ISSN: 0067-2904
GIF: 0.851

Sorption efficiency of kaolinte in removal Cd from aqueous solutions

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Abstract

Because of the contaminants represented by heavy metals in the aquatic environment have an adverse effects need to be addressed, therefore, a laboratory simulation was conducted on Cd using kaolinite that collected from Ga'ara Formation as considered as a natural sorbent material that can be used to remove heavy metals from aqueous environments. Mineralogical study was conducted on kaolinite using X-Ray diffraction (XRD), Scanning Electron Microscope (ESM) and Energy-Dispersive X-ray Spectroscopy (EDS) for the purpose of investigating the micro-texture. It was found that kaolinite has pure phase of very fine grains with a very little quantity of quartz and has a number of active sites for adsorption. Chemical analyzes were performed using atomic absorption spectroscopy (AAS), Electron Probe Micro analyzer (EPMA) and Energy-Dispersive X-ray Spectroscopy (EDS) techniques confirmed a purity of kaolinite due to high alumina content, except a rare slica content originated from quartz. Kaolinite sorption efficiency was investigated through a series of laboratory experiments. The optimal reaction conditions were determined to be as: pH 5 to 9, but the best is 9, and the eqilibrium reaction time is 40 minutes, and the solid to liquid ration is 1.25 gm to 50 ml. The effect of the initial Cd concentration on the sorption efficiency of kaolininte was also investigated and shows that the sorption proportionally increases with high concentration. All the laboratory experiments indicate that the reaction is an indothermic.

Keywords: Sorption, Cadimium, kaolinite; Aqueous solutions; Ga'ara Formation.

كفاءة إمتصاص الكاؤلينايت في إزالة الكادميوم من المحاليل المائية

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الخلاصة:

بسبب كون الملوثات المتمثلة بالمعادن الثقيلة في البيئة المائية ذات أثار سلبية تحتاج معالج، لذلك، أجريت محاكاة مختبرية على عنصر الكادميوم باستخدام معدن الكاؤلينايت التي تم جمعه من تكوين الكعرة باعتباره مادة ماصة طبيعية يمكن استخدامها لإزالة المعادن الثقيلة من البيئات المائية. أجريت دراسة معدنية للكاؤاينايت باستخدام الأشعة السينية الحائدة (XRD) والمجهر الإلكتروني الماسح (ESM) وطاقة الأشعة السينية المتشتتة من التحليل الطيفي (EDS) لغرض التحقق في النسيج المجهري للمعدن. تبين أن الكاؤاينايت ذات طور نقي تقريبا مكون من حبيبات ناعمة التحبب مع كمية ضئيلة من الكوارتز، ويحتوي على عدد من المواقع النشطة للامتصاص. أجريت التحاليل الكيميائية باستخدام مطياف الامتصاص الذري (AAS)، والمايكروبروب الالكتروني (EPMA) وطاقة الأشعة السينية المتشتتة للتحليل الطيفي (EDS) حيث أكدت نقاوة معدن الكاؤلينايت بسبب احتواءة على نسبة عالية من الالومينا، مما يشير الى انه كاؤلين نقي باشتثناء تراكيز قليلة من السليكا التي مصدرها الكوارتز. تم فحص كفاءة الامتصاص للكاؤلينايت من خلال سلسلة تجارب مختبرية. تم من خلالها تحديد ظروف التفاعل المثلى لتكون كما يأتي: الدالة الحامضية من 5 الى 9 لكن الافضل هو 9 ،

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بينما وقت التوازن للتفاعل هو 40 دقيقة، ونسبة الصلب الى السائل هي 1.25 غم : 50 مل. كما تم فحص تاثير تركيز الكادميوم الأولي في المحلول على كفاءة إمتصاص الكاؤلينايت وتبين ان الامتصاص يزداد طرديا مع زيادة التركيز، وان جميع التجارب المختبرية دلت على ان التفاعل هو ماص للحرارة.

1. Introduction

Toxic heavy metals are pollutants of water with of major concern for human health along with the environmental quality. Heavy metals are commonly found dissolved in different aqueous solution including drinking water causing dangerous for the environment. Cadmium (Cd) is known to be one of the most toxic heavy metal even found in low concentration in the aqueous environmental. It has so many impacts, where targets the nervous system, bone, and it causes hypertension in human and increase risk of lung cancer [1]. Different methods (chemical precipitation, ion exchange, filtration and membrane separation and reverse osmosis) for the removal of Cd from aqueous solution are well known. But most of these methods are costly and sometime complex and not efficient. The sorption (adsorption and absorption) method is a promising technique for the removal of Cd from aqueous solutions. This method depends on cation exchange capacity and adsorption for elimination of Cd. Kaolinite is an important raw material has many industrial uses due to its high cation exchange capacity, high specific surface area, and consequential strong adsorption capacity [2]. This study used kaolinite collected from the Ga'ara Formtion in rempval Cd from aqueous solutions. The mineralogy of kaolinite and its sorption efficiency in the removal of potentially harmful Cd ions from aqueous solutions were detail studied.

The aim of this study is to determine the optimal conditions of sorption process of Cd onto kaolinite from aqueous solutions of different concentrations.

2. Materials and methods

Kaolinite was dried and gently grinded using machine grinder, then it was investigated with the Scanning Electron Microscope **(**SEM) and Electron Probe Micro Analzer (EPMA) techniques that carried out in the Geological Faculty, Warsaw University- Poland. Polished section of kaolinite also has been done in the workshop of Warsaw University. A Philips X-ray difractometer has been applied using CuKa radiation and a normal scanning speed of I˚20/min. A powder sample of less than 0.5 gm was placed in the holder for XRD test. Stock solutions were prepared using $Cd(NO_3)_2.4H_2O)$ standard solution in a wide range of Cd concentrations ((25, 50, 75, 100, and 125 ppm). A series of laboratory experiments was conducted at the Geochemistry lab in the Department of Geology at the University of Baghdad. All experiments were done at the room temperature using batch mode. The standard solution was already acidic, then then NaOH was used to control specific pH. The measurements of pH, TDS and EC have been done using a Hanna pH-meter. The calibration solutions were used for calibrating the device according to [3].

3. Results and discussion

3.1 Mineralogy

Kaolinite has chemical formula $Al_2Si_2O_5(OH)_4$ [4]. It has a triclinic crystal system of chemical formula as $Al_2Si_2O_5\ (OH)_4$. a = 5.13Å, b = 8.89Å, c = 7.25Å $\alpha = 90°$, $\beta = 104.5°$, $\gamma = 89.8°$, Volume of the unit cell is 320.11 Å [5]. Kaolinite has a 1:1 layer belongs to phyllosilicates. One layer of the mineral consists of an alumina-octahedral sheet and a silica tetrahedral sheet that share a common plane of oxygen atoms and repeating layers of the mineral are hydrogen bonded together [6]. XRD revealed a pure phase of kaolinite with little quartz (Figure- 1).

SEM investigation of the kaolinite polished section shows very fine grains formed the whole ground mass of kaolinite. Kaolinite contains some impurities as visible crystals, but extremely rare. This visibility confirms that the kaolinite is pure deposits. Grains of less than 60 microns of grain size of non clay minerals associated kaolinite were observed; they mainly were quartz (Figure -2). EDS spectra display the main elemental composition of kaolinite where alumina dominant (Figure -3). Si and Al are major constituents of tetrahedral and octahedral sheets of kaolinite respectively. Fe, Mg, Na, K and Ti are within the interlayer indicating a good substitution can be happened and providing so many exchangeable vacant sites.

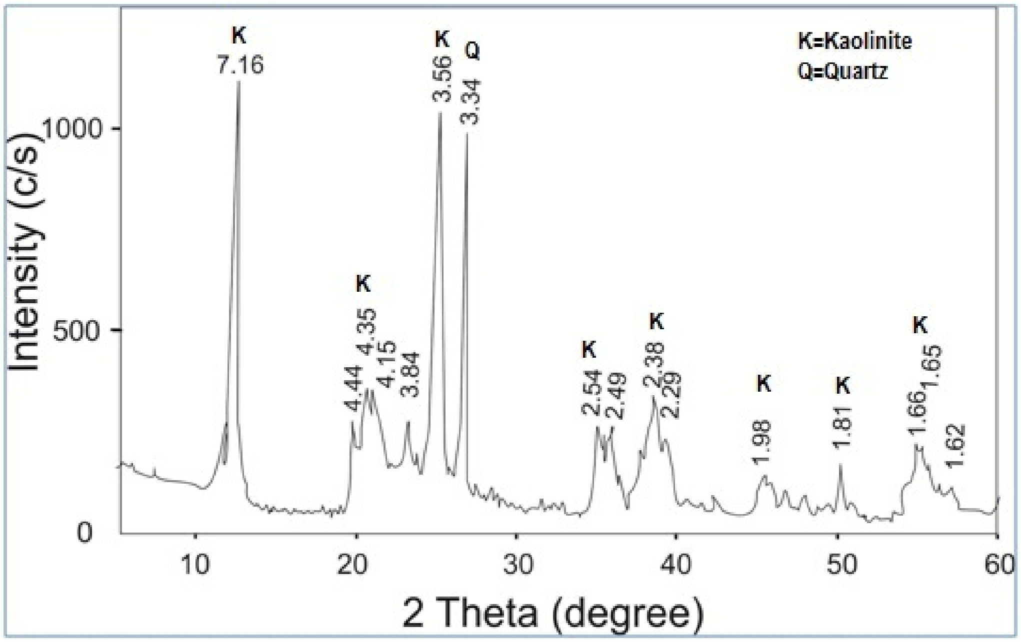

Figure 1- X-ray powder diffraction pattern of the Ga'ara kaolinite.

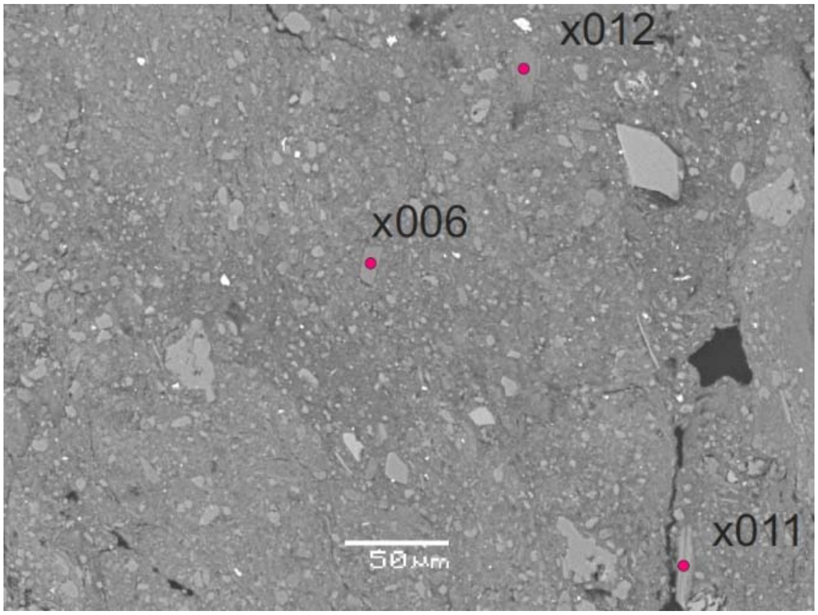

Figure 2- SEM shows the texture of the studied kaolinite using polished section.

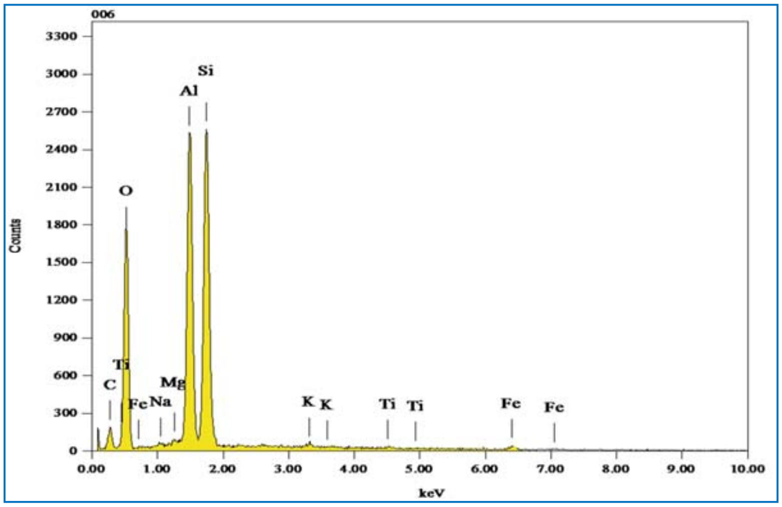

Figure 3- EDS shows the spectra of kaolinite for point 006 appeared in Figure -2.

3.2 Factor affecting sorption

3.2.1 pH effect

The cation exchange capacity (CEC) of kaolinite mainly depends on pH value [7]. A higher pH value gives rise to more negative charges, which lead to a higher CEC value.

In this paper, pH was investigated through 4 experiments presented in Table -1. So the pH value of the kaolinite slurry has been adjusted in a wide range (1.3 - 9). The response of kaolinite sorption is illustrated in Figure -4, which clearly displays how sorption affected by pH indicating a good kaolinite sorption was at pH 5, but the optimal sorption was at pH 9. There is no clear interpretation explains the reason for the low absorption at pH 7; however, it can be attributed to analyst and analytical errors.

Sorption (%) was calculated using equation below:

C (%) of heavy metal= $[(C_i - C_f)/ Ci]100$

Where C_i is the initial Cd concentration and C_f is the final Cd concentration.

Table 1- Results of sorption efficiency of kaolinite for Cd at different pH.

No.	Before experiment								After experiment						
	Time (min)	Weight mass (gm)	C_i (ppm)	Total vol. (ml)	pH	TDS (mg/l)	EC (μs/cm)	T (Cº)	pH	TDS (mg/l)	EC (μs/cm)	T (Cº)	C_f (ppm)	Sorption (ppm)	Sorption (%)
Cd1	10	2.0	100	50	1.3	9500	16150	24	1.19	5400	8750	23.9	82.75	17.25	17.25
Cd2	10	2.0	100	50	5	9500	16150	24.1	6.88	4800	7730	23.8	25.72	74.28	74.28
Cd3	10	2.0	100	50	7	9500	16150	24.2	6.86	5100	8240	23.8	29.3	70.7	70.7
Cd4	10	2.0	100	50	9	9500	16150	24	7.11	3930	6360	23.7	6.66	93.34	93.34

C_i**:** Initial Concentration.C_f**:** finalConcentration.

Many researchers; for example [8] have identified that maximum adsorption efficiency tends to occur in the range pH 6-8; the decreasing negative charge density for lower adsorption efficiency occurs above this pH [9-10]. The amount adsorbed of Cd increases with pH ranges from 1 to 7 [1]. TDS and EC after end of experiments became less in their values. This case reflects the decreasing of seed in the final solutions and eventually it is a good indicator of sorption process.

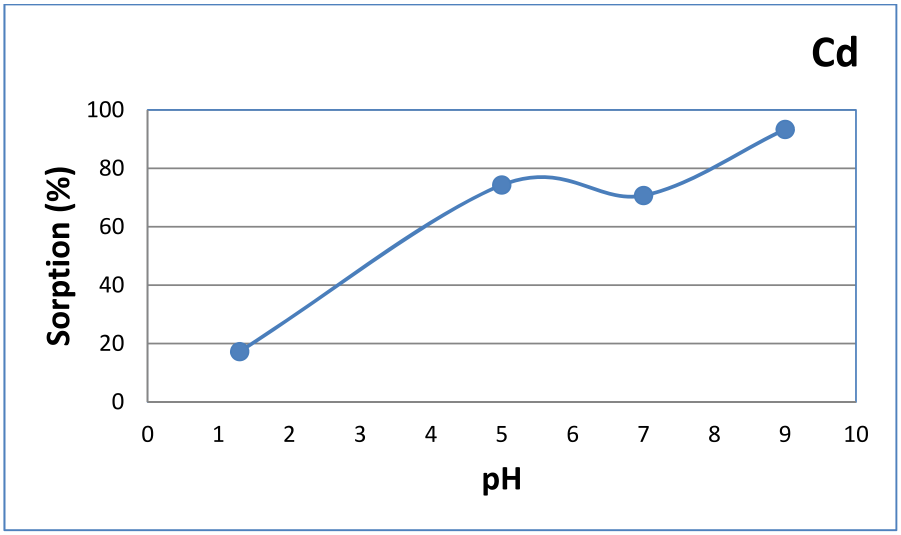

Figure 4- The effect of pH value on the sorption of Cd onto kaolinite.

3.2.2 Soild-liquid ratio

The meaning of solid-liquid ratio is a ratio of kaolinite to solution. Different doses of kaolinite (0.25, 0.5, 0.75, 1.0, 1.25, 1.5, and 2.0 gm) were investigated to clarify the best solid-liquid ratio that able to give highest sorption. Each dose was separately mixed with 50 ml of aqueous solution contained Cd of 100 ppm (Table -2) at pH 9. It was found from this experiment, the best sorption capacity of kaolinite happens with 1.25 gm (Figure -5). Then this weight is the best weight for removal Cd.

Table 2- Results of kaolinite sorption efficiency in removal Cd from aqueous solution with different dose of sorbent.

No.	**Before experiment**						**After experiment**				
	Time (min)	**Weight mass (gm)**	***C_i* (ppm)**	**Total vol. (ml)**	**pH**	**T (C°)**	**pH**	**T (C°)**	***C_f* (ppm)**	**Sorption (ppm)**	**Sorption (%)**
Cd1	10	0.25	100	50	9	15.2	1.23	15.1	68.28	31.72	31.72
Cd2	10	0.5	100	50	9	15.2	1.24	15.0	68.18	31.82	31.82
Cd3	10	0.75	100	50	9	15.2	1.12	15.1	67.69	32.31	32.31
Cd4	10	1.0	100	50	9	15.2	1.15	15.1	67.18	32.82	32.82
Cd5	10	1.25	100	50	9	15.2	1.2	15.1	65.25	34.75	34.75
Cd6	10	1.5	100	50	9	15.2	1.13	15.0	65.2	34.80	34.80
Cd7	10	2.0	100	50	9	15.2	1.19	15.0	65.18	34.82	34.82

C_i*:** Initial Concentration.C_f*:** finalConcentration.

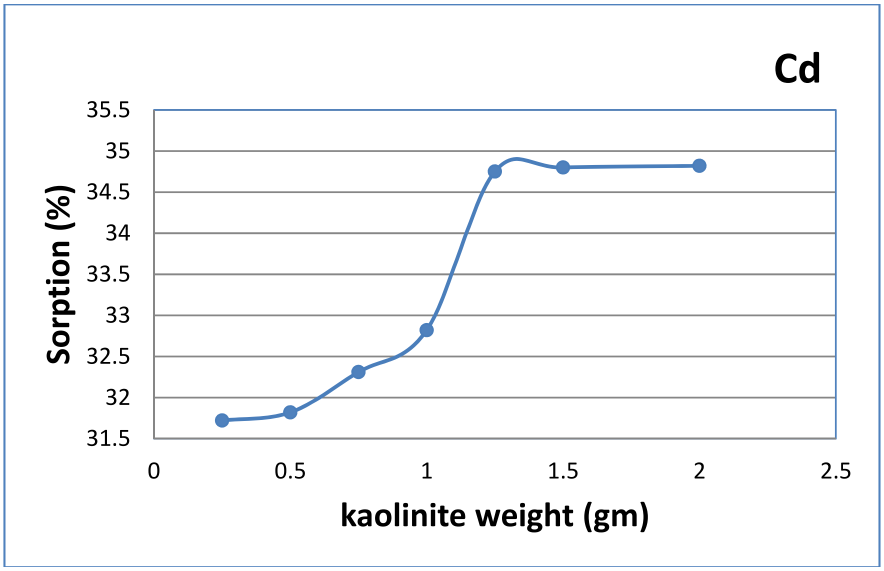

Figure 5- Effect of kaolinte does on it sorption to rremove Cd from aqueous solution at pH 9.

3.2.3 Equilibrium reaction time

For the purpose of investigation the equilibrium reaction time, eight laboratory experiments were designed and performed. Time was selected as 10, 20, 30, 40, 50, 60, 70, 80 min in order to investigate the equilibrium reaction time in which the best sorption was done (Table -3). It was found that the maximal kaolinite sorption to remove Cd from these solutions is 32.2% (Table -3). This sorption has been happened during contact time of 40 min. Thus, the 40 min was determined to be the optimal equilibrium reaction time. Figure -6 displays the kaolinite sorption increases with time from 10 to 40 min, and then it seems to be constant approximately. This relationship confirms that the 40 min is the optimal time. The time rate of sorption is often initially rapid followed by a longer time for more constant secondary phase [10].

Table 3- Results of kaolinite sorption efficiency in removal Cd from aqueous solution with different reaction time.

No.	**Before experiment**						**After experiment**				
	Time (min)	**Weight mass (gm)**	**C_i (ppm)**	**Total vol. (ml)**	**pH**	**T (°C)**	**pH**	**T (°C)**	**C_f (ppm)**	**Sorption (ppm)**	**Sorption (%)**
Cd1	10	1.25	100	50	9	22.9	1.0	22.2	78	22.0	22.0
Cd2	20	1.25	100	50	9	22.9	1.12	22.0	74.4	25.6	25.6
Cd3	30	1.25	100	50	9	22.9	1.12	22.9	69.5	30.5	30.5
Cd4	40	1.25	100	50	9	22.9	1.15	22.5	67.5	32.2	32.2
Cd5	50	1.25	100	50	9	22.9	1.15	22.0	67.9	32.1	32.1
Cd6	60	1.25	100	50	9	22.9	1.14	23.1	68.0	32.0	32.0
Cd7	70	1.25	100	50	9	22.9	1.15	22.8	67.7	32.3	32.3
Cd8	80	1.25	100	50	9	22.9	1.16	22.9	67.5	32.5	32.5

C_i: Initial Concentration; C_f: final Concentration.

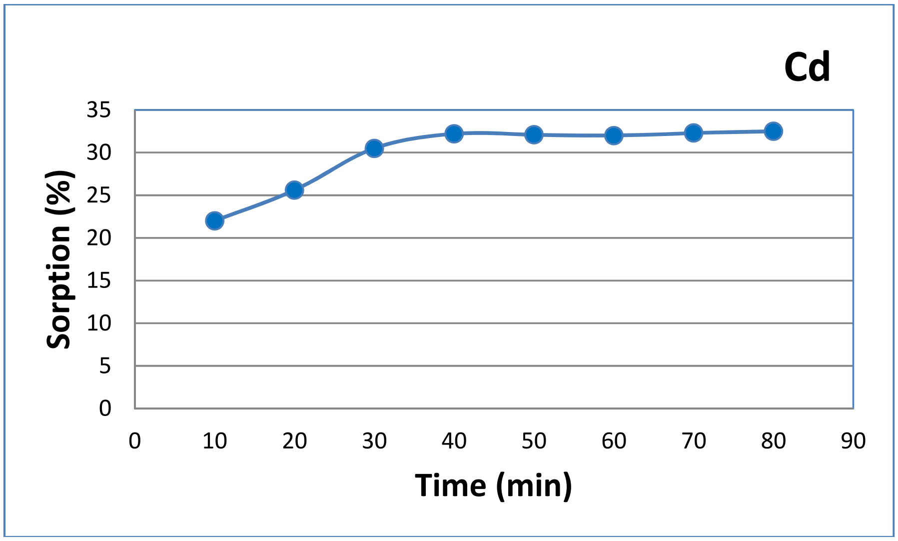

Figure 6- Effect of time on the kaolinte sorption at pH 9 and weight sorbent mass 1.25 gm.

3.2.4 Initial concentration

Data and results of laboratory experiments conducted for investigating the kaolinite efficiency in removal Cd from aqueous solutions are listed in Table -4. Five initial solutions of Cd were prepared with concentrations of 25, 50, 75, 100 and 125 ppm. Then 50 ml of each of the initial Cd solutions was treated with 1.25 gm of kaolinite under the optimal conditions (40 min at pH 9) at room temperature. After the end of experiment, the Cd concentrations in the final solutions were measured, where they are found as 0.9, 2.0, 3.3, 8.8 and 13.0 ppm respectively. The kaolinite sorption was 96.4, 96.0, 95.6, 91.2 and 89.6 % (Table -4). Reactions between Cd and kaolinite led slightly to decrease temperature (Table -4) indicating that the reaction mechanism was indothermic. The sorption efficiency of Heavy metal ions increases with pH till pH 9. Figures -7 and -8 show the kaolinite sorption (%) and sorption (ppm) respectively and confirm that the maximal sorption happened with the initial Cd concentration of 125 ppm.

Table 4- Results of kaolinite sorption efficiency in removal Cd from aqueous solution with different initial concentration.

No.	**Before experiment**						**After experiment**				
	Time (min)	**Weight mass (gm)**	**C_i (ppm)**	**Total vol. (ml)**	**pH**	**T (C°)**	**pH**	**T (C°)**	**C_f (ppm)**	**Sorption (ppm)**	**Sorption (%)**
Cd-1	40	1.25	25	50	9	15.3	8.8	15.2	0.9	24.1	96.4
Cd-2	40	1.25	50	50	9	15.4	8.8	15.2	2.0	48.0	96.0
Cd-3	40	1.25	75	50	9	15.4	8.7	15.1	3.3	71.7	95.6
Cd-4	40	1.25	100	50	9	15.5	8.1	15.2	8.8	91.2	91.2
Cd-5	40	1.25	125	50	9	15.6	8.4	15.3	13	112	89.6

C_i: Initial Concentration.**C_f:** finalConcentration.

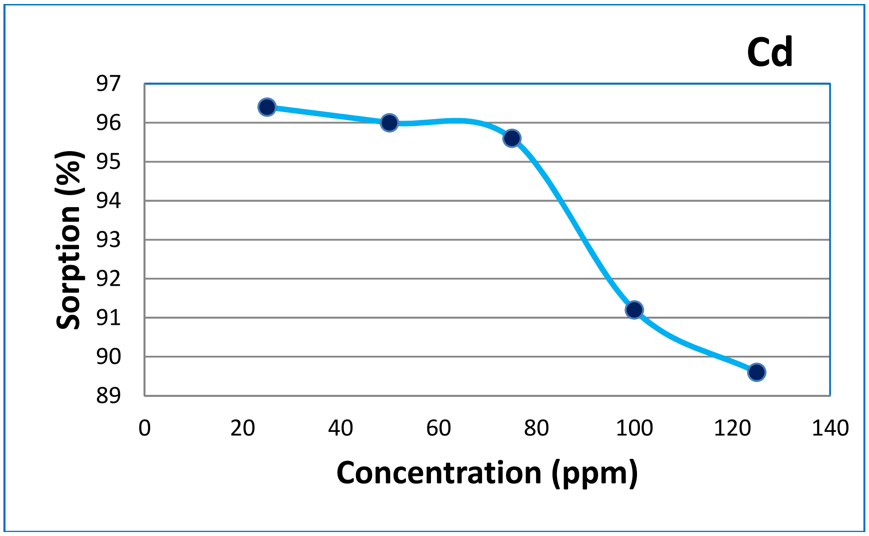

Figure 7- Sorption efficiency (%) of kaolinite in removal Cd from initial solutions of different concentrations.

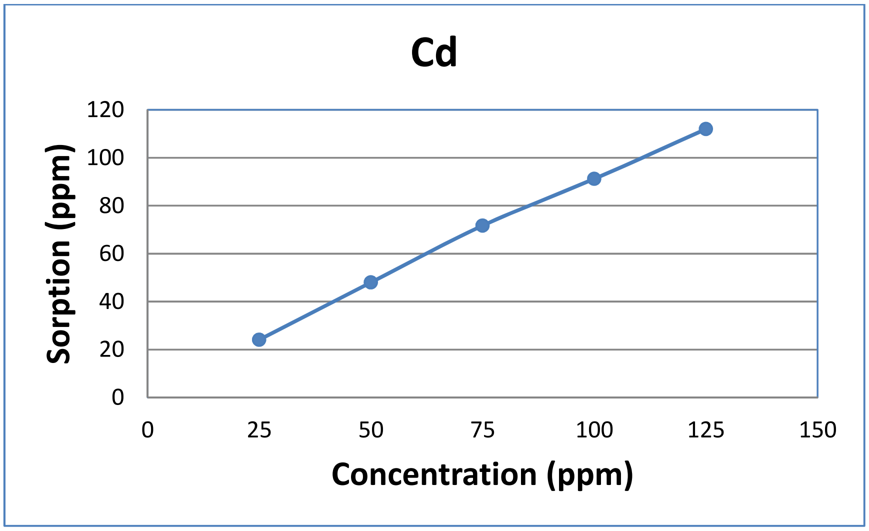

Figure 8- the relationship between intial concentrations and kaolinite sorption (ppm).

4. Discussion and conclusions

The kaolinite of fine grain particles as shown by SEM has a large surface area; thus, it considered as a good absorbent material for Cd. The scarcity of non-clay minerals such as quartz that was detected by XRD and confirming by SEM contained within kaolinite improves the absorbance characteristics of kaolinite and indicating almost a pure phase. As a result of heavy metal ions (Cd) adsorption, the amounts of H^+ ions released from the kaolinite structure yielding an increase of negative charge on the surface [11]. This mechanism was detected particularly at initial solutions of high Cd concentrations. Cations in the internal layer such as K, Ca Mg Fe played an important role in providing the negative charge on kaolinite surface as well as the OH and H^+ in both of tetrahedral and octahedral sheets. The exchangeable cations occur mostly on the edges and on the basal (OH) surfaces of the kaolinite [7].

1. The optimal sorption conditions for removal Cd from aqueous solutions are determined as: pH (9), the equilbrium reaction time is 40 min, and solid-liquid ratio is 1.25 gm: 50 ml.
2. The kaolinite sorption occurs through two major mechanisms, the initially rapid ion exchange phase happens during 10 min, and the slower inner complex forming phase happens during the 40 min.
3. It was found that the adsorption of Cd ions onto kaolinite was strongly dependent on the initial ion concentration.
4. The mechanism of Cd sorption onto kaolinite was indothermic.

5. References

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