



**Uranium Adsorption from Bahariya Oasis leach liquor via TOPO Impregnated Bentonite Material; Isothermal, kinetic and Thermodynamic Studies**



**A.M. Masoud<sup>1</sup>, Muhammad Saeed<sup>2</sup>, M.H. Taha<sup>1</sup>, M. M. El-Maadawy<sup>1\*</sup>**

<sup>1</sup>*Nuclear Materials Authority, P.O. Box-530, El Maddi, Cairo, Egypt*

<sup>2</sup>*Department of Chemistry, Quaid-i-Azam University 45320-Islamabad, Pakistan*

**T**HE current study includes the application of cost effective TOPO (tri-n-octylphosphine oxide) impregnated bentonite for efficient uranium adsorption. Various experimental parameters (pH, time, adsorbent weight, mechanical stirring, uranium concentration and temperature) were thoroughly investigated. The synthesized trioctylphosphine oxide (TOPO) based adsorbent was characterized via XRD, SEM, BET, TGA and FT-IR. The results showed 78.3% uranium adsorption can be achieved under optimized conditions (30 min, TOPO impregnated onto bentonite form 1.87M sulfate leach liquor solution of 250 mg/L at room temperature). The obtained findings fitted well with thermodynamic, isothermal ( $0 < R_L < 1$ , favorable adsorption) and pseudo second order kinetics (rate constant  $0.20 \text{ g/mg min}^{-1}$ ). In thermodynamical studies negative sign of (specified the spontaneity of process, (endothermic) and positive sign show high randomness after adsorption.

**Keywords:** Uranium, adsorption, leach liquor, TOPO, and bentonite.

### **Introduction**

In the outer layer of earth, the uranium metal is usually somewhat unfamiliar and in the form of mixture due to the presence of other elements. The physical structure of it obtains by the mega explosions of stars along with other elements which have high atomic masses than iron. Globally, the present condition actively demands the electric energy means than that of carbon dioxide, methane gas energy sources, because the production of radioactive energy sources mostly based on radioactive element i.e. uranium, due to this reason the value of such radioactive metal elements, is rising gradually [1]. Heavy metals,

dyes [2], organic compounds and radioactive elements are major factors of environmental pollution. A number of facile methods to extract uranium metal element along with other heavier elements that are present in ordinary means in addition to radioactive wrecks, but the top conventional recognized techniques are membrane treatment, chemical precipitation, ion exchange, elimination and adsorption [3-6]. To recover and separate the metal charged species, usually used techniques are ion exchange and solvent extraction. So as to obtain profitable separation of solute by liquid-liquid extraction method, that requires the multipurpose extractions of solute by back extraction methods. Furthermore, the

\*Corresponding email: [elma3dawi@yahoo.com](mailto:elma3dawi@yahoo.com)

Received 13/6/2018; Accepted 6/7/2019

DOI: 10.21608/ejchem.2019.13638.1843

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ion exchange polymeric adhesive materials that have been used for the slight careful extraction of transition metals regarding to first group metal elements [7, 8], and an additional extraction method by using an organic adhesive substance to extract precise concentration of charged metal species into the large chain molecules by clear absorption method that has been suggested by Warshawsky [9], and these substances act like a link amid liquid-liquid extraction and ion exchange method [10]. It is a useful application of ion exchange resin that the extracting agents of remarkable characteristics have been used for the synthesis of dilute mixtures, as well as their high relative partition ratio with selective properties and dissolution in an organic liquid phase with the help of tools and operational traits of solid ion exchange method [11-13]. Lately, the extracting activated resins that have been used to extract metals from a solution which contain number of constituents in many analytical fields, and they consist of acidic organophosphorous complexes and bi functional organo-phosphorus complex [14]. A few number of extracting agents like tri-n-octylamine, quaternary alkyl ammonium salts, crown ethers and tri-n-dodecylammonium chloride [15] and 1-(2-pyridylazo)-2-naphthol [16], have also been utilized.

According to research, a novel sorbent material, such as bentonite activated by the trioctylphosphine oxide (TOPO), which was familiarized to extract uranium from the filtered liquid and the impacts of adsorption variables like time, initial strength of uranium and temperature were examined. . The newly prepared adsorbent was characterized by XRD, SEM, BET, FT-IR,

and TGA to identify the formation. Isothermal and kinetic measurement was also studied. Moreover, the temperature ranging graphs at adsorption procedure, for instance two-variables (Langmuir, Freundlich) which were analyzed to discover top most adsorption methods.

### Material and Methods

All the reagents and chemicals used during this work were of analytical grade such as 2:1 type bentonite clay, trioctylphosphine oxide (TOPO) provided by *Riedel-deHaen, Co.*, acetone (99%) collected from *Adwic Co.* Uranium solution (adsorbate) was prepared from leaching Bahariya Oasis uranium ore (100 g/kg) of sulfuric acid ( $H_2SO_4$ ) under atmospheric conditions at room temperature, the chemical characteristic composition of this leach liquor is shown in (Table 1). Adsorbent was prepared by impregnation of TOPO in acetone solution (80% V/V) onto bentonite clay as following dry scheme that are widely used[17]. 50 mL of TOPO solution was immersed with 3 g of bentonite, the subsequent slurry was stirred for 24 hours, evaporation of acetone from this slurry was performed at ambient temperature ( $25 \pm 1$  °C) and then dried at 80°C. Regarding as adsorption, the 0.2g TOPO based modified bentonite was used for 10 mL leach liquor (250 ppm) solution of uranium in thermostated shaker at optimum temperature ( $25 \pm 1$ °C). The suspension solution was filtered and residual uranium concentration determined by using ICP and UV-VIS spectrophotometer (*Arsenazo-III*).

**TABLE 1** Chemical composition of sulfate leach liquor used for extraction experiments.

Component	Concentration
$SO_4^{2-}$	100.5 g/L
$Fe_{total}$	21.1 g/ L
Al	1.5 g/ L
$P_2O_5$	0.6 g/ L
Ca	0.5 g/ L
Cl <sup>-</sup>	1.4 g/ L
U	250 ppm

## Results and Discussion

FT-IR is a modern analytical technique which was used to analyze the produced vibrational bands in unmodified bentonite and TOPO (tri-n-octylphosphine oxide) impregnated bentonite were recorded by using ATI MATTSON GENESIS Series-Model-960-M009 in the range of ( $4000\text{cm}^{-1}$  to  $400\text{cm}^{-1}$ ) (with resolution  $1\text{cm}^{-1}$  and 15 scan) to get insight about functional as well as finger print region. The SEM, XRD and TGA of unmodified and bentonite with TOPO were analysed by using Philips XL-30 ESEM, Powder XRD (AXS-D8 Bruker Advance) by using ( $\text{Cu-K}\alpha = 0.15406\text{nm}$ ) and Modern Thermogram respectively. In addition, surface area was investigated before and after modification by using Brunauer Emmett Teller (BET) technique.

### Powder X-Ray Diffraction Analysis (XRD):

XRD pattern of unmodified and TOPO impregnated bentonite was recorded by using Powder X-Ray Diffraction (AXS-D8 Advance) as given in (Figure 1). The characteristic peak in spectra of unmodified bentonite appears at  $2\theta = 5.08$  with basal spacing  $1.52\text{nm}$  and shifting towards lower  $2\theta$  value ( $2\theta = 4.09$ ) with increase in basal spacing  $2.05\text{nm}$  in modified bentonite. The shifting of peak gives information that the basal spacing increase in TOPO impregnated bentonite and efficient for adsorption than unmodified bentonite. Remaining all peaks are same in both spectra due to presence of Quartz and alumina silicates observed at ( $2\theta = 31.7, 37.10, 42.44$ ) with basal spacing  $2.79, 2.38$  and  $2.062 \text{ \AA}$  respectively as confirmed by (JCPDS No. 00-006-0024).

### FT-IR Analysis:

FT-IR is advanced analytical technique used to analyze the unmodified bentonite and TOPO impregnated bentonite as given (Figure 2). Regarding as FT-IR spectra of TOPO impregnated bentonite, the peak observed at  $2830\text{cm}^{-1}$  due to  $\text{sp}^3\text{-C-H}$  stretch. In the FT-IR spectra of modified bentonite the broad band appears at  $3458\text{cm}^{-1}$  corresponds to  $\text{-OH}$  stretch, which is less intense than unmodified bentonite. In addition, the peak observed in the region of  $1500\text{-}1300\text{cm}^{-1}$  due to bending vibrations of  $\text{CH}_2$  and  $\text{CH}_3$  which are also absent in unmodified bentonite. The peak appears at  $800\text{-}700\text{cm}^{-1}$  corresponds to C-H in-plane

bending vibration [18]. The peak observed in the range of  $1100\text{-}1000\text{cm}^{-1}$  corresponds to  $\text{P=O}$  bond of TOPO in modified bentonite spectra. The Si-O-Si and Si-O-Al vibrational bands appears in the range of  $1000\text{-}900\text{cm}^{-1}$  in both spectra [19]. These results indicated the existence of the ligand on the modified clay minerals [20]. These all peaks gives confirmation the formation of TOPO impregnated bentonite.

### BET Analysis:

The BET is advanced analytical technique used to investigate the surface area of unmodified bentonite  $43.6 \text{ m}^2/\text{g}$  which leads to decrease ( $36 \text{ m}^2/\text{g}$ ) after TOPO impregnation into bentonite. The decrease in surface area generally due to the presence of hydrophobicity (familiarized into clay by organic cations) that encumbers access to the interlayer surface [21].

### Scanning electron microscopy-micrographs (SEM)

Morphological characterization studies of unmodified, TOPO based modified bentonite and uranium adsorbed impregnated bentonite were performed by (Philips XL-30 ESEM), which are shown in (Figure 3). The figure (a) shows that the unmodified bentonite is not more porous and agglomerated but shows fluffy structure. The micrograph image of TOPO impregnated bentonite in figure (b) before adsorption illustrate that the particles are more agglomerated, porous and better for adsorption than unmodified bentonite [22]. But in figure (c), the surface modification is clearly seen after the deposition of uranium onto prepared adsorbent. The above discussion clearly indicated the formation of modified bentonite with TOPO and adsorption. The further justification is discussed in XRD analysis which gives information about shifting of peak in modified bentonite to lower  $2\theta$  values.

### TGA:

Thermogravimetric analysis of unmodified and modified bentonite gives information of mass loss (%) as a function of temperature ( $^{\circ}\text{C}$ ) as shown in (Figure 4). This study illustrates that the TOPO impregnated bentonite shows following transitions; water evaluation (below  $150^{\circ}\text{C}$ ), dehydroxylation  $\text{-OH}$

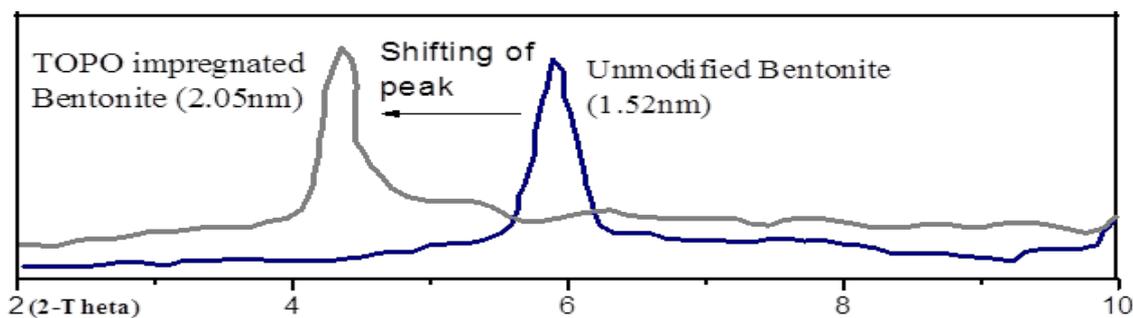


Fig. 1 Powder XRD pattern of unmodified and TOPO impregnated Bentonite

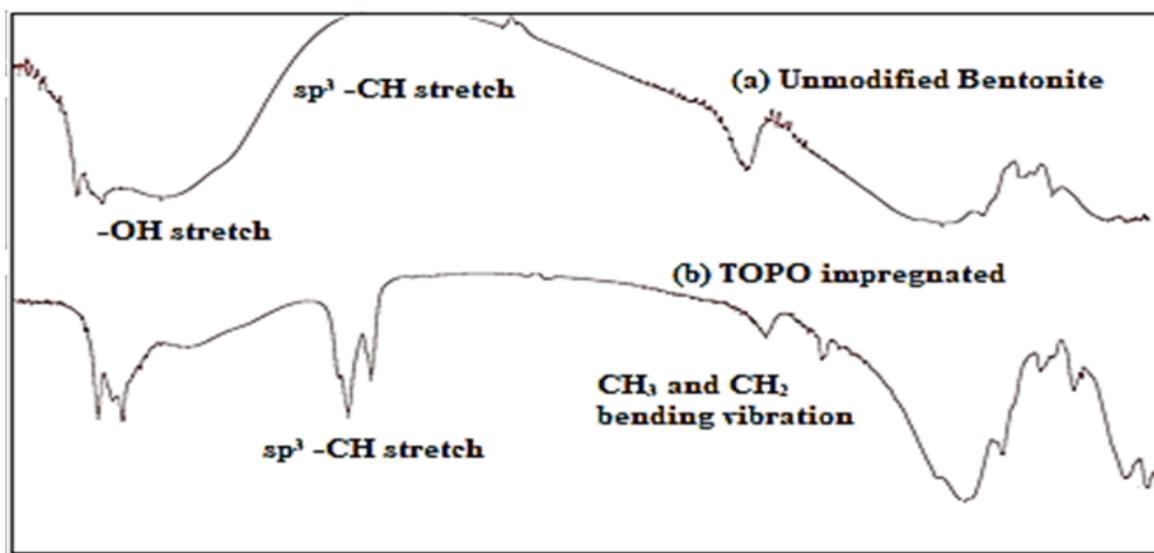


Fig. 2 FT-IR spectrum of (a) unmodified bentonite and (b) TOPO impregnated bentonite

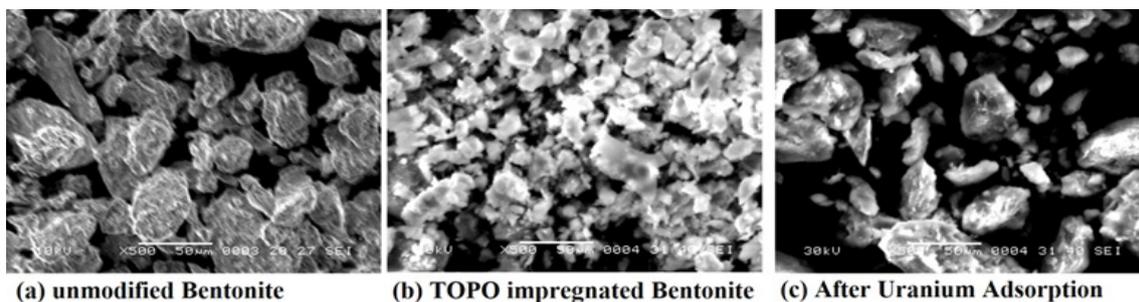


Fig. 3 SEM micrographs of unmodified bentonite (a), TOPO impregnated bentonite (b), Uranium adsorbed TOPO impregnated bentonite (c).

(400-450°C), evaporation of organic compounds impregnated between layers of bentonite (550-770°C), but in unmodified only two transitions occurs as water evaporation and dehydroxylation. The described difference give confirmation of TOPO impregnation into bentonite which is efficient for adsorption of uranium (VI).

### Optimization:

The amount of uranium adsorbed ( $q_e$ ) by using hydrazine impregnated charcoal was determined by measuring the difference between initial concentration and equilibrium concentration and represented as;

$$q_e = (C_o - C_e) \times V/m \quad (1)$$

Where  $C_e$  and  $C_o$  corresponds to equilibrium and initial concentration in mg/L respectively,  $m$  is the mass of adsorbent and  $V$  corresponds to volume of solution (L). The removal percentage efficiency and distribution coefficient ( $K_d$ ) of concerned ions was determined by following equations (2) and (3) respectively;

$$\text{Uranium adsorptin (\%)} = (C_o - C_e)/C_o \times 100 \quad (2)$$

$$K_d = (C_o - C_e)/C_o \times V/m \quad (3)$$

### Investigation of TOPO-Impregnation onto Bentonite

#### Effect of TOPO concentration

Various experimental results are collected by using 1.0g bentonite, TOPO concentration 0.05-0.5 M in acetone, solvent/bentonite (10 mL:1.0 g), time 2 hours at 200rpm and room temperature. There is a direct relationship between concentration of TOPO impregnated bentonite and amount of TOPO which is explained in the form of results in (Figure 5). These results show that, when amount of TOPO augmented from 0.05 to 0.4 M along with increased impregnation from 0.1 to 1.2 g bentonite, correspondingly but the additional amount of TOPO do not give any outcome on the impregnated TOPO. The 0.4 M of TOPO concentration is the optional concentration that is used for the other experiments of bentonite impregnation.

#### Effect of impregnation contact time:

Various experiments were approved at different time ranges from 0.5 to 8hr and amount of TOPO 0.4 M in acetone, at 25°C temperature with stirring speed of 200 rpm, and solvent/bentonite, (V/ m, ml/ g), ratio of 10 ml/ 1.0 g, all these test just to examine the effect of time onto the concentration of TOPO impregnated, g/1.0 g. The (Figure 6) illustrate that, at initial hour the impregnation of TOPO solvent proceeds and it was reached on a stage where 1.05g TOPO/1.0g bentonite, then after 4 hrs it gradually increased from 1.28g/1.0g bentonite. Moreover, the increased time of impregnation and TOPO impregnation at the concentration of 1.29g/1.0g bentonite which reveals that there are some slight impacts on the impregnation process of bentonite when gradual increase in time more than 4 hrs. For that reasons, the 4 hrs time signifies the favored chemical reactions specifically to take full advantage from the impregnation process of bentonite.

#### Effect of TOPO solvent/ Bentonite, (V/ m, ml/ g), ratio

The relative amount of bentonite, (V/m, ml/g) has some effects of TOPO solvent but the concentration of TOPO impregnated, (g/1.0g bentonite) which was analyzed between the range of 4.0ml/1.0g to 20.0ml/1.0g along with constant amount of TOPO 0.4M in acetone at a 4hrs reaction time, 200rpm is stirring speed and temperature of 25°C. The obtained results (Figure 7) reveal that, the increasing amount of solvent in bentonite (V/m, ml/g) relative amount i.e. 4.0ml/10.0g, the additional concentration of TOPO impregnated (g/1.0g bentonite) ranges between 0.41 to 1.29 and the more augment of solvent in relative amount to bentonite, (V/m, ml/g) that has negligible impacts on the concentration of TOPO impregnated, (g/1.0g bentonite). In some other experimental calculations of bentonite impregnation procedures, the most significant and ideal ratio that is used to determine the solvent to bentonite, (V/ m, ml/ g), relative amount is of 12.0 ml/ 1.0 g.

#### Temperature Effect:

To investigate the influence of temperature onto the concentration of TOPO

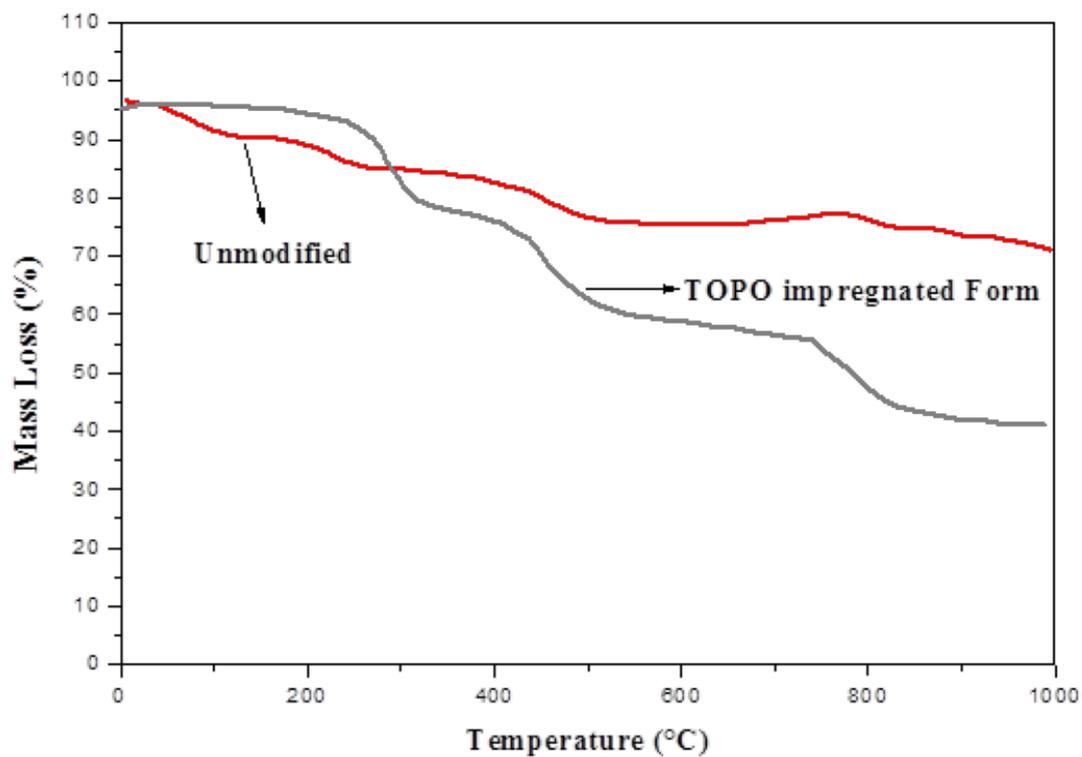


Fig. 4 . TGA thermograph of unmodified and TOPO impregnated Bentonite

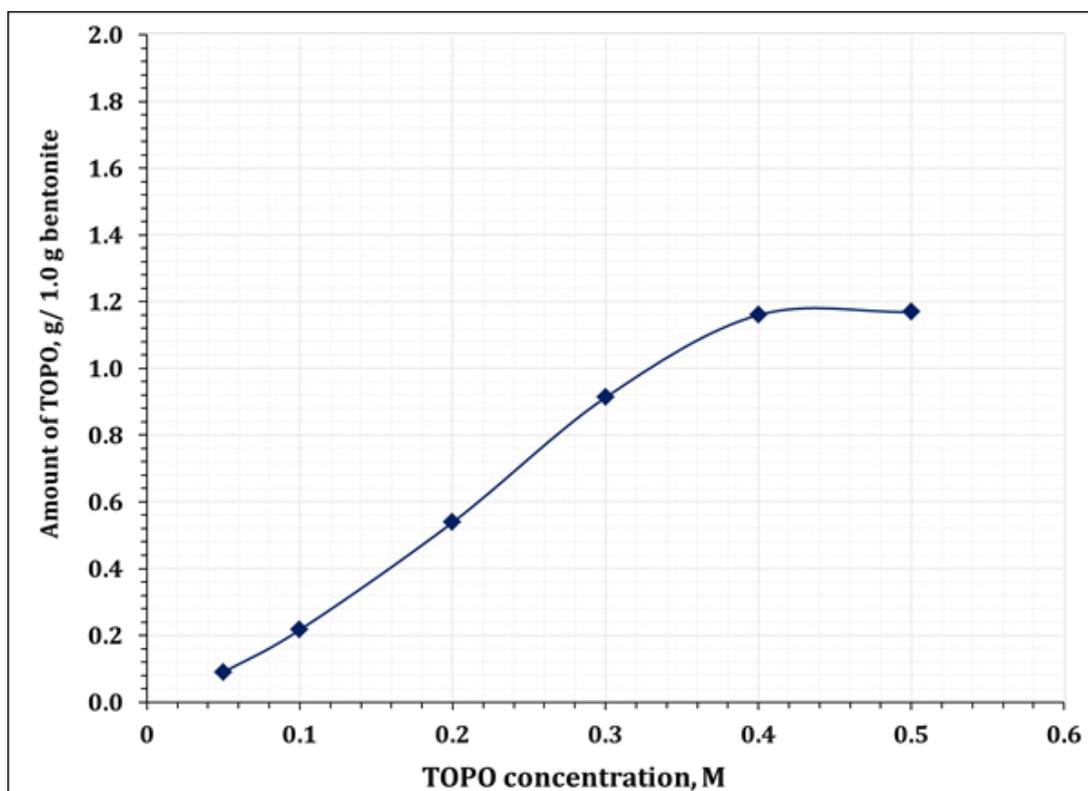


Fig. 5. Effect of TOPO concentration on amount of TOPO impregnated

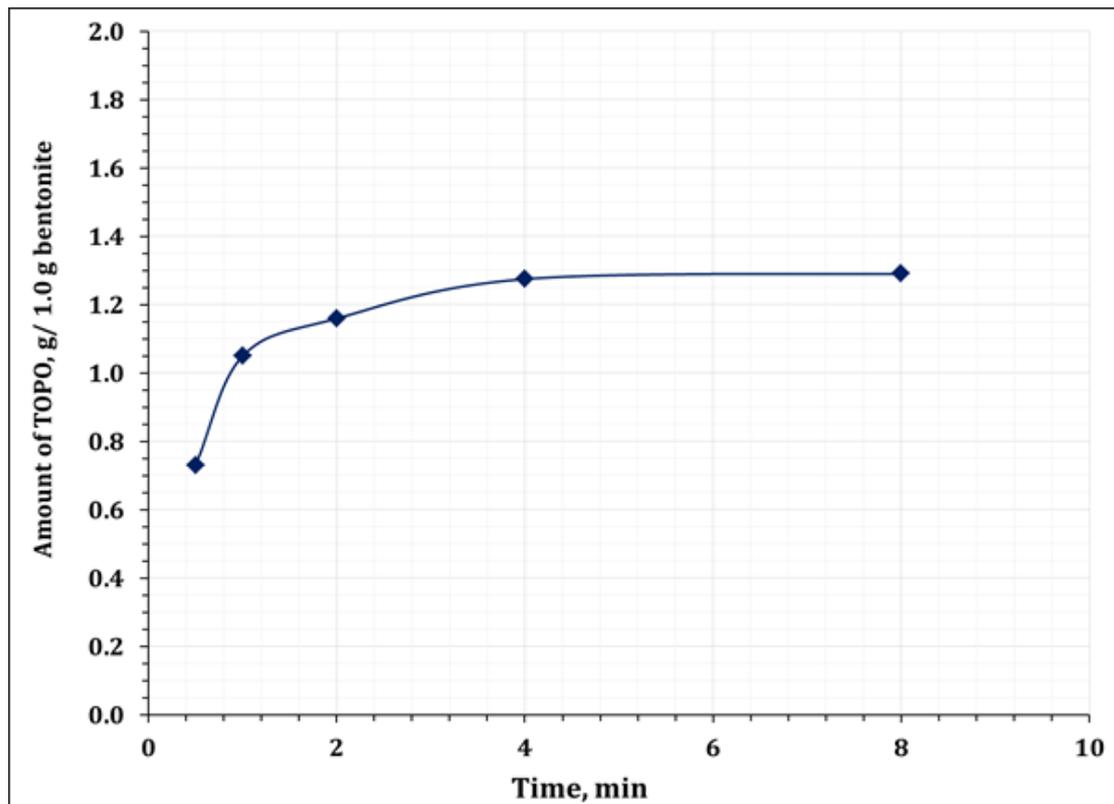


Fig. 6. Effect of time on amount of TOPO impregnated

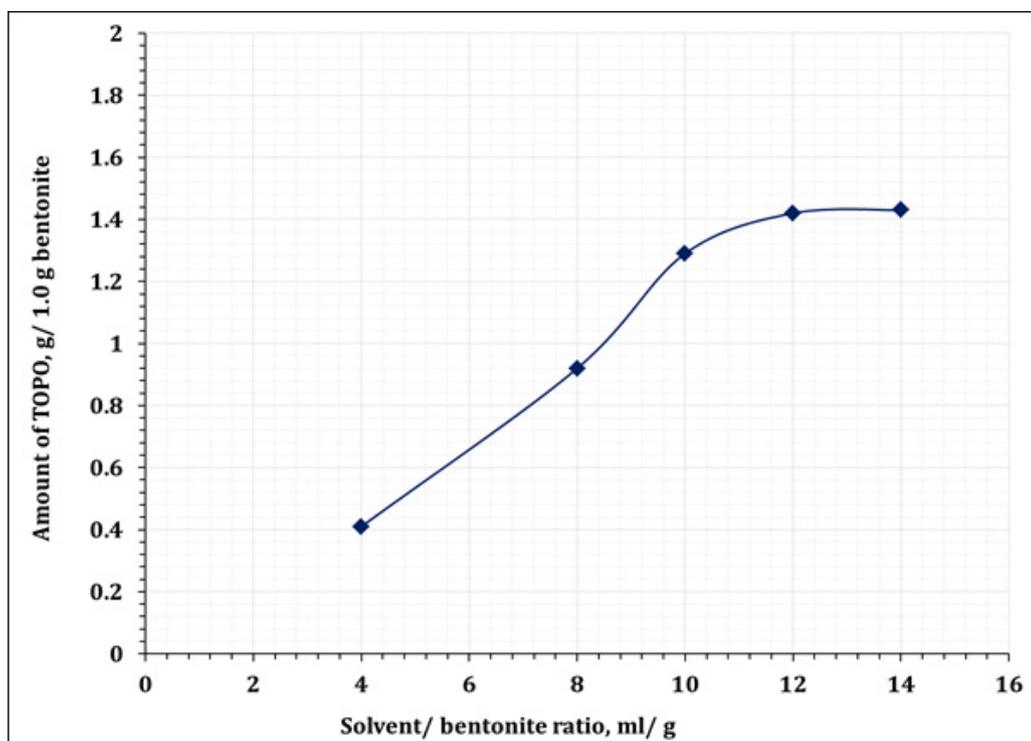


Fig. 7. Effect of Solvent/bentonite ratio on amount of TOPO impregnated

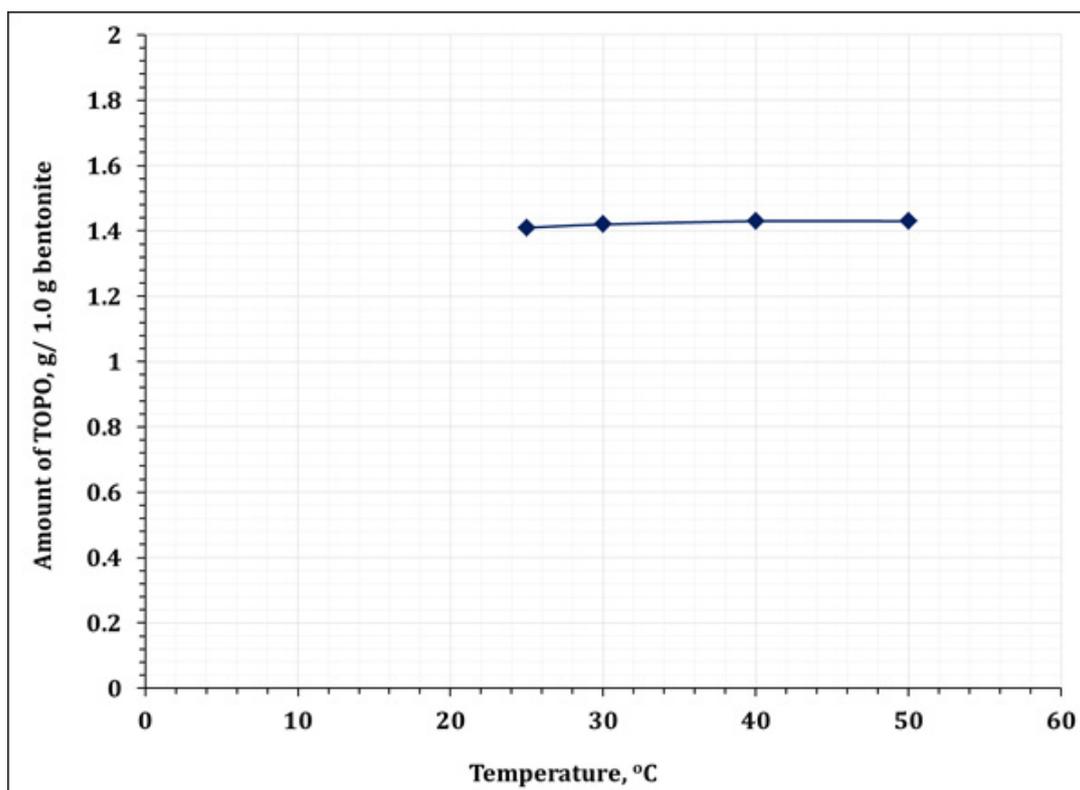


Fig. 8. Effect of temperature on amount of TOPO impregnated

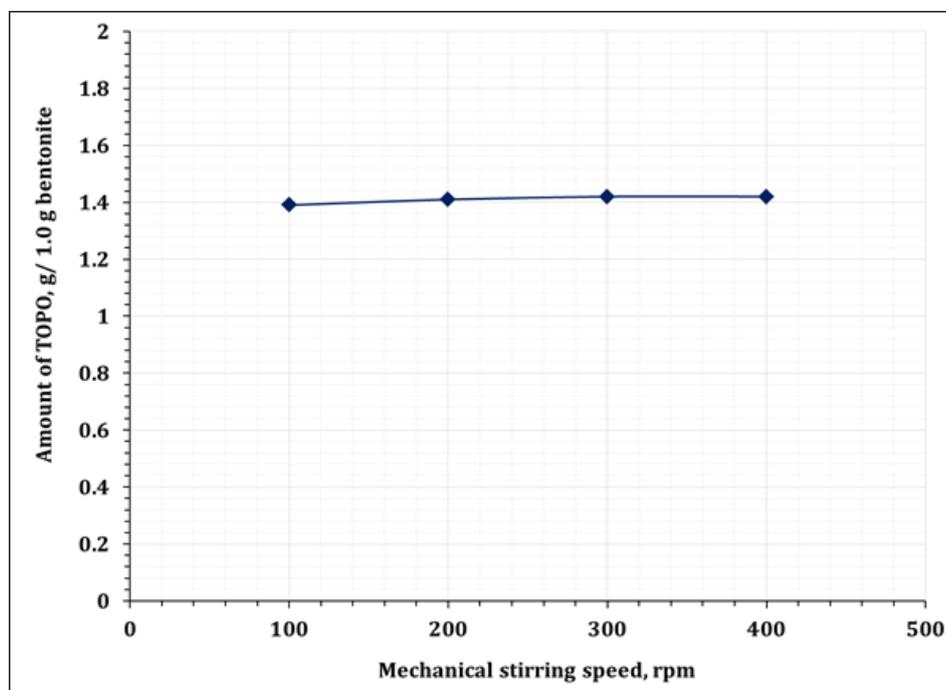


Fig. 9. Mechanical stirring speed on amount of TOPO impregnated

impregnation, (g/1.0g bentonite) various experiments were performed at different temperature ranges 25-50°C, with constant amount of TOPO 0.4M in acetone and solvent/ bentonite, (V/m, ml/g), ratio of 12ml/ 1.0 g, at 4hrs reaction time and continuous stirring speed of 200rpm at 25°C. The relation between concentrations of TOPO impregnated g/1.0 g bentonite and solvent to temperature, which is shown below in (Figure 8) as consequences of these experiments. The increase in temperature from 25°C to 50°C the amount of TOPO impregnated, (g/ 1.0 g bentonite) with increasing concentration from 1.41 to 1.43 remains ineffective at this temperature range, because moderate changes in temperature doesn't matter. Thus, various experimental processes were carried out at room temperature (25°C).

### Mechanical Stirring

Various tests were proceeded at different stirring (100-400rpm), with constant amount of TOPO 0.4M in acetone solvent/ bentonite, (V/ m, ml/ g), relative amount of 12 ml/ 1.0g, at 25°C and 4hrs of reaction time. All these calculations were done to examine the consequences of mechanical stirring speed onto the concentration of TOPO impregnated (g/1.0g bentonite). (Figure 9) shows the relation between the concentrations of TOPO impregnated g/1.0g bentonite and mechanical stirring speed of liquid. So the experimental results reveal that, when the powered stirring speed increases 100 to 400rpm and the concentration of TOPO impregnated (g/1.0 g bentonite) value increases from 1.39 to 1.42. It gives the significant information that this powered stirring speed is slightly effectual onto the increasing concentration of TOPO impregnated (g/1.0g bentonite). According to above information, a point becomes clear that 200rpm stirring speed is appropriate.

### Uranium Adsorption Studies

#### Time effect on uranium adsorption

The adsorbed amount of uranium by using TOPO impregnated bentonite increases directly at initial 5min with the removal efficiency of uranium is 73.9% that expressed in (Figure 10), subsequently to attain the equilibrium position time factor is increased from 5 to 30min with 78.3% removal efficiency of uranium. This

presentation could be clarified where the sites of surface adsorption were exhausted due to the dependence on lapse of time. The empty sites were considered as problematic complex residual which occupied with positive ions due to unlike attraction between the solid adsorbent and bulk forms [23].

#### pH effect on uranium adsorption

The adsorption experiments were performed to examine the initial pH influence and efforts were made during the experiments (in acidic medium just to inhibit the possible precipitation) as the reaction proceeded with the addition of 0.2 g of TOPO-B to 10 mL percolated liquor which holding the 250 ppm amount of uranium. By using the 0.1N HCl or 0.1N NaOH solutions, the pH of the solution was modified from 0.73 to 1.7. So the obtained outcomes indicated in (Figure 11) by increasing the pH values from 0.73 to 1.71 the slight decrease occurs in absorption efficiency from 78.26 to 69.57%. Similarly, some changes may be happened by enhancing the pH value, the protonated affinity of adsorption sites decrease and many complex anions sites developed. Further, there is a competition between the number of protons ( $H^+$ ) and uranium (VI) in sorption decreasing sites[24].

#### Effect of temperature on uranium adsorption

The temperature effect from 20–50 ±1°C was studied on adsorbed uranium from aqueous solution by using TOPO impregnated bentonite. The reaction conditions which were used the initial amount of uranium (VI) in leach liquor of 250ppm and the adsorbed amount of 0.2g/10ml with 30min contact time. The percentage (%) efficiency of uranium adsorption reduces as the temperature range boosted and the nature of reaction was exothermic, this is explained in (Figure 12). Moreover, the low temperature is favorable for the elimination of each metal ion from solutions. These obtained results were established and corresponding with research of uranium (VI) removal from aqueous solution on adapted bentonite[25]. As adsorption reduces, when temperature increases and it's reason lies behind the relative improvements of metal charged species which have the avoidance ability from the

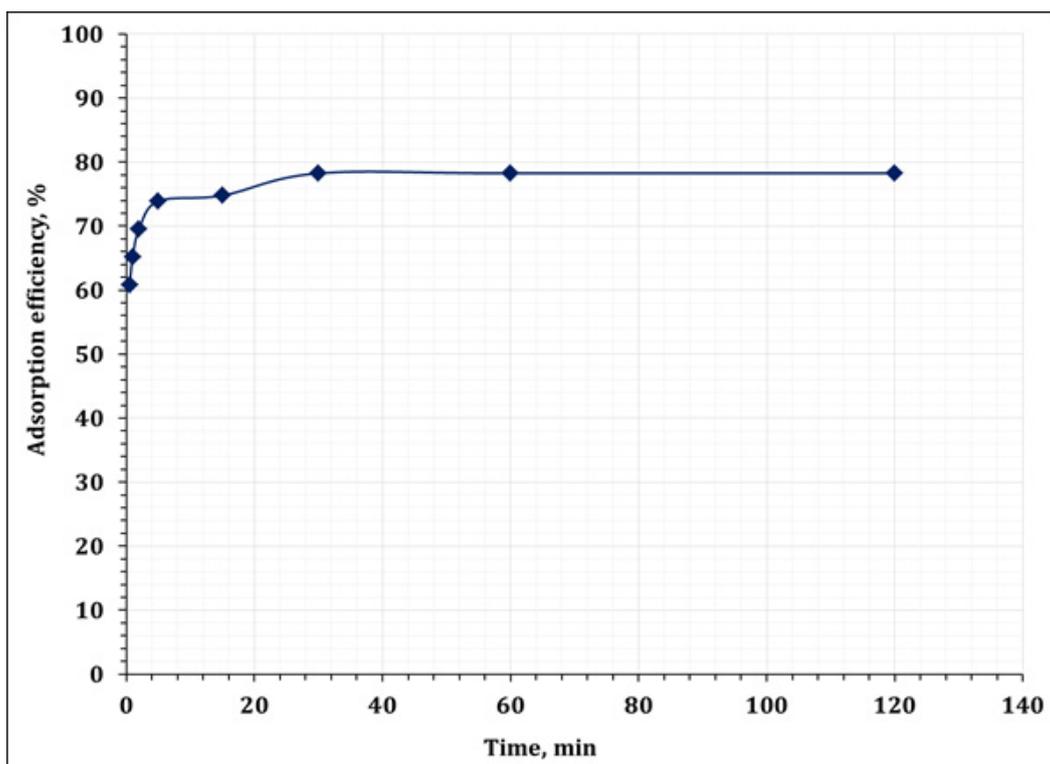


Fig. 10. Effect of time on adsorption of uranium

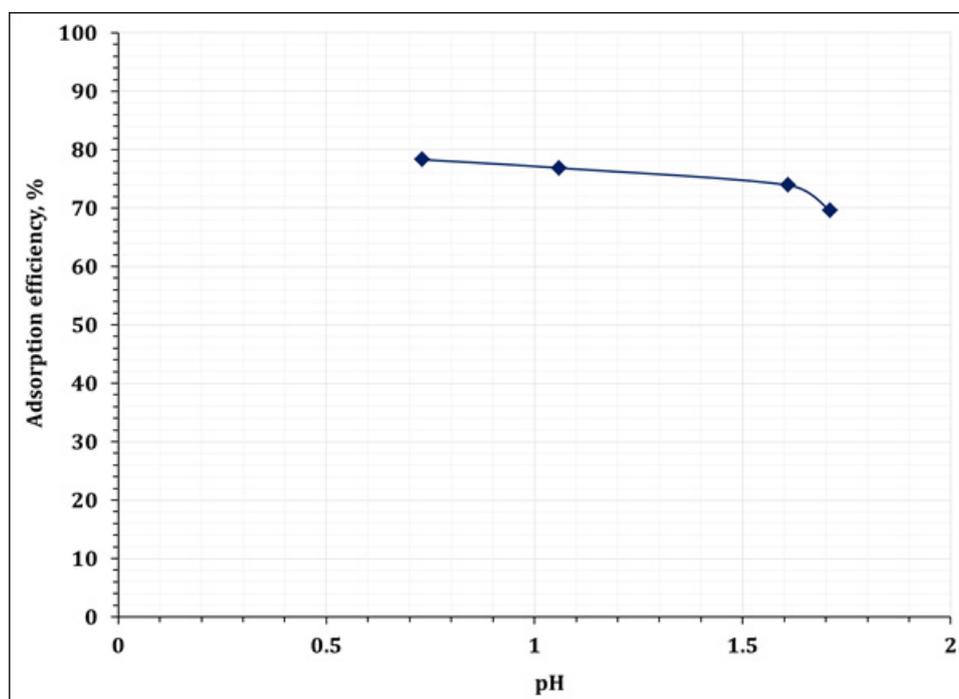


Fig. 11. pH effect on adsorption of uranium

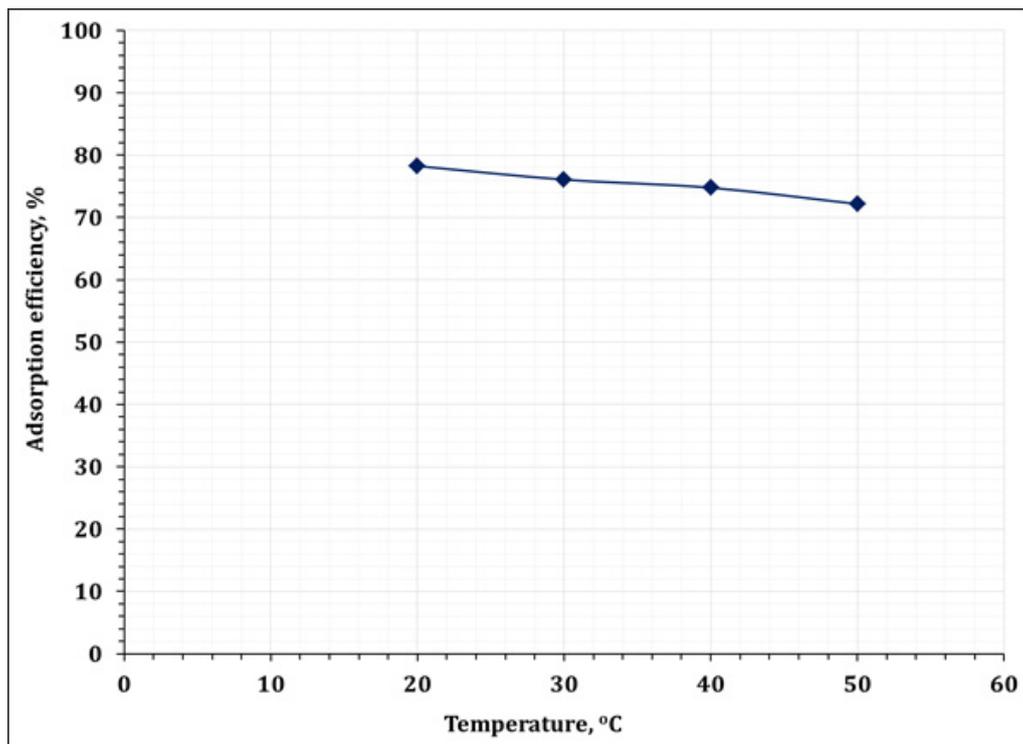


Fig. 12. Effect of temperature on adsorption of uranium

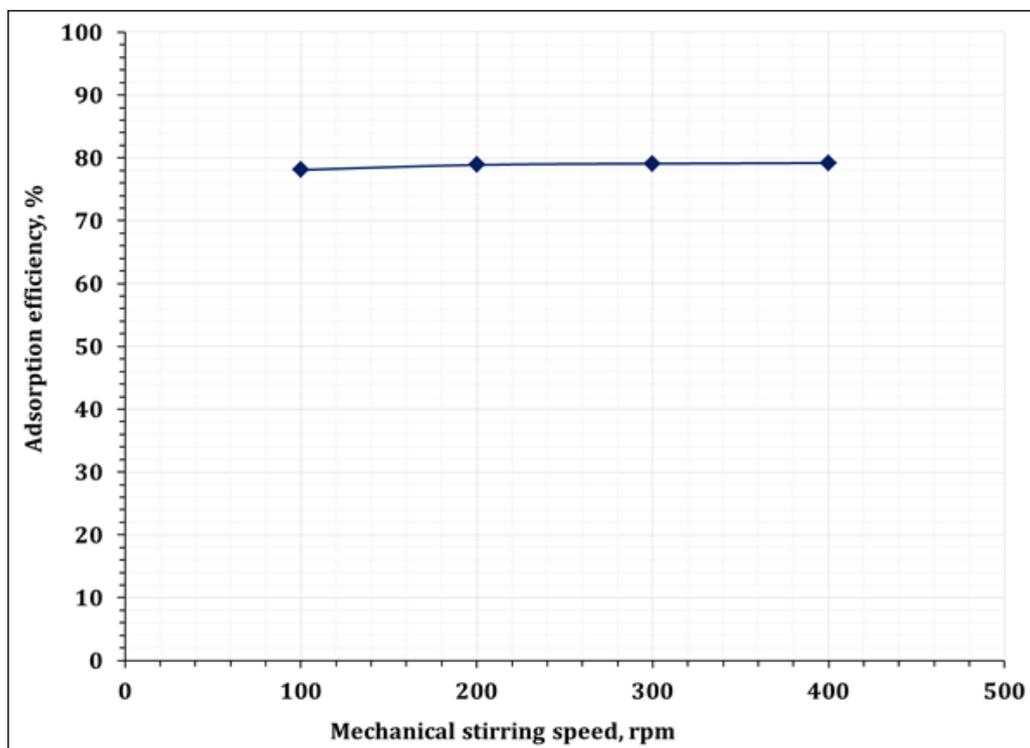


Fig. 13. Effect of mechanical stirring speed on adsorption of uranium

solid form to bulk state and it may be due to weak modified attractions amid the reactive sites of adsorbent and species of adsorbate along with the infectious elements of adsorbed form[26].

#### Effect of Mechanical stirring speed:

The influence of mechanical stirring rate was analyzed on uranium sorption method from percolated liquor on TOPO impregnated bentonite and also on variable stirring speed from 100 to 400rpm. Though, some other parameters were fixed at mud concentration by adding 0.2g/10ml, with 30min of contact time at 25 °C. A relation amid sorption efficiency of uranium and powered stirring rate reveals that the stirring speed enhanced from 100 to 400rpm, with minor changes which were observed from 78.1 to 79.2% in efficiency of uranium process and these conclusions of experiments are given below in (Figure 13). Hence, the changed mechanical stirring rate has some mild influence on uranium sorption process. So, the more favorable preferred stirring rate was 400rpm in sorption process.

#### Uranium (VI) concentration effect:

Number of experiments were performed by attaining the equilibrium concentration of 0.2g TOPO impregnated bentonite, 10ml of sulphate from percolated liquor solutions which consisting different concentrations of uranium charged species vary from 100 to 1500ppm, at 25 °C for 30min contact time, these calculations was done just to investigate the influence of initial concentration of uranium and adsorption efficiency on TOPO impregnated bentonite. A relationship between uranium adsorption efficiency and uranium ion concentration was explained in (Figure 14). According to above information, it was approved clearly that adsorption efficiency of uranium reduced with escalating its primary concentration. Moreover, the modified bentonite has the adsorption capacity for increased uranium (VI) concentration with some rising initial concentration of uranium and this outcome is harmonizing to that reported literature by Kütahyalı and Eral (2004) and the work based on discriminating adsorption of uranium from liquor solutions by using the activated element of carbon which was synthesized from charcoal with the help of chemical reactions[5].

#### Effect of adsorbent amount:

A chain of adsorption trails was carried out by using various modified clay concentration ranges from 0.02 to 0.3g clay/10ml in addition to variable parameters which were kept constant as at 250ppm, initial amount of uranium, contact time of 30min and at 25 °C. The collected information is recorded graphically in (Figure 15) with the help of this data observations can be clear that adsorption efficiency of uranium enhanced comparatively with rising adopted clay concentration. The rising concentration of impregnated adsorbed clay beyond the amount (dose) of 0.2g/10ml, which provide weak developments in percentage adsorption efficiency of uranium, due to the addition of unwanted reactive sites more than the fixed amount (0.2g) of uranium in the constant fractions (10ml) of solution.

#### Adsorption kinetics

To study the nature of adsorption (Physiosorption or chemisorption), the adsorption kinetics was studied for the adsorption of uranium (VI) by using TOPO impregnated bentonite. The process of adsorption is amalgamation of resistance series due to mass transfer, diffusion and intraparticle diffusion which van dominated through one stage either pseudo first-order[27] and pseudo second order kinetics[28]. The kinetic activity for the adsorption of uranium (VI) ions by using TOPO impregnated bentonite was analyzed from pseudo first (Lagergren) and second order (Ho and McKay-1999) that are represented in equation respectively.

$$\text{Log}(q_e - q_t) = \text{Log} q_e - K_2 / 2.303 t$$

$$(t/q_t) = 1/(K_2 q_e^2) + 1/q_e t$$

Where  $q_e$  and  $q_t$  in (mg/g) corresponds to equilibrium adsorption capacity and at time (t),  $K_{p1}$  ( $\text{min}^{-1}$ ),  $K_2$  ( $\text{g}/(\text{mg min}^{-1})$ ) represents the rate constant of pseudo first and pseudo second-order kinetic model. The linear plots of both pseudo first and second order are shown in Figure (16, 17). Regarding as kinetic study, it was observed that the pseudo second order kinetics study is better fit for uranium adsorption, which indicate that chemisorption behavior. The linear regression coefficient ( $R^2$ ) and  $q_e$  values for pseudo second order is better than pseudo first order. The modeled

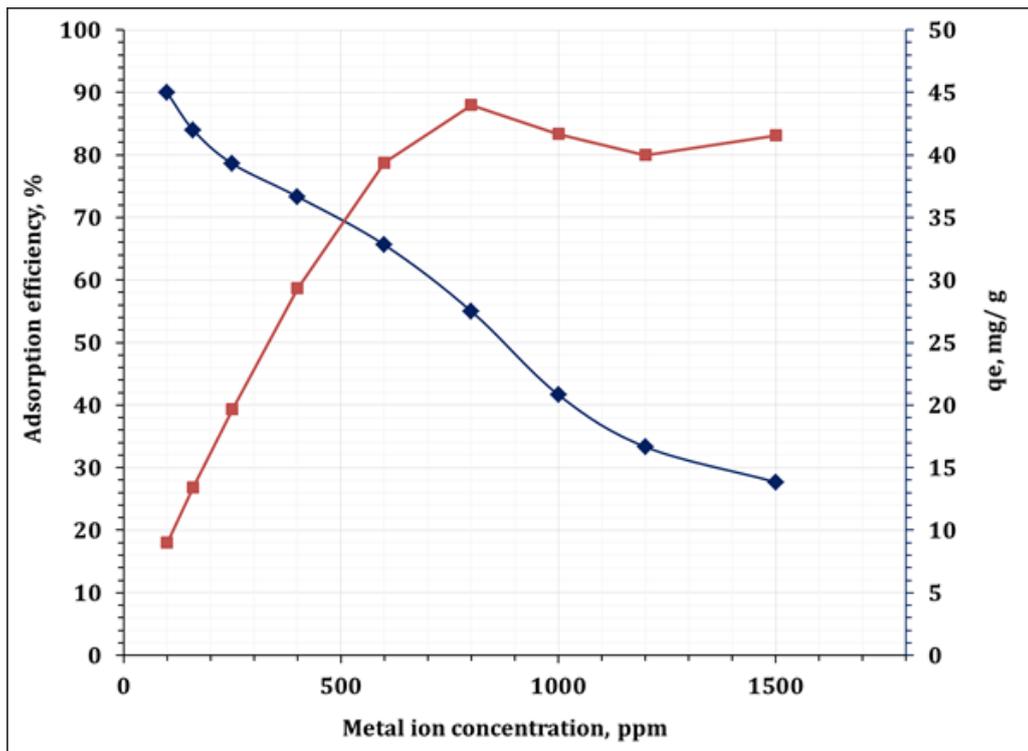


Fig. 14. Effect of uranium concentration on adsorption of uranium

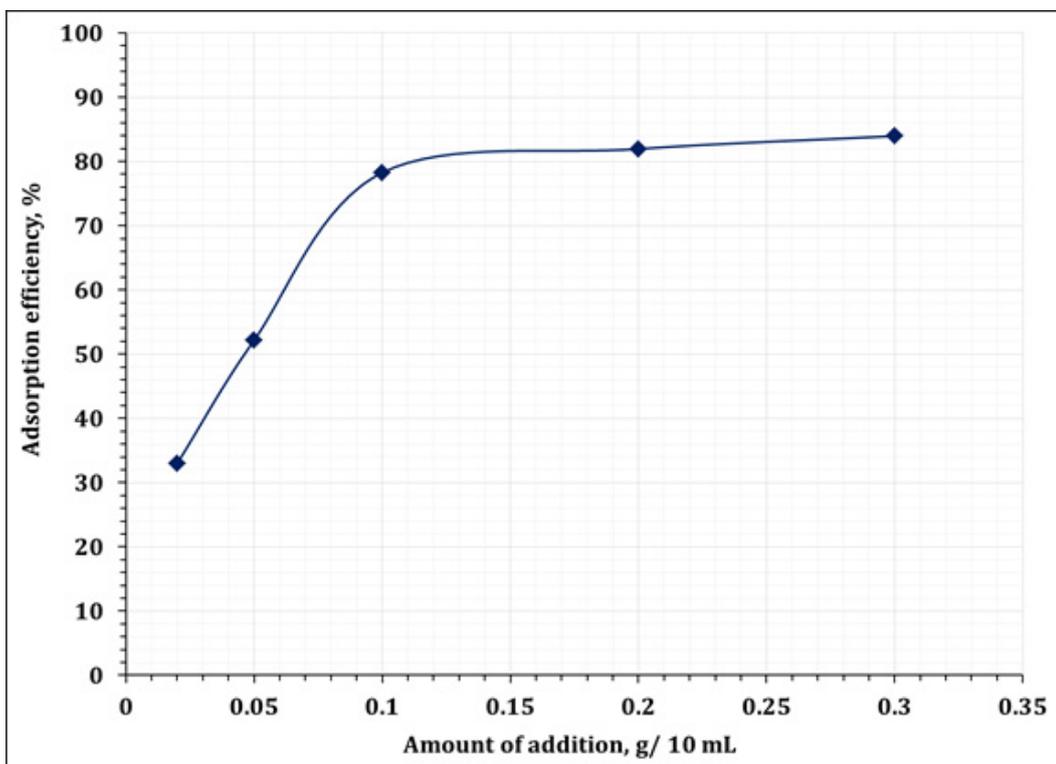


Fig. 15. Effect of adsorbent amount on adsorption of uranium

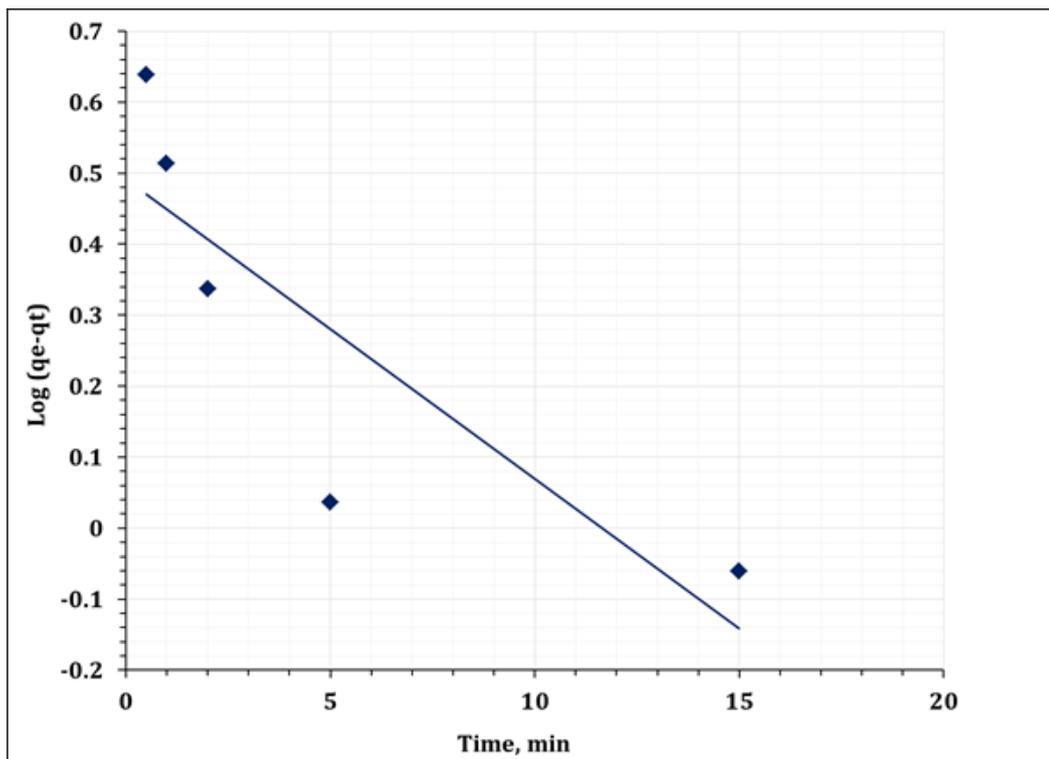


Fig. 16. Lagergren plot for adsorption of uranium using TOPO impregnated bentonite

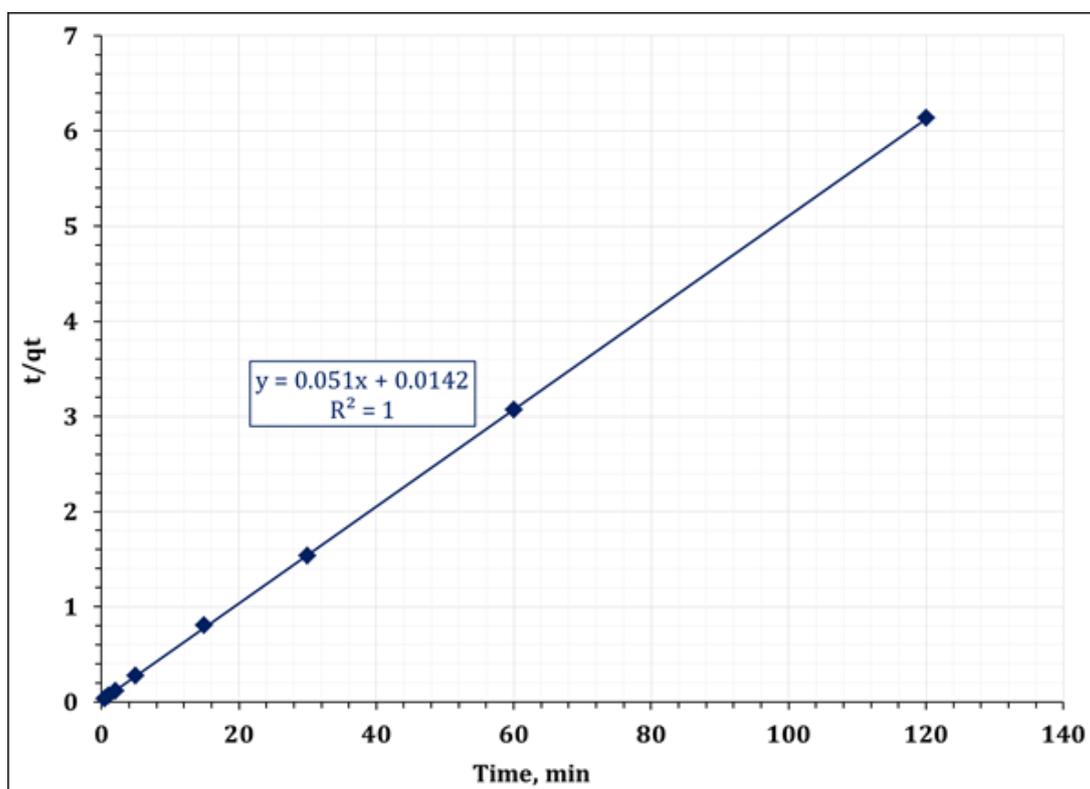


Fig. 17. Pseudo second-order plot for uranium adsorption using TOPO impregnated bentonite

curves using the  $q_e$  and  $k_s$  parameters in (Table 2) were compared with the experimental points that has also been reported that the pseudo-second-order kinetic model fit better uranium sorption data than that of the pseudo-first-order model[29]. The accuracy of the pseudo second order model in predicting kinetic data suggests that the rate of uranium sorption may be prearranged by chemisorption mechanism.

## Theory of adsorption isotherms

### Langmuir isotherm

For the selection of adsorbent and equilibrium method for adsorption, the isotherm models play crucial role. These isotherm models are very significant for adsorption as they give information about nature of adsorption (homogeneous and heterogeneous). Langmuir (1918) and Freundlich (1906) models were applied for investigating the homogeneous and heterogeneous nature respectively. The linear equations of Langmuir isotherm and Freundlich isotherm models are shown below respectively;

$$\frac{C_e}{q_e} = \frac{1}{b q_{\max}} + \frac{C_e}{q_{\max}}$$

$$h q_e = h K_F + \frac{1}{n} h C_e$$

Where  $q_e$  represents the adsorbed amount of uranium (mg/g),  $C_e$  represents the equilibrium conc. of uranium (mg/L),  $q_{\max}$  and  $b$  correspond the monolayer capacity of adsorption and Langmuir constant respectively.  $K_F$  and  $n$  represents the Freundlich constants correlated with adsorption capacity and intensity respectively. Figures (18, 19 and 20) and Table (3) shows linear plot of Langmuir and Freundlich isotherms models and correlation coefficient ( $R^2$ ). The effect of isotherm shape can be used to predict whether a sorption system is "favorable" or "unfavorable" both in fixed-bed systems [30], as well as in batch processes as shown in (Figure 18-19). According to [31], the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter  $K_R$ , which is defined by the following relationship:

$$K_R = \frac{1}{1 + K_a C_0} \quad (4)$$

where  $K_R$  is a dimensionless separation factor,  $C_0$  initial metal ion concentration (mg/L) and  $K_a$  Langmuir constant (L/mg). The separation

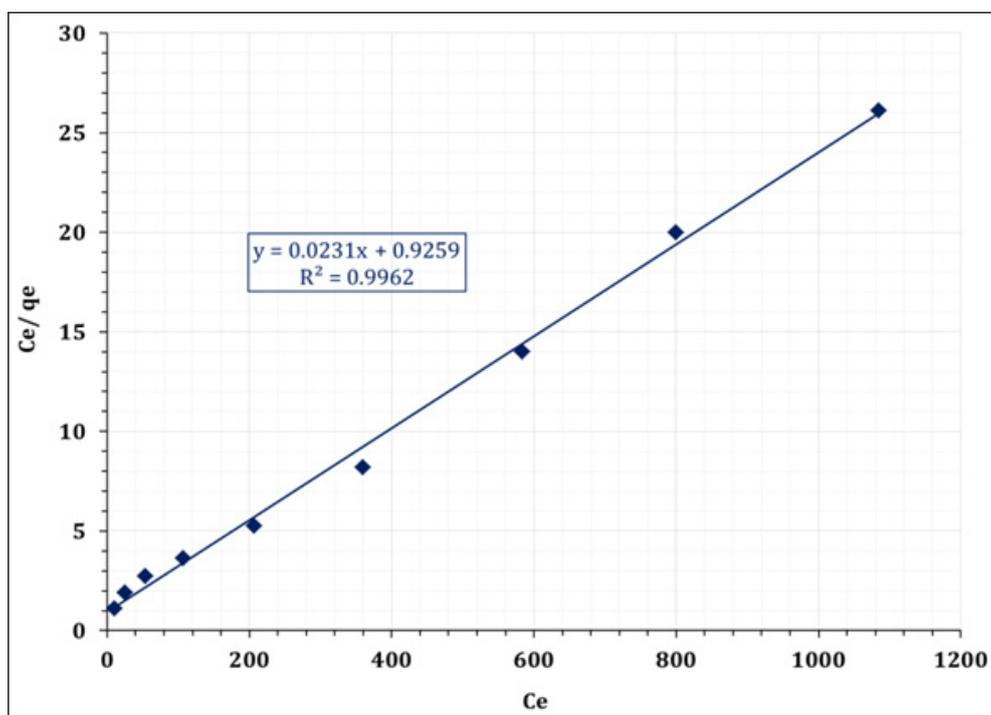


Fig. 18. Langmuir adsorption isotherms for uranium (VI)

**TABLE 2** The values of the pseudo second order ( $k_2$ ) and their corresponding correlation coefficient ( $R^2$ )

Pseudo second-order			
$K_2$ ( $\text{min}^{-1}$ )	$q_{e_{\text{cal}}}$ (mg/g)	$q_{e_{\text{exp}}}$ (mg/g)	$R^2$
0.20	18.05	18.00	1.00

**TABLE 3** Langmuir and Freundlich isotherm constants for uranium (VI) adsorption onto TOPO impregnated bentonite.

<b>Freundlich isotherm model</b>	$K_f$ (mg/g)		4.91	
	$n$		2.94	
	$R^2$		0.89	
<b>Langmuir isotherm model</b>	$Q_m$ (mg/g)		43.29	
	$b$ (L/mg)		0.025	
	$R^2$		0.99	
	<b>RL</b>	<b>Co</b>		
		100		0.286
		160		0.200
		250		0.138
		400		0.091
		600		0.063
		800		0.048
1000			0.039	
<b>Dubinini-Radushkevich (D-R) isotherm model</b>	$\beta$ ( $\text{mol}^2 \text{KJ}^2$ )		24.50	
	$q_m$ (mmol/g)		30.67	
	$R^2$		0.64	

factor  $K_R$  value confirms the adsorption to be unfavorable ( $K_R > 1$ ), linear ( $K_R = 1$ ), favorable ( $0 < K_R < 1$ ) or irreversible ( $K_R = 0$ ) as shown in (Figure 20) and (Table 3).

It was observed for the collected data that the uranium adsorption by using TOPO impregnated bentonite followed Langmuir Model than Freundlich isotherm model which is the indicative of homogeneous nature of adsorption. The calculated  $q_m$  value (43.29 mg/g) through Langmuir Model is very close to experimental value for the adsorption of uranium. The maximum adsorption capacity for the adsorption of uranium by using TOPO modified adsorbent exhibits high amount of uranium was adsorbed and results are better form previous study. The value of  $R_L$  for various experiments is less than one which is indicative of favorable adsorption of uranium on TOPO impregnated bentonite.

### Adsorption thermodynamic studies

In order to investigate the spontaneity ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ), the thermodynamical parameters were applied on adsorption of uranium at equilibrium by changing the temperature. Regarding as thermodynamic study, the distribution coefficient correlates with change in enthalpy and entropy at equilibrium and optimum temperature as given in equation;

Where  $\log K_D$  correspond the distribution coefficient ( $\text{cm}^3/\text{g}$ ),  $\Delta S^\circ$  and  $\Delta H^\circ$  indicate the standard entropy and enthalpy,  $T$  is optimum temperature (K) and  $R$  represents the gas constant in (KJ/mol. K). The Gibbs free energy ( $\Delta G^\circ$ ) was determined by using standard equation as given;

The values of change in entropy and enthalpy were calculated from linear plotted

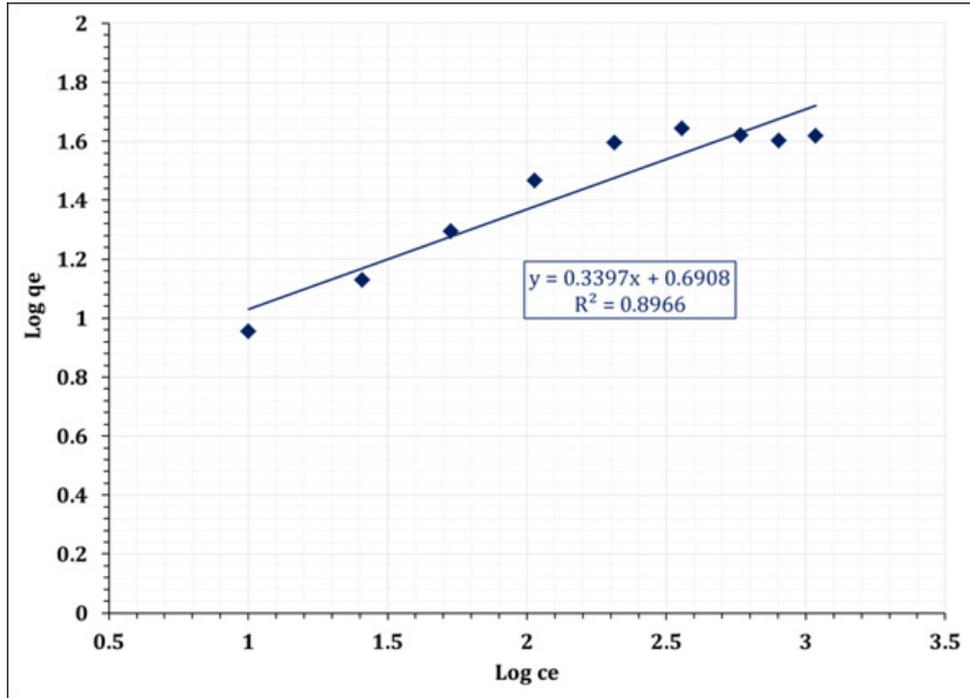


Fig. 19. Freundlich adsorption isotherms for uranium (VI) adsorption

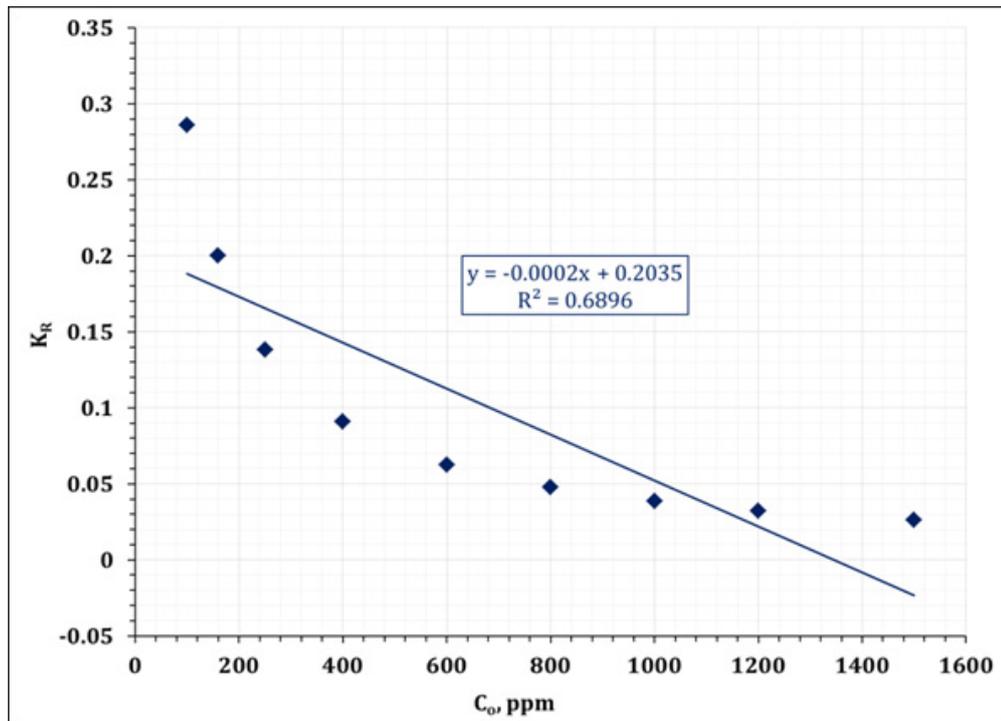


Fig. 20. Separation factor RL of uranium adsorbed

slope ( $\log K_d$  vs  $1/T$ ) as shown in (Figure 21). The calculated parameters from thermodynamics study are given in (Table 4). It is observed that the uranium adsorption onto TOPO impregnated bentonite is an exothermic process due to negative values of  $\Delta H^\circ$ . In addition the calculated value of  $\Delta G^\circ$  is negative which corresponds to spontaneous adsorption process and more positive value of  $\Delta S^\circ$  (standard entropy) indicates the randomness behavior of adsorbent after adsorption of uranium [32].

#### Effect of elution and Adsorbant reusability

Take 0.1g from loaded uranium onto impregnated bentonite (4mg U/2g material) and add 10ml from (0.5M HCl, 0.5M HNO<sub>3</sub>, 0.5M H<sub>2</sub>SO<sub>4</sub>, 0.1M NaCl and H<sub>2</sub>O) and stirring for 60min at room temperature. Desorption tests were investigated through TOPO impregnated sample (0.1 g) and 0.5 M eluent solution (10 mL). The systematically calculated efficiency (96.5%) reveals that H<sub>2</sub>SO<sub>4</sub> is significant solution for elution from uranium loaded onto modified bentonite as shown in Table 5. Regarding as reusability of adsorbent for elution of uranium ions has been estimated by using H<sub>2</sub>SO<sub>4</sub>

(regenerating agent), as after kinetic study the adsorbent (0.05g) was mixed with acidic solution of 250 mg/L (10mL) for 120min and washed with deionized water to maintain pH 5-6. For ensure of complete recovery of adsorbed ions on modified material the uranium ions in regenerating solution was determined.

#### Conclusion

New solid phase extraction and cost effective method has been developed via TOPO impregnated bentonite for investigating uranium adsorption from leach liquor acidic solution. The results of present study showed promising achievement (78.3% uranium) under optimized operating conditions. The current study showed direct dependence of adsorption efficiency with time, adsorbent weight and mechanical stirring and is indirectly related to pH and concentration of uranium. Adsorption kinetics study follows pseudo-second-order-kinetic model (rate constant 0.20 g/mg min<sup>-1</sup>) which shows chemisorption behavior of uranium adsorption from leach liquor. The isothermal results follow Langmuir model than Freundlich model with maximum uranium

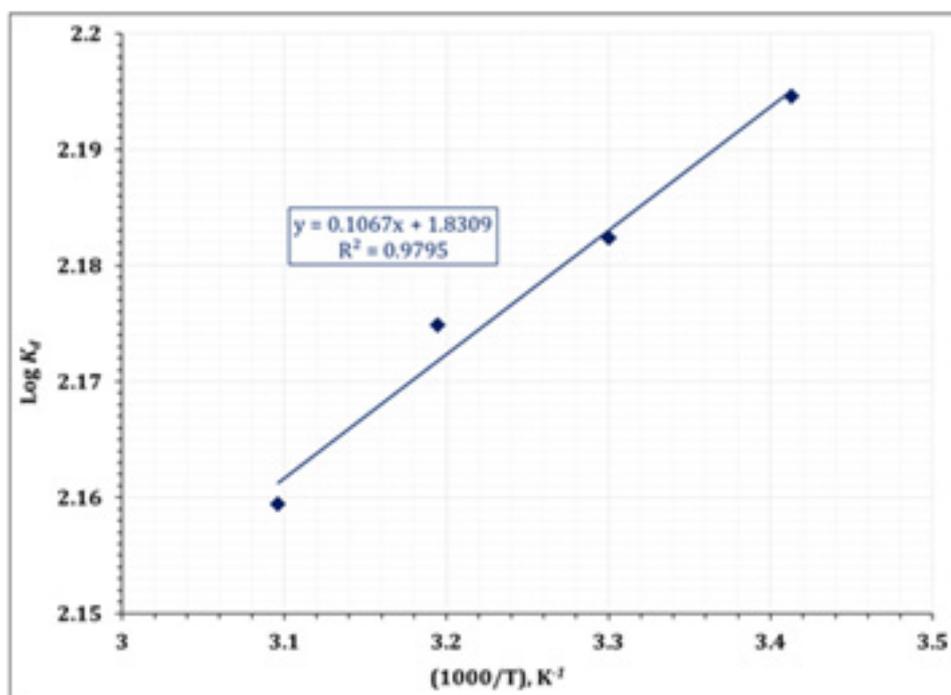


Fig.21 Plot of LogK<sub>d</sub> versus 1/T for uranium sorption onto TOPO impregnated bentonite

**TABLE 4** Thermodynamics parameters for uranium (VI) adsorption on B-TOPO.

	$\Delta G$ (kJ/ mol)				$\Delta H$ (kJ/ mol)	$\Delta S$ (J/ mol K)
	20 °C	30 °C	40 °C	50 °C		
U	-12.31 ± 0.04	-12.66 ± 0.04	-13.03 ± 0.04	-13.35 ± 0.04	-2.04 ± 0.02	35.04 ± 0.5

**TABLE 5:** Effect of uranium elution efficiency from the loaded B-TOPO

Eluent	efficiency %
0.5 M HNO <sub>3</sub>	66.6
0.5 M HCL	40
0.5 M H <sub>2</sub> SO <sub>4</sub>	96.6
0.1M NaCl + 0.5 H <sub>2</sub> SO <sub>4</sub>	55.6
H <sub>2</sub> O	16

adsorption capacity predicting the homogeneity in system. However present data fits very well with isothermal (Langmuir Model where  $0 < R_L < 1$ , shows favorable adsorption) and thermodynamic studies (exothermic and spontaneity in system). The synthesized adsorbent TOPO impregnated into bentonite would be a promising candidate for solid phase extraction of uranium from sulfate leach liquor solution holding uranium.

#### **Conflict of Interest:**

All the authors have no conflict of interest.

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