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Analytical and Isothermal Studies of Equilibrium Sorption of Cr (VI) and p-nitrophenol onto organokaolin

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Abstract

Removal of toxic heavy metals and organic pollutants from contaminated water is of great interest in the field of water handling. Organoclays have unique adsorption behavior towards hydrophobic organic contaminants. Thus, the present study focus on separation of Cr(VI) from Cr(III) and *p*-nitrophenol (PNP) from the aqueous solutions using new organokaolin synthesized for the first time from local clay. The method is based on using Iraqi's kaolin in the presence of hexadecyltrimethyl ammonium bromide as surfactant. Infrared spectroscopy and x-ray diffraction are employed to characterized innovated clay. The optimum adsorption conditions for the removal of Cr(VI) and PNP were: mass of organokaolin, 0.5 g; pH, 1 & 11, Temp. 15 & 35 °C; contact time, 80 min for the removal of Cr(VI) and *p*-nitrophenol, respectively. Under the optimum conditions, removal rate of 96%for the adsorption of Cr (VI) and PNP was achieved. Higher value of r^2 refers to the goodness of fitting of Langmuir equation rather than Temkin and Freundliche equations for the sorption of Cr(VI) on the organokaolin. From the calculated thermodynamic parameters, ΔG, ΔH and ΔS values, the adsorption process has been found endothermic in nature. The developed method was applied successfully for the analysis of 15 water samples collected from areas of Baghdad. Good recoveries were obtained ranging from 97.4-101.1% (RSD < 2.15%) and 97.8-100.1% (RSD= 1.8%) for Cr(VI) and PNP, respectively.

KEYWORDS: Adsorption, Organokaoline, Chromium, p-nitrophenol, Clay.

Introduction

Water pollution is one of the most serious problems due to occurrence of inorganic and organic wastes that discharged to the aquatic environment either in water-soluble or insoluble forms. Therefore, elimination of toxic heavy metals and organic pollutant from wastewater and water becomes an important environmental concern for water pollution and human health protection. Moreover, difficult degradation and accumulation of heavy metals in living organisms cause various diseases and disorders while the organic

pollutants disorder to biological degradation [1, 2]. Among the organic and heavy metals pollutants, phenol and chromium (Cr) are considered the most toxic and hazardous to the environment.

Chromium is the common contaminant in groundwater and soil, especially in industrial regions. It is classified by the US Environmental Protection Agency (EPA) as one of 126 high-priority pollutants. Furthermore, Cr is also listed among the 25 hazardous substances thought to pose the potential threat to human health at priority superfund sites. Some chromium compound, such as $Cr_2O_7^{2-}$ is carcinogenic and known as a most toxic species with high mobility [3], while Cr^{3+} is less mobile and less available to biological systems [4].

Phenol compounds such as *p*-nitrophenol (PNP) is considered toxic and has been implicated in carcinogenesis, teratogenesis and mutagenesis. It has also been listed by the US EPA as priority contaminants. In addition, it is harmful to plants, animals and humans health, even at low concentrations. In case of acute exposure to PNP, it is known to cause blood disorder, liver and kidney failure, anemia, skin and eye irritation and systemic poisoning [5,6]. Due to its slow degradation, PNP readily enter the environment by agricultural runoff of pesticides, effluents from oil refineries and plastic industries [7,8]. Consequently, attention has paid to develop method for the effluent treatment in the era of industrial and social development.

Different methods for the water treatment have been proposed. The principle of pollutant removal process generally is based on precipitation and coagulation, chemical oxidation, sedimentation, filtration, adsorption, osmosis, ion exchange reduction, ion exchange, membrane technologies and electrolysis [9-13]. Among these techniques, adsorption technology using solid adsorbents shows potential as one of the most efficient methods used extensively for the removal of organic and inorganic micropollutants. Adsorption has advantages over the other methods because of simple design and can involve low investment in term of both initial cost and land required. Various absorbents were used such as activated carbon [14], cement-based materials [15] biomass [2] synthetic resins [16], multi-walled carbon nanotubes [17] clays and clay mineral [18,19]. The sorption capabilities of clay minerals in particular, come from their high surface area and exchange capacities. [20]. In addition, negative charge on the structure of clay minerals gives clay the capability to be modified by surfactant. In general, clay minerals can be modified using a variety of chemical/physical treatments to achieve the desired surface properties for best immobilization of diverse contaminants. Furthermore, modification of the clay minerals with organic substances such as quaternary ammonium compounds results in products commonly known as organoclays (OC). The modification enhances the affinity of OC toward diverse pollutants since it involves changing in the nature of clay mineral from hydrophilic to hydrophobic [4].

OC formed by replacing inorganic cations (sodium and calcium) that present on the surfaces and interlayer spaces of clays by the nitrogen end of a quaternary amine [21-24]. A quaternary ammonium salts such dimethyl ammonium, methyl benzyl ammonium, dibenzyl methyl ammonium, and benzyl dimethyl ammonium quaternaries [23] are the most commonly used as organic compound to modify clays. These salts contain organic nitrogen in the center of molecular structure attached with four organic groups.

Therefore, the surface active side becomes cationic and capable to coordinate with other compounds which preferred for the adsorption process. Moreover, the hydrophobic property makes OC more attractive to poorly water-soluble organic molecules [25].

Thus, in this study a new organoclay called organokaolain was chemically modified by mixing Iraqi's kaolin with hexadecyltrimethyl ammonium bromide (HDTAB) as surfactant (Figure 1). The optimum conditions for the adsorption and removing of PNP and Cr(VI) will be evaluated. Moreover, isothermal study will perform using Langmuir, Temkin and Fruinlich equations.

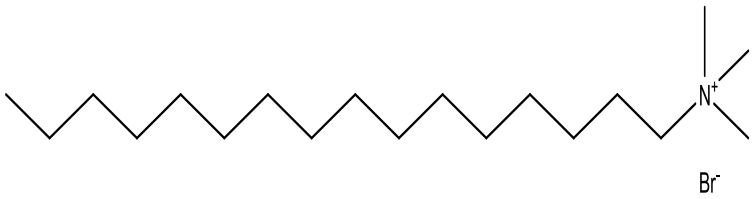


Figure 1. Chemical structure of HDTAB

Experimental

Chemicals and materials

All chemicals, solvents, reagents used were of analytical grade: hydrochloric acid (HCl) 37%. Sodium hydroxide (NaOH), potassium chromate (K_2CrO_4), hexadecyltrimethyl ammonium bromide were purchased from Sigma–Aldrich (St. Louis, MO, USA). Kaolin clay was obtained from Geological Survey and Mining (Baghdad, Iraq). The composition of kaolin clay is shown below:

Constituent	SiO_2	Al_2O_3	L.O.I	Fe_2O_3	TiO_2	Na_2O	MgO	CaO	K_2O
Wt%	48.57	35.05	11	1.56	1.19	0.96	0.77	0.6	0.08

L.O.I, Loss on ignition

Instruments

The spectrophotometer model was Double Beam UV-Visible recording Spectrophotometer (Shimadzu, UV-260). Electronic balances (Sartorius Lab. CE, Germany) and FTIR spectrophotometer equipped with Attenuated total reflection (ATR), Shimadzu, 8400S (Japan). pH meter (WTW pH 7110, Germany). X- Ray diffraction Shimadzu, 6000 (Japan). AAS, Shimadzu 670, Japan.

Preparation of solutions

Approximately 3,650 µg mL^{-1} of stock solution of HCl (37%) was prepared by transferring aliquot volume of concentrated acid into 250 mL calibrated flasks.

Approximately 4,000 µg mL^{-1} of sodium hydroxide was prepared by dissolving appropriate weight of sodium hydroxide in distilled water and made up into 250 mL calibrated plastic flask.

Stock solution of 1000 µg mL^{-1} of Cr(VI) was prepared by dissolving 3.727 g of K_2CrO_4, in distilled water and made up into 500 mL calibrated flask.

A stock solution of 1000 µg mL^{-1} of PNP prepared by dissolving 1 g of *p*-nitrophenol in distilled water and diluted to 1000 mL with distilled water in calibrated flask.

Preparation of organokaolin:

4 g of kaolin was washed first using 100 mL distilled water then heated at 40-80°C using magnetic stirrer and kept a side in beaker (250 mL) for next step. In another beaker (500 mL), 2 g of HDTAB was dissolved in 60 mL of distilled water followed by mixing slowly drop by drop the content of first beaker with second using continuous stirring and heating. The final solid was then filtered and dried at 100 °C.

Adsorption batch procedure

Adsorption experiments were carried out under optimized conditions using synthesized organkaolin as adsorbent in a vibrated water bath set at 25 °C for 60 min. A 0.5 g of organokaolin was thoroughly mixed with 25 mL of the water river containing known amount of Cr(VI). The pH value 1 was used in adsorption system. The mixture was continuously shaken at 120 rpm for ٦٠ min. Then, the mixtures were filtered. The remaining chromium ion was measured using atomic absorption technique. All adsorption experiments were conducted in triplicates. Adsorption procedure for the PNP removal was performed keeping the steps mentioned above for the chromium determination except one parameter i.e., pH adjusted to 11 and the remaining PNP was determine spectrophotometrically at the optimum $\lambda_{max.}$ Adsorption capacities (q, mg g^{-1}) were calculated form the following equation [15]:

$$q = \frac{C_o - C_e}{M}\ x\ V \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

where $C_o$is the initial concentration (mg L^{-1}), C_e is the concentration at equilibrium (mg L^{-1}), V the volume of liquid phase (L) and M the mass of the adsorbent (g).

Removal rates (*R%*) were evaluated as percentage as follows:

$$R\% = \frac{C_o - C_e}{C_e}\ x\ 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Results and discussion

FTIR Characteristics

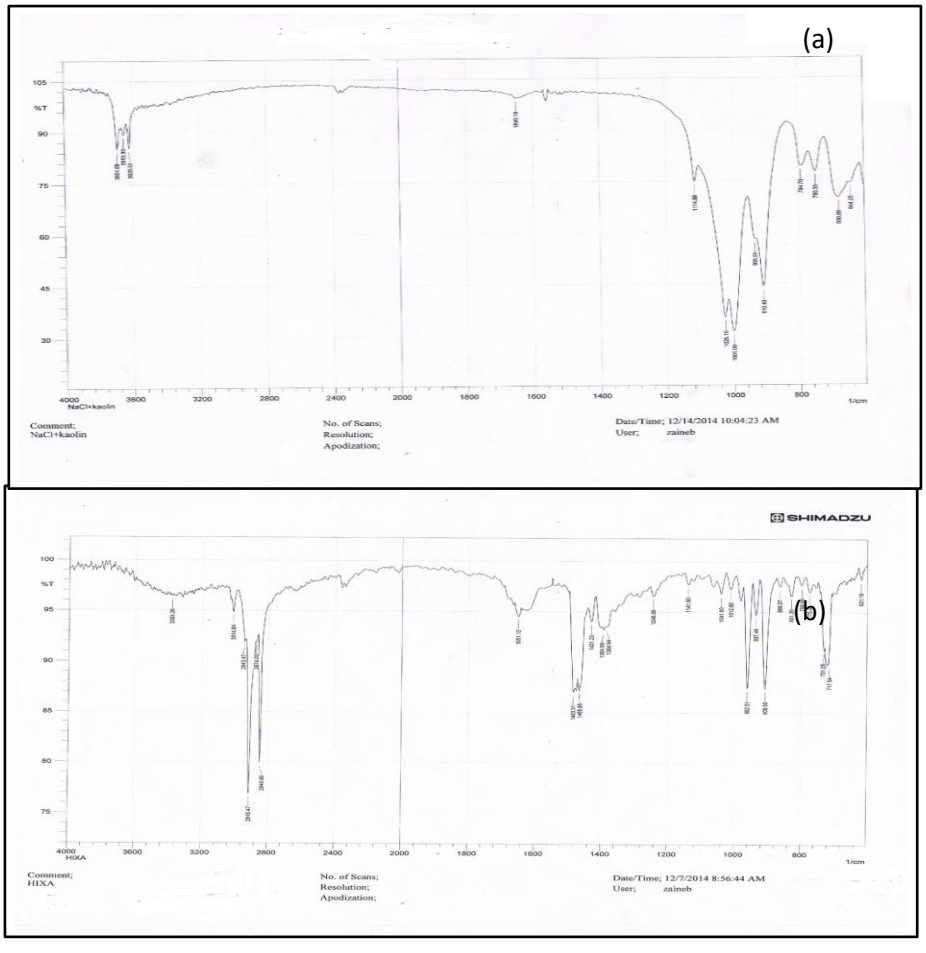
Infrared spectroscopy is an essential technique widely used to probe the molecular environment of the intercalated surfactant for the organoclays mineral structure. Figure 2 (a,b and c) shows the FTIR spectra of natural kaolin clay, HDTAB and kaolin-

organoclay, respectively. The FTIR spectrum between 4000 and 600 cm^{-1} for natural clay. Multi peaks of natural kaolin correspond to 650, 684, 752, 798, 831, 910, 933, 1004, 1028, 3620, 3651 and 3691 cm-1 are shown in Fig. 2a.

Fig. 2b shows the peak at 1465, 1483 and 1651 cm^{-1} are belong to C=C aromatic while 2848, 2874 cm^{-1} peaks that related to -CH_2 variation band and symmetrical -CH_3 stretching absorption band, respectively. Besides, 2916 and 2943 cm^{-1} peaks are assigned to -CH stretching band in HDTAB compound.

The organoclay mixtures showed CH_2 asymmetric and symmetric stretching vibrations (Fig. 2c) which proved the presence of the organic surfactant molecules on their structures. Though not significant, the peaks indicated a gradual shift to lower frequencies with increasing surfactant loadings. The band shifts to lower wave number demonstrated a gradually built conformation of the surfactant molecules in the organoclays. Moreover, the organoclay mixtures showed a transformation from low packing density and ordering to high packing density and ordering of the organic molecules with increasing surfactant loadings in the individual organoclays.

The organic matter peaks at 1487, 2848 and 2916 cm^{-1} were sharper than those of the natural clay. The CH_3, CH_2 and CH bands confirmed the alkylammonium intercalation in the interlayer galleries of the clay mineral, and lower intensity of the characteristic clay mineral peaks indicated the organoclay nature of the treated clay.



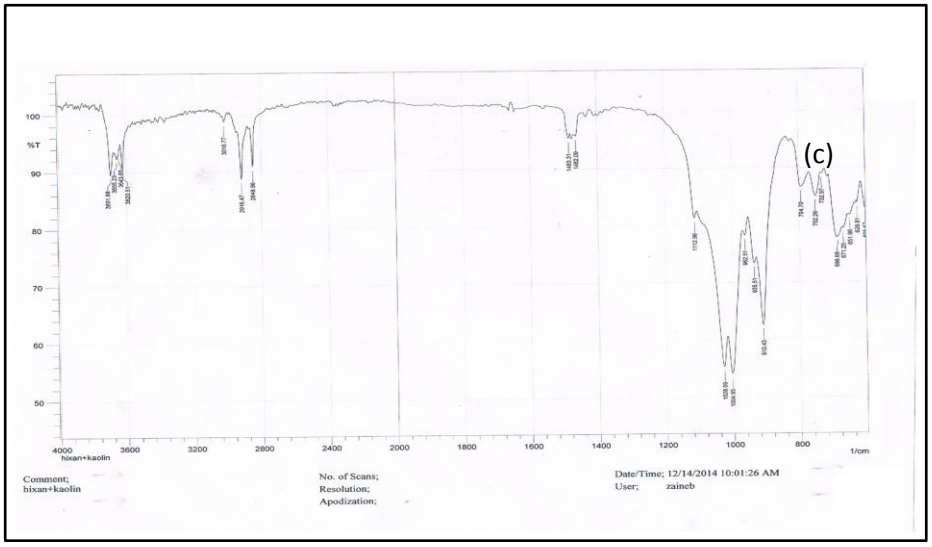


Figure 2. FTIR spectra of (a) natural kaolin clay (b) HDTAB and (c) organokaolin

X – Ray Diffraction (XRD) Measurements

The interlayer spacing of natural kaolin, HDTAB and organokaolin are shown respectively in Figure 3 (a, b and c). 2Ɵ=26.6490, d=3.34236 peaks of the surface of natural kaolin is attributed to QuartzSiO_2 while 2Ɵ=12.3232, d=7.17673 and 2Ɵ=24.9637, d=3.56405 refer to the presence of kaolinite group (Figure 3 a). The interlayer distance or reflection baseband for kaolin is 7.17673 Aº, but reflection baseband for HDTAB is 12.6597Aº. Moreover, the overlap between the particles of kaolin and HDTAB is shown in Figure 3c. Thus, when kaolin interacts with organic matter that occurs is aching in the crystal structure of organic matter and not the chemical composition. However, the results of Figure 3 show that there is no significant change in 2Ɵ value of the detected peaks of XRD pattern of kaolinite group (i.e., 2Ɵ=12.3232 and 2Ɵ=24.9637). While a significant change in d spacing was observed due to filling of porous of kaolin by surfactant (i.e., 2Ɵ=3.6432, d=24.2327).

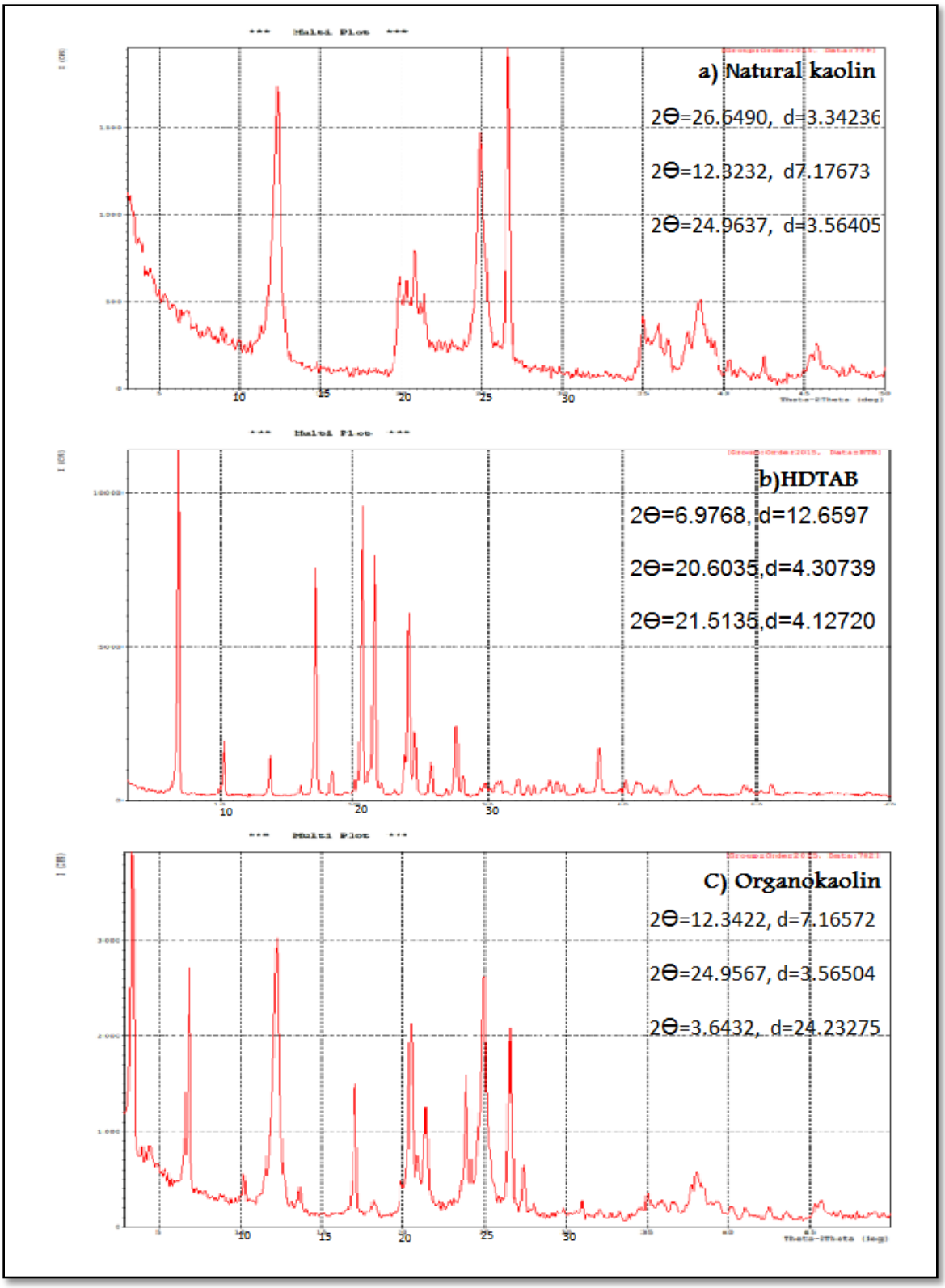


Figure 3. XRD of (a)natural kaolin, (b) HDTAB and (c) organokaolin

Studying the optimum conditions for the adsorption isotherms

The optimum conditions for the adsorption of chromium and PNP by organo kaolin were performed using the following preliminary conditions: initial concentration, 60 µg mL^{-1}; final volume, 25 mL and stirring speed, 120 rpm.

Effect of pH

The pH of adsorption of Cr & PNP should adjusted to ensure that the analytes are removed totally from pollutant solution so that it can be efficiently transferred into the organoclay. The effect of pH (1-6) and (2-11) were investigated for Cr and PNP, respectively. Figure 4 shows that high removal percentage of Cr ion at pH =1 but drops abruptly thereafter and high percentage of PNP removal was achieved at the alkaline conditions (pH=11). The reason behind this is due to electrostatic attraction between negative charge of $HCrO_4^-$ with the positive charge of the functional amino group which presented on the adsorbent surface (i.e., organoclay surface) [26]. Different formula of chromium ion such as $HCrO_4$, HCr_2O_7, Cr_2O_7 and CrO_4^{-2} has also been accumulated at the organoclay surface. As we mentioned earlier, sodium ion in the organoclay active side was replaced by quartery amine which help to attract hydrophobic compounds. Therefore, at the basic conditions, the presence of negative charge on the PNP molecule accelerates adsorption process on the organoclay surface.

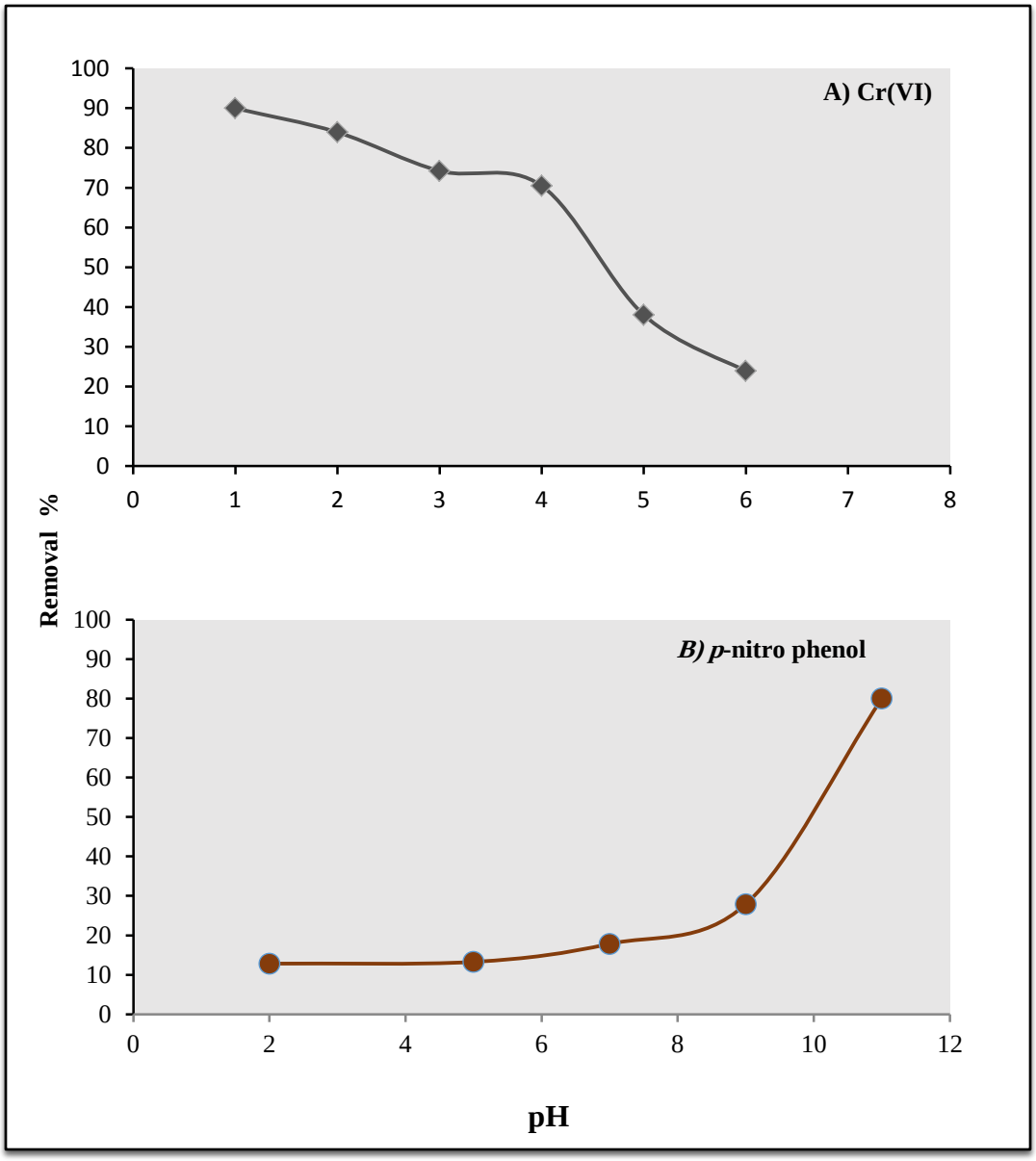


Figure 4. Effect of pH on the adsorption of A) Cr(VI), and B) p-nitrophenol

Effect of contact time

The equilibrium time for adsorption systems is an important factor. Increasing the removal percentage of analyes is due to physical and chemical properties of the organoclay surface. In addition, using HDTAB via preparation of organoclay improves hydrophobic interaction between the adsorbed molecules and organoclay. Moreover, the degree of Cr (VI) and PNP sorption depends on the amount of the surfactant ions in the kaolin layer sites [27]. Therefore, the removal percentage was found to increase with increasing extraction times from 10-80 min for the adsorption of Cr(VI) and PNP (Figure 5). Thus, 80 min was selected for the subsequent experiments.

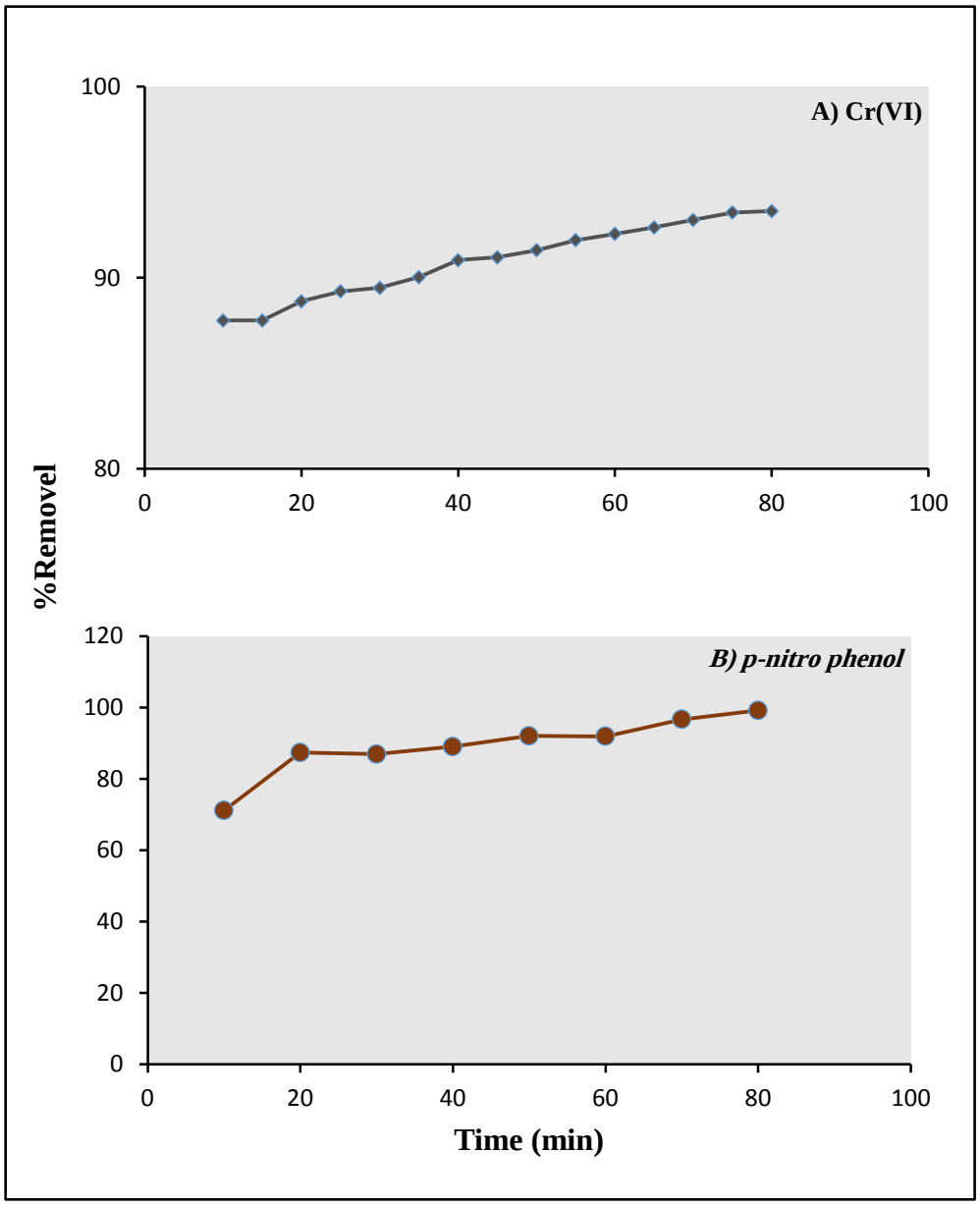


Figure 5. Effect of contact time on the adsorption of A) Cr(VI), and B) PNP

Effect of Temperature

Effect of different temperature (15, 25, 35 and 45 Cº) on the adsorption of Cr(VI) and PNP were studied. At low Temp., increasing percentage removal up to 97% for the adsorption of Cr(VI) and at high temperature increasing percentage removal up to 98% for the adsorption of PNP. Nomination the heat criterion is to understand the adsorption process either endothermic or exothermic. It seems that the reaction is exothermic since

high temperature increases the kinetic energy of the adsorbed molecules which enhance admission of extracted ions via the pores of the solid phase sorbent.

Effect of adsorbent mass

The effect of adsorbent mass (0.1–0.5 g) on the removal of Cr(VI) and PNP was investigated. As expected, as the mass increased, higher removal percentage was obtained due to increasing in the number of active sites on the surface of adsorption. However, when more than 0.5 g was used, no additional enhancement was observed. Therefore, 0.5 g was selected for the further experiments.

Adsorption isotherm

Fig. 6A explained that the adsorption isotherm of Cr (VI) using organokaolin surface which is ideal for microporous surface. In the other hand, Figure 6B showed that the adsorption isotherm of PNP refer to the third type which indicate that mesoporosity surface when capillary condensation take place with high adsorption capacity and flat region of control that compatible with the formation of unilateral layer followed by the formation of multiple layers.

Different mathematical models were applied to describe experimental data of adsorption isotherms such Freundlich, Langmuir and Temkin models which usually employed to analysis adsorption occurred in the experiment.

Table I: Adsorption isotherms calculations of Cr (VI) & PNP on organokaolin surface

Pollutants	[C◦] (µg mL $^{-1}$)	[Ce] (µg mL $^{-1}$)	Log Ce	Qe (mg g^{-1})	Log Qe	Ce/Qe	ln Ce
Cr	10	0.7586	0.1199	2.3103	0.36367	0.3283	
	20	1.7827	0.2510	4.5543	0.6584	0.3914	0.5781
	30	3.9413	0.5956	6.5146	0.8138	0.6050	1.3715
	40	9.5517	0.9800	1.2013	0.0796	1.2548	2.2567
	50	19.4517	1.2889	7.6370	0.88292	2.5470	2.9679
PNP	10	2.0652	0.3149	1.9837	0.2974	1.04108	0.7252
	20	3.9057	0.5917	4.0235	0.6046	0.9707	1.3624
	30	5.5144	0.7415	6.1213	0.7868	0.9008	1.7073
	40	7.2463	0.8601	8.1884	0.9132	0.8849	1.9805
	50	21.413	1.3306	7.1467	0.8541	2.9961	3.0639

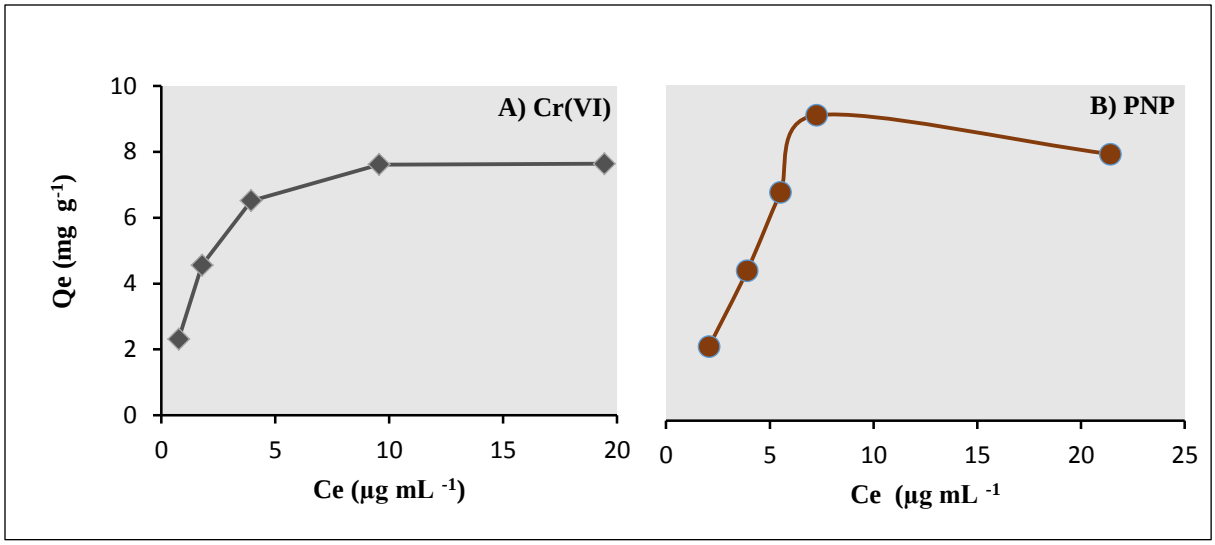


Figure 6. Isotherms adsorption of A) Cr (VI) and B) PNP

Langmuir and Freundlich and Temkin equations

To quantify the amount of adsorbate on an adsorbent and to describe quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, Langmuir model was applied. It is offer the equilibrium distribution of metal ions between the solid and liquid phases. However, it designed for monolayer adsorption onto a surface containing a finite number of identical sites. While, Freundlich equation describes the adsorption characteristics for the heterogeneous surface. In addition, it represents by
curve relating the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact [28,29]. Langmuir represented by the following equation [17]:

$$\frac{Ce}{Qe} = \frac{1}{Q_{\circ}K} + \frac{Ce}{Q_{\circ}} \text{.....2}$$

Where:

C_e : Equilibrium concentration of the metal in solution (mg L^{-1})

Q_e: Amount absorbed at equilibrium (mg g^{-1})

$Q_{\circ}$: Sorption capacity (mg g^{-1})

$\boldsymbol{K}$ **:** Langmuir constants (L mg^{-1})

The linearized Langmuir adsorption isotherms of chromium ion and PNP are presented in Fig. 7 (A). Freundlich adsorption isotherms were also utilized to the removal of Cr(VI) and PNP using organoclay. It was calculated using equation below [28]:

$$\boldsymbol{Q_e = K_f C_e^{1/n}} \text{.....3}$$

where:

$\boldsymbol{Q_e}$: Amount of metal ion adsorbed at equilibrium (mg g^{-1})

$\boldsymbol{C_e}$: Equilibrium concentration of metal ion in the solution (mg L^{-1})

K_f : Freundlich isotherm constants (mg g^{-1})

n: adsorption intensity

Freundlich adsorption parameters were determined by transforming the Freundlich equation (3) into logarithm form:

$$Log\ Q_e = Log\ K_f + {}^{1}/_{n}\ Log\ C_e \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 4$$

$K_f$is an approximate function of adsorption capacity, whereas ${}^{1}/_{n}$ is a indicator of the strength of adsorption in the adsorption process. If ${}^{1}/_{n}$ value is lower than one indicates that adsorption capacity is slightly suppressed at lower equilibrium concentrations and doesn't forecast any saturation of the sorbent therefore, infinite surface coverage is predicted ispredicted mathematically, multilayer adsorption on the surface will occur [17, 28].

Figures 7B present application of Freundlich adsorption isotherms of the

removal Cr(VI) and PNP. The Temkin isotherm model given by the following equation:

$$Q_e = Bln\ A_T + B \ln C_e \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 5$$

Where A_T and B are the Temkin isotherm constant (L g^{-1}) and heat of sorption (J mol^{-1}) respectively. R is the gas constant, B can calculate from $B = RT/b_T$……6

where:

b_T: Temkin isotherm constant

T: Temperature at 298 K.

The plot of Qe against ln Ce for Cr (IV) and PNP sorption on organokaolin is shown in Figure 7C.

Table II summarized the values that estimated from Langmuir, Freundliche and Temkin plots. It is clear that the Langmuir isotherm is best fitted for the sorption of Cr(VI) on the organokaolin. Moreover, when the system is in the equilibrium state, the distribution of Cr(VI) between the organokaolin and the Cr(VI) solution is of fundamental importance in determining the maximum sorption capacity of organokaolin for the chromium ion from the isotherm.

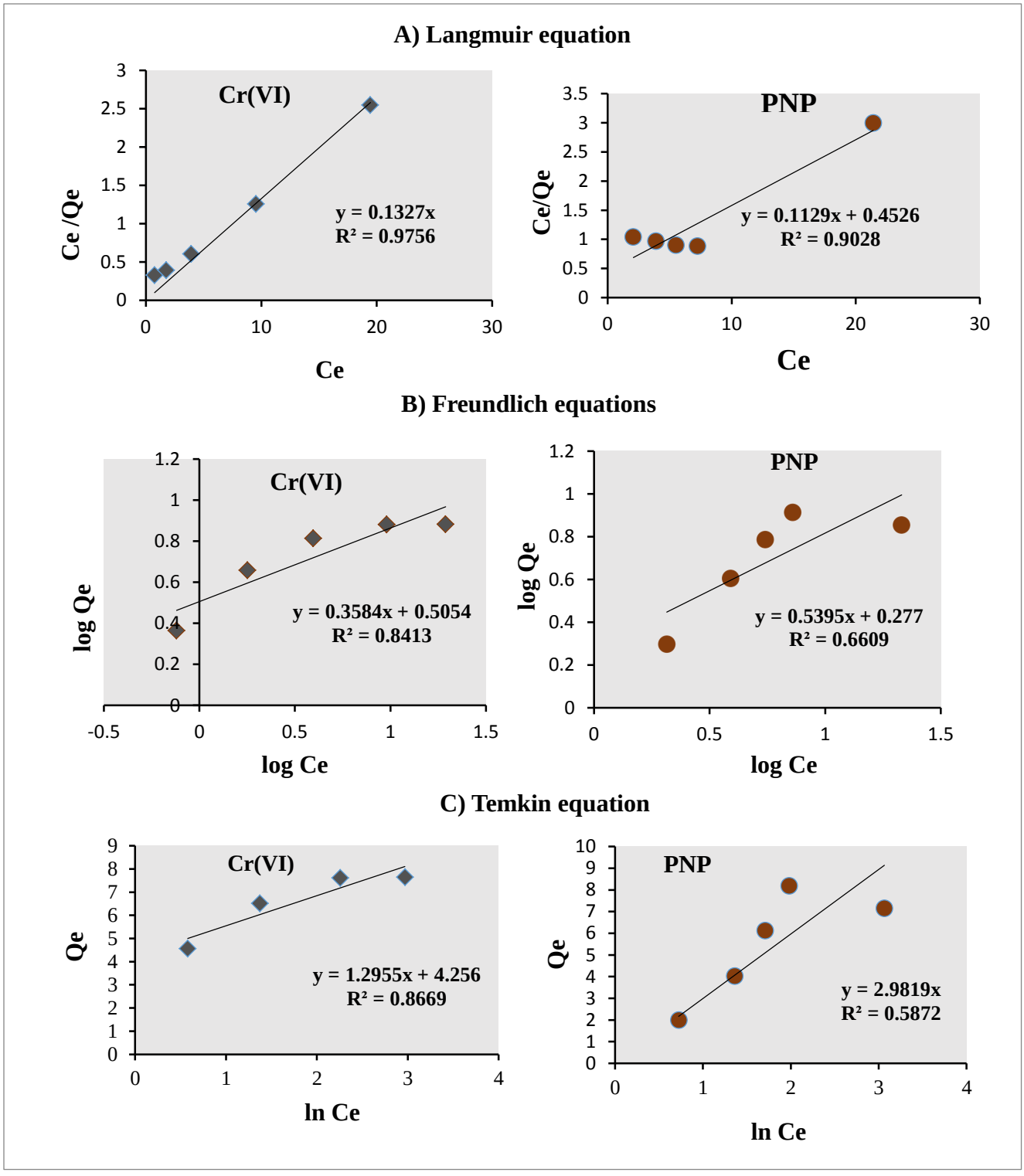


Figure 7. Langmuir (A), Freundlich (B) and (C) Temkin isotherms for the adsorption of Cr(VI) and PNP onto organokaolin

١ **Table II: Constants and parameters of Langmuir, Freundich and Temkin for the adsorption of Cr(VI) and PNP onto**
٢ **organokaolin.**

Pollutant	Langmuir			Freundlich			Temkin		
	K_a (L mg^{-1})	Q_o (mg g^{-1})	R^2	n	K_f (mg g^{-1})	R^2	A_T (L mg^{-1})	B (J mol^{-1})	R^2
Cr	1.4333	5.8139	0.9756	2.7901	1.6576	0.8413	3.2852	1.2955	0.8669
PNP	4.0089	2.2094	0.9028	1.8535	1.3191	0.6609	0.5928	2.326	0.5872

K_a, Langmuir constant ($L\ mg^{-1}$); Qo, sorption capacity (mg g-1); n, adsorption intensity;
K_f, Freundlich isotherm constant ($mg\ g^{-1}$); A_T, Temkin isotherm constant ($L\ mg^{-1}$); B, heat of sorption (J/mol)

Thermodynamic of Adsorption Process

Estimation of equilibrium constants changing as a function of temperature can be performed using thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). Thus, free energy changes of the sorption reaction are given by the following equation:

$$\Delta G° = -RTlnK \quad \text{.....} \quad \mathbf{5}$$

where ΔG°is the standard free energy change (J), R is the universal gas constant, 8.314 J mol^{-1} K^{-1} and T is the absolute temperature (K).

$$\Delta G° = \Delta H° - T\Delta S° \quad \text{... ... ...} \mathbf{6}$$

Equilibrium constant (K) can be estimated using enthalpy changing as a function of temperature:

$$lnK = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{.....} \mathbf{7}$$

Adsorption ability of Cr(VI) and PNP onto organokaolin at different temperature was shown in Figure 8. However, the negative values of ΔG° at various temperatures indicated the spontaneous nature of the adsorption process while the negative value of ΔS° indicated that there is decrease in the degree of freedom of the adsorbed species during the adsorption process. Moreover, the positive value of ΔH° indicated that the adsorption was endothermic (Table III).

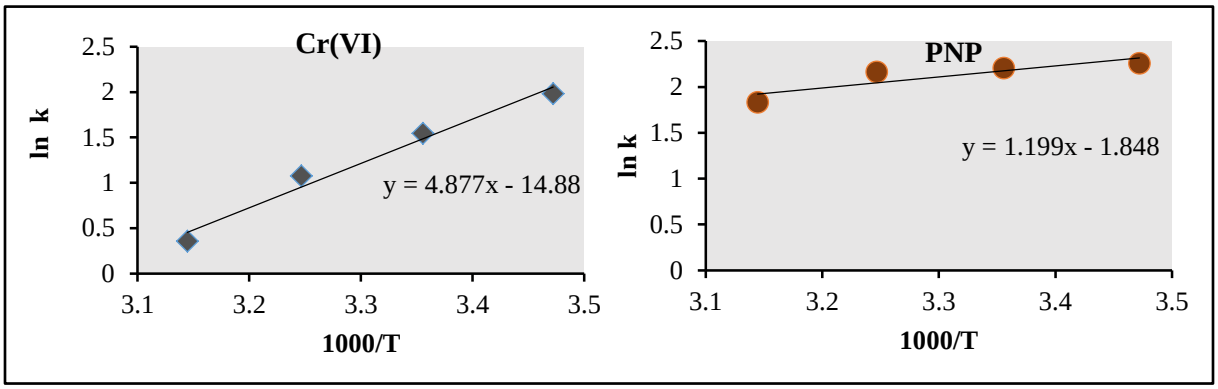


Figure 8. Adsorption ability of A) Cr(VI) and B) PNP onto organokaolin surface

Table III: Thermodynamic parameters for the adsorption of Cr(VI) and PNP onto organokaolin at different temperature

Pollutants	Temp. (K)	1000/T (K^{-1})	k	Ln k	ΔG (KJ mol^{-1})	ΔH (KJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
Cr	288	3.4722	7.2461	1.9804	-4.74210	-40.547	-447.376
	298	3.3553	4.6772	1.5427	-3.82215		
	308	3.3695	2.9261	1.0737	-2.74943		
	318	3.1446	1.4247	0.3539	-0.9356		
PNP	288	3.4722	9.5821	2.2599	-5.41117	-9.968	-15.364
	298	3.3553	9.0704	2.2050	-5.46304		
	308	3.3695	8.6949	2.1627	-5.53805		
	318	3.1446	6.2410	1.8311	-4.84115		

Analysis of real samples

In order to test the usefulness of the developed method, it was applied for the analysis of Cr(IV) and PNP that was spiked to water samples. A total of 15 samples collected from different areas of Baghdad were analysed under optimum conditions. It was found that no Cr(IV) or PNP were detected in the analyzed samples.

Initially, water samples filtered using a Whatman filter paper (No.4), spiked with pollutants and subjected to the suggested removal procedure. Good recoveries with

acceptable RSD% values were obtained for all water samples (Table IV). However, the results do not show any interference suggesting the capability of organoclays to overcome the matrix effects.

Table IV: Recoveries of pollutants spiked to water samples

Area of water samples	Mean recovery%, (RSD %) (n=3)	
	Cr(IV)	PNP
Bab Al moatham (2)	97.4 (2.15)	98.3 (1.8)
Al kadhim city (3)	101.1 (1.15)	99.2 (0.78)
Water drainage (4)	98.7 (0.98)	97.8 (1.3)
Tap water Palestine street (2)	100.4(0.65)	100.0 (0.54)
Tap water 14 Ramadan (4)	99.5 (0.25)	100.1 (0.18)

No. in the brackets refers to the analysed sample and each sample was repeated 3 times; all samples spiked with 10 µg mL-1 of pollutants.

Conclusion

Effective organoclay modified by hexadecyl trimethylammonium bromide named organokaolin were introduced for the adsorption of Cr(IV) and PNP from pollutant water. The synthesized organokaolin is capable to eliminate interferences effect from the water sample. The developed method is remarkably simple, fast and economic since it required only 0.5 g of modified clay and the removal of organic and inorganic pollutants was performed at acidic conditions. Isothermal study using Langmuir, Freundliche and Temkin equations showed that the Langmuir isotherm is best fitted for the sorption of Cr(VI) on the organokaolin. Thermodynamic calculations showed that the sorption process of Cr(VI) and PNP onto organokaolin had exothermic and spontaneous nature. The developed method gives useful knowledge for the development of remediation technology either to remove cationic and anionic metal elements simultaneously from various industrial wastewaters using a single adsorbent or for in situ immobilization of heavy metals and metalloids in contaminated soils and sediments.

References

1. Kumar, P. S., Ramakrishnan, K., Kirupha, S. D., and Sivanesan, S. Thermodynamic and kinetic studies of cadmium adsorption from aqueous solution onto rice husk. *Brazilian Journal of Chemical Engineering* (2010) **27**, 347-355

2. Abdel-Aty, A. M., Ammar, N. S., Ghafar, H. H. A., and Ali, R. K. Biosorption of cadmium and lead from aqueous solution by fresh water alga Anabaena sphaerica biomass. *Journal of advanced research* (2013) **4**, 367-374

3. Zhitkovich, A. Chromium in drinking water: sources, metabolism, and cancer risks. *Chemical research in toxicology* (2011) **24**, 1617-1629

4. Sarkar, B., Naidu, R., and Megharaj, M. Simultaneous Adsorption of Tri-and Hexavalent Chromium by Organoclay Mixtures. *Water, Air, & Soil Pollution* (2013) **224**, 1-10

5. Navarro, A. E., Cuizano, N. A., Lazo, J. C., Sun-Kou, M. R., and Llanos, B. P. Comparative study of the removal of phenolic compounds by biological and non-biological adsorbents. *Journal of hazardous materials* (2009) **164**, 1439-1446

6. Nwokem, C., Gimba, C., Ndukwe, G., and Abechi, S. Process optimization for the removal of p-nitrophenol and p-nitroaniline by hexadecyltrimethylammonium-bentonite from single and binary solute systems. *Advances in Applied Science Research* (2014) **5**, 268-278

7. Allen, S. J., Koumanova, B., Kircheva, Z., and Nenkova, S. **2005.** Adsorption of 2-nitrophenol by technical hydrolysis lignin: kinetics, mass transfer, and equilibrium studies. *Industrial & engineering chemistry research* (2005) **44**, 2281-2287

8. Kilduff, J. E., and King, C. J. **1997.** Effect of carbon adsorbent surface properties on the uptake and solvent regeneration of phenol. *Industrial & engineering chemistry research* (1997) **36**, 1603-1613

9. Esalah, J. O., Weber, M. E., and Vera, J. H. **2000**. Removal of lead, cadmium and zinc from aqueous solutions by precipitation with sodium Di- (n- octyl) phosphinate. *The Canadian Journal of Chemical Engineering* (2000) **78**, 948-954

10. Zouboulis, A., Matis, K., Lanara, B., and Loos-Neskovic, C. Removal of cadmium from dilute solutions by hydroxyapatite. II. Flotation studies. *Separation Science and Technology* (1997) **32**, 1755-1767

11. Canet, L., Ilpide, M., and Seta, P. Efficient facilitated transport of lead, cadmium, zinc, and silver across a flat-sheet-supported liquid membrane mediated by lasalocid A. *Separation Science and Technology* (2002) **37**, 1851-1860

12. Toles, C. A., and Marshall, W. E. Copper ion removal by almond shell carbons and commercial carbons: batch and column studies. *Separation science and technology* (2002) **37**, 2369-2383

13. Ravindran, V., Stevens, M. R., Badriyha, B. N., and Pirbazari, M. Modeling the sorption of toxic metals on chelant- impregnated adsorbent. *AIChE journal* (1999) **45**, 1135-1146

14. El-Sadaawy, M., and Abdelwahab, O. **2014.** Adsorptive removal of nickel from aqueous solutions by activated carbons from doum seed (Hyphaenethebaica) coat. *Alexandria Engineering Journal* (2014) **53**, 399-408

15. Wang, X., Chen, J., Kong, Y., and Shi, X. Sequestration of phosphorus from wastewater by cement-based or alternative cementitious materials. *Water research* (2014) **62**, 88-96

16. Lin, S.-H., and Juang, R.-S. Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: a review. *Journal of environmental management* (2009) **90**, 1336-1349

17. Mobasherpour, I., Salahi, E., and Ebrahimi, M. Thermodynamics and kinetics of adsorption of Cu (II) from aqueous solutions onto multi-walled carbon nanotubes. *Journal of Saudi Chemical Society* (2014) **18**, 792-801

18. Ko, C. H., Fan, C., Chiang, P. N., Wang, M. K., and Lin, K. C. p-Nitrophenol, phenol and aniline sorption by organo-clays. *Journal of Hazardous Materials* (2007) **149**, 275-282

19. Zhu, R., Zhu, J., Ge, F., and Yuan, P. Regeneration of spent organoclays after the sorption of organic pollutants: A review. *Journal of environmental management* (2009) **90**, 3212-3216

20. Gonen, Y., and Rytwo, G. Using the dual-mode model to describe adsorption of organic pollutants onto an organoclay. *Journal of colloid and interface science* (2006) **299**, 95-101

21. Li, F., Jiang, Y., Xia, M., Sun, M., Xue, B., and Ren, X. A high-stability silica–clay composite: Synthesis, characterization and combination with TiO 2 as a novel photocatalyst for Azo dye. *Journal of hazardous materials* (2009)**165**, 1219-1223

22. Mishra, T., and Parida, K. Transition metal pillared clay 4. A comparative study of textural, acidic and catalytic properties of chromia pillared montmorillonite and acid activated montmorillonite. *Applied Catalysis A: General* (1998) **166**, 123-133

23. Sanabria, N., Centeno, M., Molina, R., and Moreno, S. Pillared clays with Al–Fe and Al–Ce–Fe in concentrated medium: Synthesis and catalytic activity. *Applied Catalysis A: General* (2009) **356**, 243-249

24. Sapag, K., and Mendioroz, S. Synthesis and characterization of micro-mesoporous solids: pillared clays. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (2001) **187**, 141-149

25. Barrault, J., Gatineau, L., Hassoun, N., and Bergaya, F. Selective syngas conversion over mixed aluminum-iron pillared laponite clay. *Energy & fuels* (1992) **6**, 760-763

26. Gao, Y., Wahi, R., Kan, A., Falkner, J., Colvin, V., and Tomson, M. Adsorption of cadmium on anatase nanoparticles effect of crystal size and pH. *Langmuir* (2004) **20**, 9585-9593

27. Yantasee, W., Warner, C. L., Sangvanich, T., Addleman, R. S., Carter, T. G., Wiacek, R. J., Fryxell, G. E., Timchalk, C., and Warner, M. G. Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles. *Environmental science & technology* (2007) **41**, 5114-5119

28. Dada, A., Olalekan, A., Olatunya, A., and Dada, O. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn2+ unto phosphoric acid modified rice husk. *Journal of Applied Chemistry* (2012) **3**, 38-45

29. Rahimi, M., Vadi, M., Branch, S., and Sarvestan, I. Langmuir, Freundlich and Temkin Adsorption Isotherms of Propranolol on Multi-Wall Carbon Nanotube. *Journal Of Modern Drug Discovery And Drug Delivery Research.* (2014) **1**, 1-3