as well as droughts [1-3]. There are different types of contaminates present in the water as heavy metals, inorganic compounds, organic pollutants, and many other complex compounds [4-6]. Each type of these contaminants has harmful and ecological environmental effects on human beings. For that reason, the presence of these contaminants should be minimized to the lowest concentration.

Several techniques have been used by researcher in order to remove these contaminants, including photo catalytic oxidation, bio-remediation and adsorption processing [7-11]. Among the powerful adsorbents used for heavy metal ions removal, polymeric adsorbents with high surface area and pore structure is confirmed to be the favorable candidates [12]. Polymers like poly acetylene, poly vinyl alcohol (PVA) and poly-aniline (PANI), gained much research concern in a wide range applications such as rechargeable batteries [13], electromagnetic interference (EMI) shielding [14], optical devices [15] and removal of heavy metals [16]. Poly-aniline has been commonly mixed with thermoplastic polymers to increase its process competence, since poly aniline is characterized by poor solubility in the common solvents. PANI thermoplastic composites are common because different characteristic matrix can be produced [17–19].

PVA characterized by its chemical resistance, mechanical property, film forming capability, and biocompatibility and is biodegradable [20]. These properties enhance its industrial uses and increase its uses in preparing environmental un-harmful materials [21–23]. PVA is an inert material, so it is prerequisite to enhance its reactivity through chemical modification, which can be performed through its hydroxyl group. Etherification and acetalization are the popular reaction used for PVA modification [24]. Several studies have been performed on the modification of PVA through amidation like the work introduced by Awada and Daneault [25], the later investigates the reaction between the azido PVA and the porpargyl amine by click reaction in order to introduce the amine function on the PVA polymer chain. The involvement of amine moiety permits the reaction of PVA with polymer or molecules containing acid carboxylic function by amidation. The amidation can also be happened in water using a carbodiimide mediated route [26].

This study aims to synthesize PVA/PANI composite depending on the chemical oxidative polymerization of aniline in the presence of poly vinyl alcohol in an aqueous acidic medium using $NaHClO_4$, as oxidant. The resultant material has been subjected to different techniques like FT-IR, SEM, and BET in order to confirm the chemical modification. The uranium removal efficiency of the modified PVA has been tested through batch experiments techniques, where the controlling factors (pH, contact time, initial uranium concentration, temperature, and adsorbent dosage) will be studied in detailed. Adsorption isotherm, kinetics and thermodynamic of the reaction will be also investigated.

2-Materials and Methods

2.1. Materials

Poly vinyl alcohol was purchased from local factory (Giza governorate, Egypt), and used as received. Sodium hypo chlorite and aniline were purchased from Aldrich. Aniline was distilled twice until it become colorless. Other chemicals were of analytical reagent grade and were used directly without further purification.

2.2. Synthesis of Poly-vinyl alcohol / poly-aniline composite

Poly-vinyl alcohol / poly-aniline (PVA/PANI) composite were synthesized by modifying the method obtained by Salem [27], depending on the chemical oxidative polymerization of aniline in the presence of poly vinyl alcohol in an aqueous acidic medium using $NaHClO_4$, as oxidant. A general polymerization reaction was carried out as follows: three gram from Poly vinyl alcohol were placed in addition to sodium hypo chlorate (2.44 g, 32.9 mmol) in a beaker (500 mL) containing 190 mL from 0.53 mol L^{-1} HCl. The mixture was stirred by a magnetic stirrer. Aniline (3 mL, 32.9 m-mol) were then added drop by drop with continuous stirring. The polymerization process was allowed to proceed for 1 h at 25 °C. The formed PVA/PANI composite was collected by filtration and washed thoroughly with a dilute HCl (0.53 mol L^{-1}) in the reaction medium until the acid filtrate became colorless. The prepared composite was air dried overnight and the yield was noted.

2.3. **PVA/PANI composite characterization**

The morphology of PGC is observed using Scanning Electron Microscope (SEM model Philips XL 30ESEM), while FTIR spectra is measured on a Thermo Scientific Nicolet IS10 and The N_2 adsorption–desorption isotherms have been used to predict the pore size distribution. The specific surface area (BET) has been recognized from the linear segment of the N_2 adsorption isotherms by applying Brunauer–Emmett–Teller (BET) theory.

2.4-**Batch adsorption experiments**

The interaction between PVA/PANI composite and uranium was figured by spectrro-photometer using the method of Merchzenko [28]. PVA/PANI (0.01g) was placed into a number of conical flasks (50 mL) followed by the addition of different volumes from the uranium bearing solution (3.75ml to 45 ml). The mixture was immediately shaken with mild shaking speed (140 rpm) for time range between 5 and 180 minute. The pH was studied in the range 0.8 to 9 and was adjusted by 0.1 M from NaOH or HCl. thermodynamic study was done by varying the temperature range from 25 to 60 °C.

The adsorbed uranium amounts obtained from the different investigation were determined using the following function:

$$q_e = V(Co - Ce)/M$$

where q_e is the adsorption amount in mg/g, M is the weight of the adsorbent (g), V is the volume of solution (L) and C_0 and C_e are the initial and equilibrium concentrations of uranium ions in solution.

2.4.1- Adsorption isotherm

The U (IV) ions adsorption onto PVA/PANI composite were investigated by using different isotherm models as:Langmuir[29] to study single layer sorption[30], Freundlich[31] that figured various adsorption features[32] and Temkin adsorption model**[33]** using the following equation**:**

Langmuir Isotherm

$$C_e/q_e = C_e/Q_m + 1/Q_m b \qquad (1)$$

Where Q_m is the saturated monolayer adsorption (mg/g), b is the Langmuir constant related to the affinity of binding sites and is a measure of the adsorption energy (mL/mg).

Freundlich Isotherm

$$\text{Log } q_e = \text{Log } K_f + 1/n \text{Log } C_e \qquad (2)$$

Where K_F is the adsorption capacity (mg/g) and 1/n is the Freundlich constant indicating adsorption intensity.

Temkin] Isotherm

$$q_e = B \ln (A+Ce) \qquad (3)$$

Where B = RT/b

Where B is the Temkin constant related to heat of sorption (J/mol), A is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol K), b is Temkin isotherm constant and T is the temperature (K) [34, 35].

2.4.2. Kinetics study

The adsorption mechanism has been studied by applying the following equations [36 and 37]:

$$\text{Pseudo-first-order: } \ln (qe - qt) = \ln qe - k_1 t \qquad (4)$$

$$\text{Pseudo-second-order: } t/qt = 1/K_2 q_e^{2} + t/q_e \qquad (5)$$

Where q_t and q_e are the amounts of uranium ions adsorbed (mg g^{-1}) at time t (min) and at equilibrium time, respectively; k_1 (min^{-1}) and k_2 (gmg^{-1} min^{-1}) are the pseudo-first-order and the pseudo second- order sorption rate constant, respectively.

2.4.3. Thermodynamic parameters

The Van't Hoff plot has been used to calculate the thermodynamic parameters ΔS, ΔH° and ΔG° applying the following equation:

$$\text{Ln } K = \frac{\Delta S}{R} - \frac{\Delta H}{R} \qquad (6)$$

$$\Delta G° = -RT \text{ Ln } K \qquad (7)$$

where ΔG° is the standard free energy, R the universal gas constant (1.987 cal/mol K or 8.314 J/mol K) and T is the absolute temperature in Kevin (K). The value of Δs and ΔH° are obtained from the slope and intercept of the relation between ln K with the reciprocal temperature 1/T.

2.4.4. Equilibration calculation

All uranium speciation in this study were performed with Hydra-MEDUSA, a chemical equilibrium calculation program [38].

3. Results and Discussion

3.1- Structural characterization

The prepared composite had micro-porosity with reference to the IUPAC classification since the values of pore diameters were 0.2 nm [38], where the obtained pore diameter was ≤0.003. The obtained data shows that BET constant value (c =21.649), which is related to the affinity of the solid with adsorbate (Figure 1). The higher the value of c is the higher the interaction. Also, figure 1 gives an indication that N_2 adsorption isotherms of the PVA/PANI composit**e** are type I curve. The later depicts monolayer adsorption and this graph can be easily explained using Langmuir adsorption isotherm, when P/P˚<1 and c>1 in BET equation, then it leads to monolayer formation and Type I Adsorption Isotherm is obtained. The BET surface area was 8.537e+00 m²/g, total pore volume was3.364e-02 cc/g and pore size of this material was 7.880e+01 (Figure 1).

The change in physical characteristics of the composite was due to to the different morphology from its associates (Figure 2). The swelling ratio was 160% for the prepared composite. It was clear that the composite had high water imbibing capacity from its poly vinyl alcohol component.

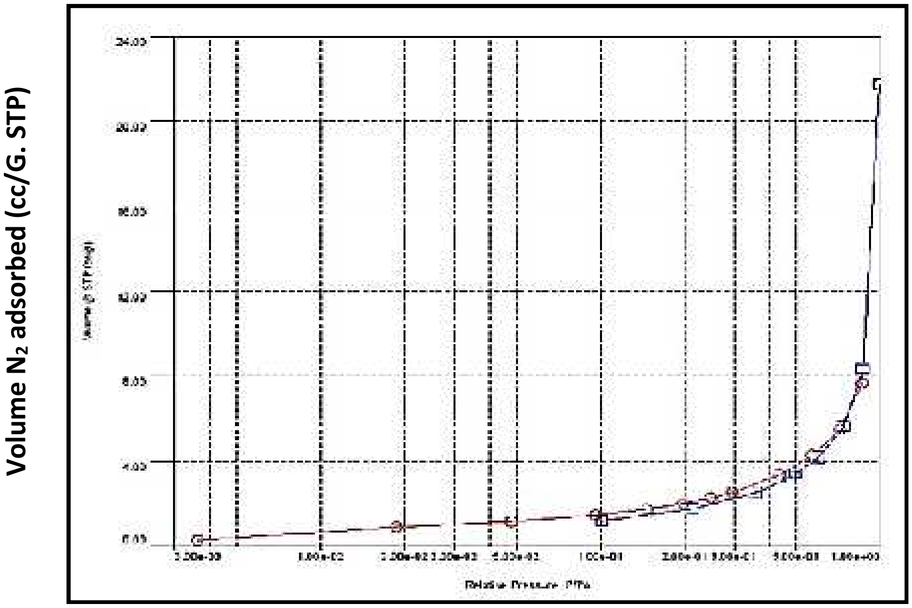

Fig (1): N_2 adsorption-de-sorption isotherms for the PVA/PANI composite.

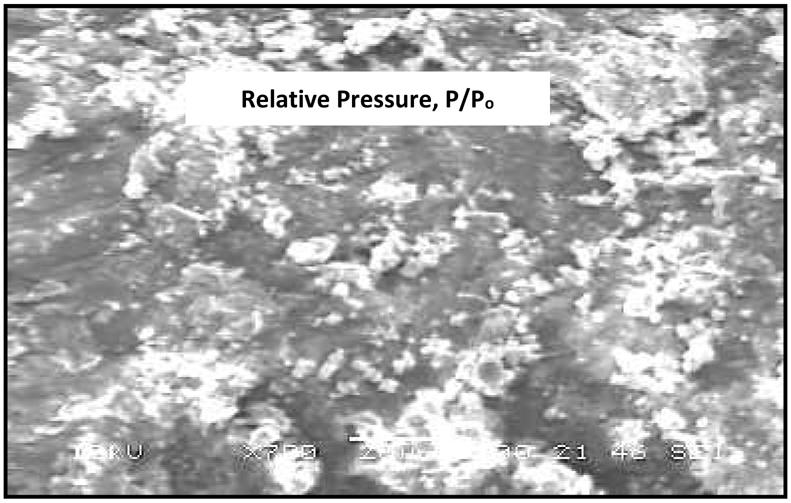

Fig (2): SEM of the prepared PVA/PANI composite

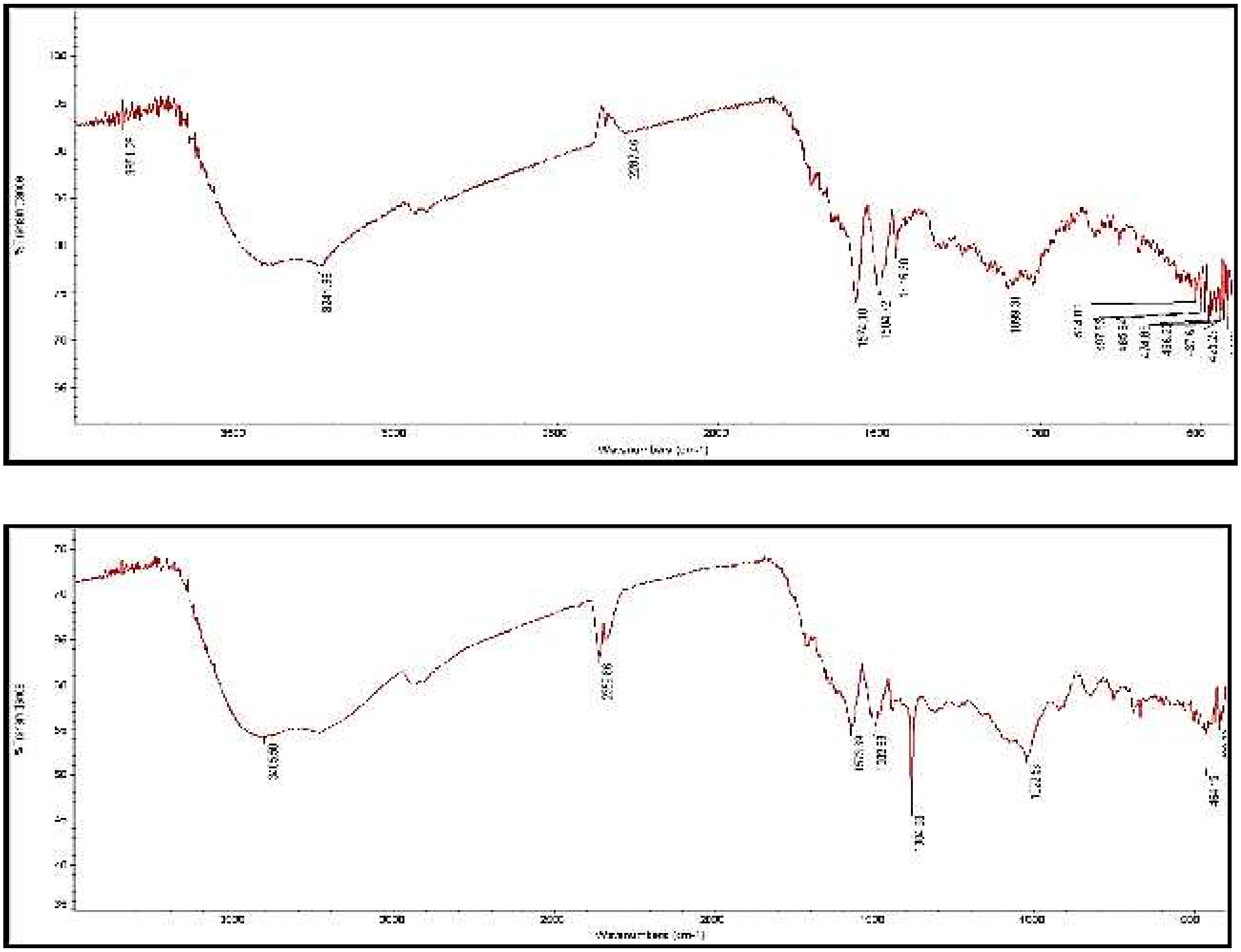

Fig (3): FT-IR of PVA/PANI composite before and after uranium ions adsorption

FT-IR investigation

The FTIR spectra of PVA/PANI composite before and after uranium adsorption were illustrated in Fig 3. The counters at 3405, 3241 and 1022cm $^{-1}$ were assigned to the vibrations NH stretch groups in PVA/PANI composite spectra, while the bands at 1446 cm $^{-1}$ was regarded to NH bending. The absorptions beak at 1649 cm $^{-1}$ was back to amide (C=O stretching and N–H bending. The bands at 2287, 1502, 1570, 1091 cm $^{-1}$ were associated to C=C stretch. After adsorption the bands at 2287 cm $^{-1}$ was shifted to 2358. The band at 1649 cm $^{-1}$ disappeared, while the band at 1460 cm $^{-1}$ was shifted to 1384 cm $^{-1}$ and became more sharpened.

3.2. Effect of controlling factors

3.2.1. Effect of initial uranium concentration

The initial uranium concentration has an important role in the adsorption capacity of the adsorbent. The effect of initial uranium concentration on its adsorption onto PVA/PANI composite has been investigated and the results are plotted in Figure 4. It can be seen that the initial U (VI) concentration provides the necessary driving force to overcome the resistance of mass transfer from the aqueous phase to the solid phase. It can also be seen that the higher the initial concentration is, the greater the adsorption capacity becomes. With further increase of uranium concentration, the adsorption capacity reached a plateau, indicating that the saturation of the available active binding sites on the PVA/PANI composite.

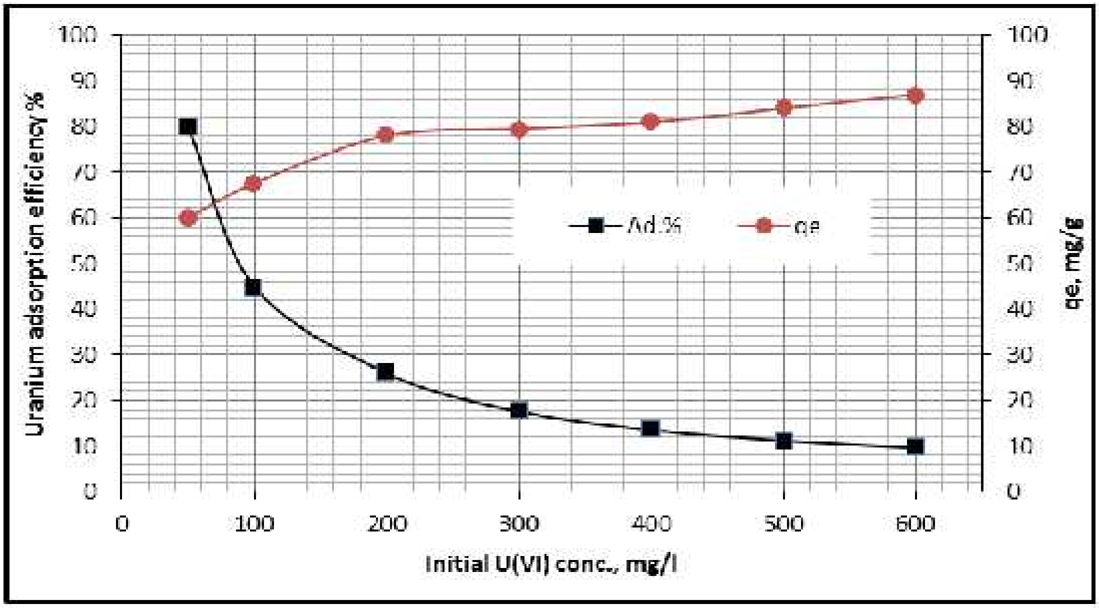

Fig (4): Effect of initial U (VI) concentration on its adsorption onto PVA/PANI composite.
(pH 5, S/L ratio 0.01g/15 ml, room temperature and 1.5 h as contact time).

3.2.1.1. Adsorption isotherms

To understand the adsorption process, different adsorption isotherms have been investigated and the results are tabulated in Table 1. The obtained results show that under the experimental conditions listed previously, the data correlate better with Langmuir isotherm rather than the other isotherms, although the correlation coefficient (R^2) for all isotherms is above 0.97 but the experimental data here is the controlling factor. The maximum adsorption value obtained in accordance to langmuir is 87.79 mg/g. The obtained value of n in freundlich isotherm is less than 1 indicating normal adsorption [39]. While in Temkin isotherm the value of its constant A and B are 5.7 and 7.8 respectively, which give an indication of the heat of sorption revealing a physical adsorption process [40].

Table 1: Parameters for plotting Langmuir, Freundlich and Temkin adsorption isotherms of U (VI) ions onto PVA/PANI composite

Langmuir pararmeters		Freunlich pararmeters		Temekin pararmeters	
q_{max}(mgg^1)	87.79	K_f (mg g-^{1})	48.0	B(j/mole)	6.651
B (Lmg^{-1})	0.062	n	0.092	A_t (L/mg)	0.8
R^2	0.99	R^2	0.985	b_t	372
				R^2	0.97

3.2.2. Effect of contact time

The results of time influence on the adsorption of U (VI) onto PVA/PANI composite are presented in figure 5. As the agitation time increases, uranium ions adsorption increases rapidly at the first 60 minute, which might be due to the surface adsorption of U (VI) on PVA/PANI composite. Then the increase in adsorption percent decreases gradually till it approaches a nearly constant value, denoting equilibrium attainment after 120 minute where no further increase in the adsorption occurs.

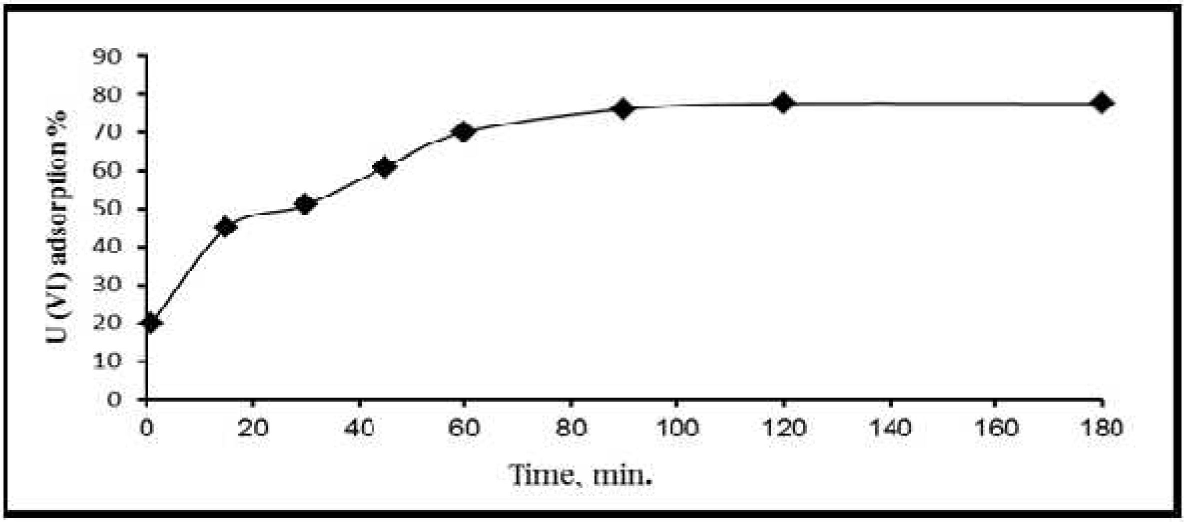

Fig (5): Effect of contact time on U (VI) adsorption onto PVA/PANI composite.
(pH 5, S/L ratio 0.01g/15 ml, room temperature and 200 mg/g U concentration).

3.2.2.1. Adsorption Kinetics

To determine the mechanism of adsorption, certain constants of adsorption are determined by using a pseudo first-order equation and pseudo second-order equation [41]. The kinetic data for adsorption of U (VI) by PVA/PANI composite are given in Table 2. Based on the obtained R^2, the kinetic data is in good agreement with pseudo second-order model as it can be noticed that the experimental q_e value is closer to that calculated by pseudo second-order equation, declaring that adsorption process is ion concentration dependent and chemical sorption is the rate-controlling step. Similar results are obtained by Zhu et al [42], where they study the removal of Co bt PVA/ chitosan beads from radioactive waste water.

Table 2: Kinetic model parameters applied to U (VI) sorbed PVA/PANI composite

First order			Second order		
q_e (mgg^{-1})	K_1 (min^{-1})	R^2	q_e (mgg^{-1})	K_2 (g mg^{-1}.min^{-1})	R^2
157.2	0.014	0.91	250	0.004	0,99

3.2.3. Effect of pH

The pH of the solution has an important role in the adsorption process, due to its effect on the speciation of metal ions, surface charge of the adsorbent and the degree of ionization of the adsorbent during the adsorption process [43]. It can be stated that two pH dependent factors have an effect on the U(VI) adsorption efficiency: Point of zero charge (pH pzc) of the adsorbent and U (VI) speciation. The results of pH influence on the adsorption of U (VI) onto PVA/PANI composite (Figure 6) indicate that with the increase in the pH, the adsorption percent increases and reach its maximum value at pH 5.1. This may be attributed to the following: At low pH, the adsorption percent is minimum, which is regarded to the protonation of –NH- to form –NH$^+$- and the competition of H$^+$ with U (VI) for the adsorption sites on the PVA/PANI composite surface. With the increase in the pH to 5.1, the competition effect decreases but in the same time the surface charge of the adsorbent is positive and accordingly more attractive to U (VI), that appears in the form of UO_2 $(SO_4)^{2-}$ (Figure 7).When pH value exceeded pH 5.1 the surface sites became negatively charged causing repulsive electrostatic effect towards U (VI) species as verified by the decrease in the adsorption efficiency.

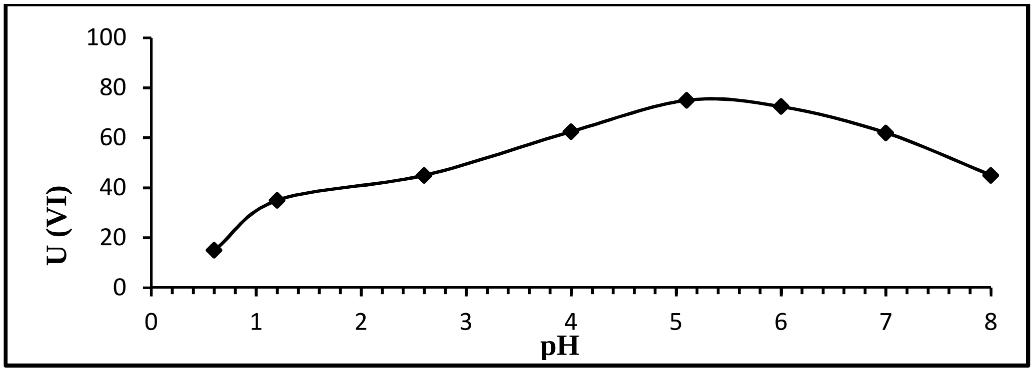

Fig (6): Effect of pH on U (VI) adsorption onto PVA/PANI composite.
(1h contact time, S/L ratio 0.01g/15 ml, room temperature and 200 mg/g U concentration).

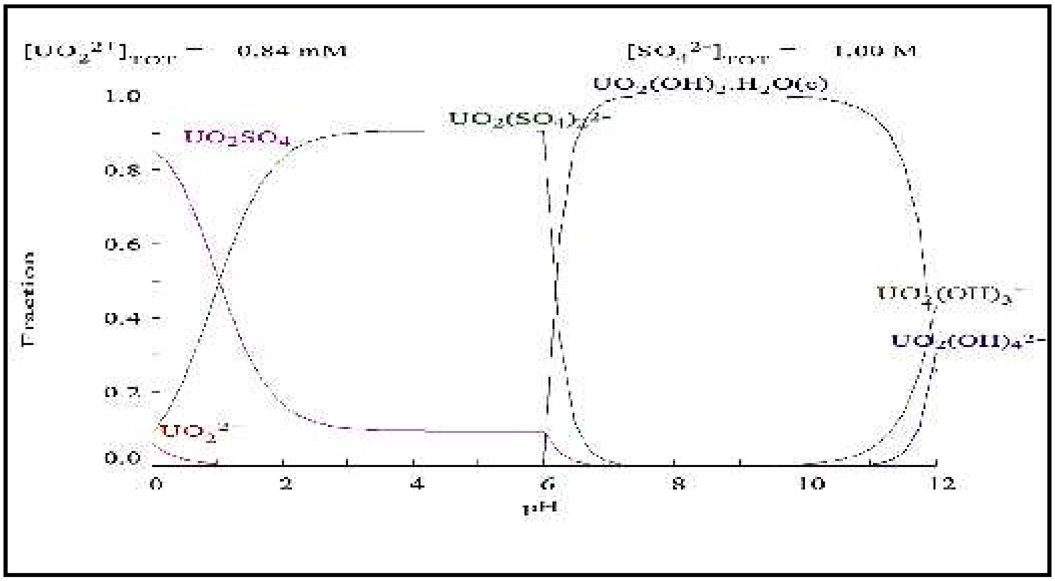

Fig (7): Expected aqueous speciation of uranium (200 mg/L) as a function of pH in 1 M H_2SO_4
using Medusa and Hydra program[38]

The aqueous speciation distribution of uranium was calculated and represented in Figure 7. The results showed that the complexes of UO_2SO_4 and $UO_2(SO_4)_2^{2-}$ were the predominant species at the pH range from 0.0 – 6 with mean total percent of 85 and 10% respectively at pH 0 while 10 and 90 % at pH 6. U-hydroxide complexes start to dominate the aqueous phase at pH near 7. The dominate complex of $UO_2(OH)_2.H_2O$ became the major specie with about 100% of total concentration at pH range from 7 to 11. After pH 12, $UO_2(OH)_4^{2-}$ and UO_2OH^{3-} became the major species. According to the initial pH of 4-6.5, the following adsorption scheme is more appropriate to be considered and the possible coordination mechanism for the interaction between $UO_2(SO_4)_2^{2-}$ and the PVA/PANI composite is followed:

$$(PVA)NH^+ + UO_2(SO_4)_2^{2-} = ((PVA)\ NH^+)\ 2UO_2(SO_4)_2^{2-}$$

3.2.4. Effect of volume/mass ratio

The obtained results in figure 8 show that with increasing the V/m ratio from 3.75 ml/ 0.01 g to 30 ml/ 0.01 g, the adsorption percent increase reflecting an increase in the adsorption capacity and attained constant adsorption after a certain V/M ratio (optimum ratio) beyond where there is no significant increase in the adsorption. The obtained results may be due to the influence of several factors as the limited adsorption sites during the adsorption reaction [44]; (ii) the aggregation/agglomeration of sorbent particles at higher doses, which would lead to a decrease in the surface area and an increase in the diffusion path length [45].

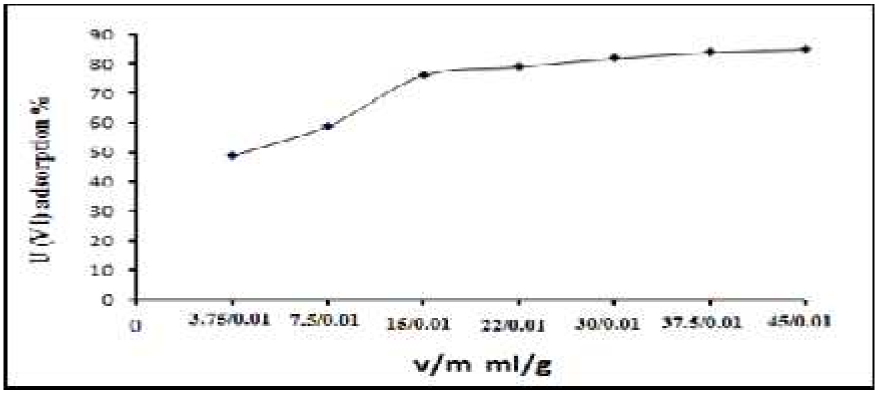

Fig (8): Effect of V/M ratio on U (VI) adsorption onto PVA/PANI composite.
(1h contact time, pH 5, room temperature and 200 mg/g U concentration).

3.2.5. Effect of temperature

The obtained results of the influence of temperature on the adsorption of U (VI) onto PVA/PANI composite show that with the increase in the temperature the adsorption percent decreases reflecting a negative affect of the temperature (Figure 8). The negative values of ΔH (-11.4 kJ mol^{-1}**)** indicates that the process is exothermic [46]. The entropy value is negative (-24J mol^{-1} K^{-1}) and gives an indication that the internal structure of PVA/PANI composite has not been changed during the adsorption [47] and the sorbate ions are stable on the adsorbant resulting loss of freedom degrees at solid/liquid interface [48]. The sorption process causes an increase in the order of the system. The small and negative value of Δ G (-3.99 kJ mol^{-1}) at lower temperature indicates the feasibility of the process and the spontaneous nature of adsorption especially at low temperature, i.e. the adsorptive forces are strong enough to overcome the potential barrier [49].

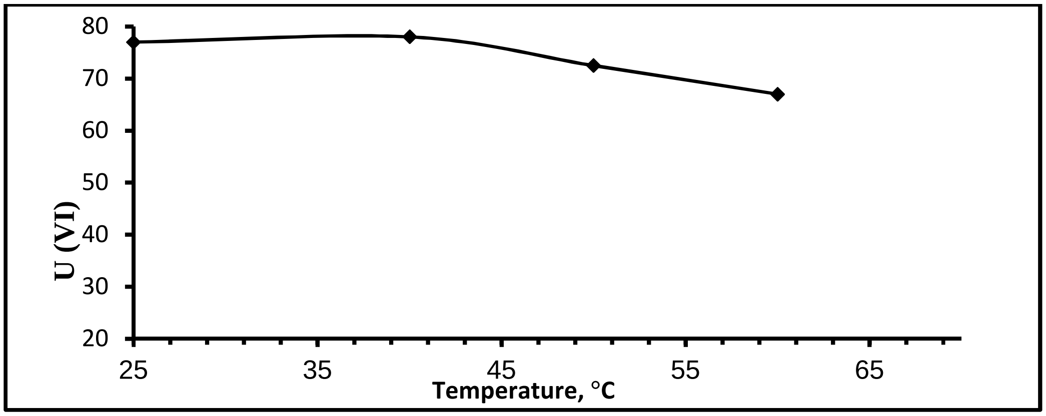

Fig (9): Effect of temperature on U (VI) adsorption onto PVA/PANI composite. (1h contact time, pH V/m 15/0.01 and 200 mg/g U concentration).

3.4. Mechanism

The adsorbent chemical composition plays an important role in expressing the adsorption mechanism. Several possible reactions may interfere for the removal of uranium ions by adsorption, from such actions are acid–base interactions, ion exchange, coordination/ chelation, complexation, precipitation, physical adsorption, and electrostatic interactions [50]. In this study, the electrostatic interaction is prospected to be the maim mechanism for uranium ions removal by PVA/PANI composite, depending on the existence of –NH$^+$– centers on the polaron/bipolaron forms of PVA/PANI composite and different uranium ions obtained with the pH variation. As the uranium ions reach to PVA/PANI composite surface, they access to the NH$^+$ centers and react with them. In the tested composite, the reaction is found to obey pseudo- second-order kinetics where the reaction rate is measured from the increased amount of adsorbed ions on the PVA/PANI composite along the time of contact. Generally, pseudo-second-order kinetics indicate that a chemical adsorption is taking place [51].

4. Conclusion

The present study deals with the preparation of polyvinyl alcohol / Poly-aniline composite by oxidative polymerization in order to examine its applicability for uranium ions removal from liquid solutions. The obtained results can be concluded in the following:

1. The adsorption of uranium ions on polyvinyl alcohol / Poly-aniline composite depends on pH while the temperature has a negative effect.
2. The adsorption of uranium ions on the prepared composite surface obeys the Langmuir isotherm rather than the other investigated isotherms.
3. The adsorption process is expressed well by pseudo – second order

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