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Sorption Efficiency of Bentonite in Removal Cd from Aqueous Solutions

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Abstract

A series of adsorption laboratory experiments were conducted to study the sorption efficiency of bentonite in removal Cd from aqueous solutions. The bentonite was found to be a good receptive to the adsorption of Cd under specific laboratory conditions. The sorption capacity for Cd onto bentonite was investigated through the variation in pH and initial Cd^{2+} concentration. The sorption efficiency onto bentonite was examined as a function of pH, initial ion concentration, equilibrium reaction time and solid mass/ liquid volume ratio. The maximum sorption (%) of Cd from solutions were determined when solid to liquid ratio is 2 gm of bentonite versus 50 ml solution, the equilibrium reaction time is 50 minute at pH ranges from 5-7. The sorption was gradually increased with increasing concentrations of Cd in solution, it was found that the highest sorption was 81.7% when the Cd concentration in the solution was 80 ppm, but it suddenly declined to 72% with highest concentrations (100 ppm Cd) because of competing cations on the negative sites on the surface of clay minerals.

Keywords: sorption, cation exchange capacity, Cd, bentonite, aqueous solutions

كفاءة امتصاص وامتزاز البنتونايت في ازالة الكادميوم من المحاليل المائية

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الخلاصة

أجريت سلسلة من التجارب المختبرية لدراسة كفاءة إمتزاز وإمتصاص البنتونيت في إزالة الكادميوم من المحاليل المائية. تبين أن البنتونيت تتقبل جيداً لامتزاز الكادميوم تحت الظروف المختبرية الخاصة. تم التحقيق من قدرة أمتصاص وأمتزاز البنتونايت لأيونات الكادميوم من المحاليل المائية من خلال تغاير درجة الحموضة والتراكيز الأولية للكادميوم. تم فحص كفاءة البنتونيت للامتصاص والامتزاز بوصفها دالة لدرجة الحموضة، وللتركيز الابتدائية للأيونات، وزمن التفاعل في حالة الاتزان، ونسبة حجم كتلة / السائل الصلبة. تبين ان أقصى إمتصاص وإمتزاز للكادميوم (%) يحصل عندما تكون نسبة الصلب إلى السائل 2غرام الى 50 مل (بنتونيت : محلول) عند زمن تفاعل قدره 50 دقيقة في ظروف دالة حامضية تتراوح بين 5 الى 7. تبين ان الامتصاص والإمتزاز يزدادان تدريجيا مع زيادة تركيزات الكادميوم في المحلول، وإن أعلى نسبة كانت 81.7٪ عندما كان تركيز الكادميوم في المحلول 80 جزء في المليون، ثم تراجع فجأة ليكون 72٪ مع التركيز الأعلى (100 جزء في المليون الكادميوم) بسبب تنافس الكاتيونات (الأيونات الموجبة فيما بينها) على المواقع السالبة الموجودة على سطح المعدن الطيني (البنتونايت).

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Introduction

Heavy metal pollution has become increasingly serious with the increase in industrialization and urbanization contained many heavy metals. Furthermore, they have negative impact on the environment and toxic for humans, animals, and plants because they aren't biodegradable [1].

The use of clay minerals has been extensively studied because of their high specific surface area, cation exchange capacity, and adsorption capacity [2-6]. Bentonite which consists mainly of montmorillonite has a wide range of industrial uses [7].It is unstable with increasing age, consequently, it is absent in sediments of pre-Mesozoic age [8], while in Jurassic is known, but the commercial deposits are Cretaceous or younger in age. Cd and Ni are bio-accumulators can inter human, animal and plant bodies via the food chain and most dangerous due to the long-term toxic effect. Consequently, developing an adsorption method that can be used for removing heavy metals from aqueous solutions is very important because it is cheaper than other used method like chemical precipitation and membrane methods.

This paper is to design and discuss an optimize laboratory experimental conditions including the sorbent mass (solid: liquid ratio), equilibrium reaction time and pH, to provide further insight of Cd adsorption on bentonite at different concentrations.

Materials and methods

A bentonite sample was prepared in the Laboratory of Geochemistry, Department of Geology, College of Science, University of Baghdad. Preparation processes included drying using an electric oven at 80°C for 3h, and then gentle grinding**.** The sample is not so hard; it was dismantled after drying process, and then gently ground using agate mortar and electrical grinder (FW 135).The XRD analysis was performed at the X-Ray laboratories, at Department of Geology, College of Science, University of Baghdad. A powder samples was mounted on holders, and then it subjected to XRD test with source consisted of Cu Kα radiation (λ=1.54 Å). Each sample was scanned with 2-theta range of 2-50 degrees.

The laboratory experiments of Cd sorption are carried out by preparing 5 stock solutions of different concentrations (20, 40, 60, 80, and 100 ppm). These stock solutions were prepared from main standard solution Cd $(NO_3)_2.4H_2O$ that has concentration 1gm/L. many laboratory experiments were conducted to test the sorption efficiency of bentonite for removing Cd from aqueous solutions and to find the optimize conditions (mass weight of adsorbent, volume of liquid, equilibrium reaction time and pH).

Mineralogy of bentonite

Bentonite a montmorellonite- rich rock, it has 2:1 (tetrahedral: octahedral sheets) layer phylosilicate class, it composed of alternating octahedral and tetrahedral sheets. The general chemical formula is $X_{0.7}\,Y_{4\text{-}6}\,Z_8\,O_{20}\,(OH)_4.\,nH_2O$, where X (Ca and Mg) is an exchangeable cations, Y $(Al\ and\ Mg)_4$ and Z $(Si)_8$are structural octahedral cations. It has a surface charge ranges between 0.2-0.6. The layers and major elements in montmorillonite are shown in table 1.

By XRD examination, the basal divalent (Ca^{2+} and Mg^{2+}) appear at 15.4 d-space, whilst the basal monovalent appears at 12.6 [7]. In the mixed monovalent/divalent, the d_{001} spacing is between 15.4 and 12.6. XRD confirmed that the bentonite is of Ca- type, because the basal space (d_{001}) of monovalent is 12.5 figure 1.

Because the Na-type of bentonite is unstable, therefore it can be suggested that the Ca-type of bentonite was Na at the beginning; then it has been converted to Ca-type due to easy replaced Na ion by Ca and Mg ions under leaching. Differences in charge and degree of chemical substitution and the type of impurities determine the physical and chemical properties of bentonite [8].The Al^{3+} can substitute Si^{4+} in the crystal lattice depending on the lower valency cations [7]. Accordingly, an unsatisfied negative charge will be yielded, and it will be balanced by loosely the exchangeable cations (Na^+, Ca^{2+}, Mg^{2+} and H^+) occupied the interlayer crystal surfaces. Chemistry of bentonite confirmed that bentonite is Ca-bentonite not Na-bentonite, where CaO is 9.91% but Na_2O is only 1.17% table 2. The mineralogical composition of the raw bentonite is mainly composed of montmorellomite (71%), with little quantity of palygorskite (14%), calcite (7%), quartz (3%) and dolomite (5%).

Table 1-Layers of montmorellonite according it is crystal structure.

Sheets	**Montmorillonite**
Octahedral (Y-site)	4O + 2 OH 4 (Al + Mg)
Tetrahedral (Z-site)	6O 4Si
Interlayer (X-site)	(Ca, Na, Mg)

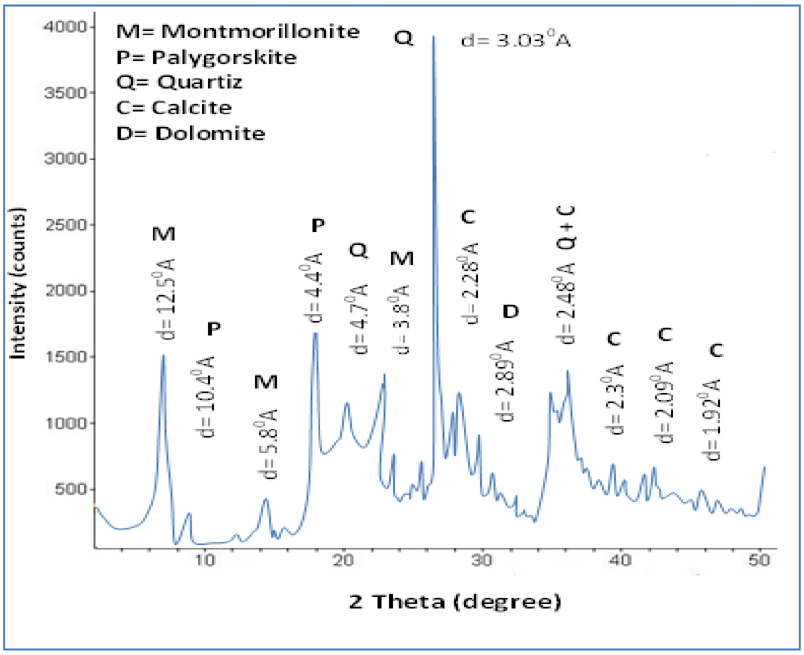

Figure 1-Difractogram shows the mineralogical composition of bentonite.

Table 2-Chemistry of bentonite.

Oxides	**(%)**
SiO_2	41.63
Al_2O_3	13.15
CaO	9.91
MgO	4.11
Fe_2O_3	3.88
Na_2O	1.17
K_2O	0.43
TiO_2	0.63
Cl	1.01
SO_3	0.21
L.O.I	23.87
Total	100

Sorption laboratory experiments

Many batch sorption experiments were carried out on the bentonite to investigate its sorption efficiency for Cd from aqueous solutions. Equilibrium reaction time, effect of the sorbent mass (solid to liquid ratio), concentration, and pH are tested.

Equilibrium reaction time

Many laboratory experiments are performed to determine the best time required for complete sorption (adsorption and absorption) of heavy metals on bentonite. The effect of time on Cd sorption (%) onto bentonite was determined. Results of equilibrium time are listed in table 3. The sorption (%) increases proportionally to the time, where the maximum sorption (%) can be seen at 50 minutes figure 2. Accordingly, 91.3 % of Cd was removed from solution onto bentonite during50 min reaction time.

Table 3-Results of laboratory experiments of Cd sorption on bentonite in ten solutions for different reaction times.

S. No.	Before experiment								After experiment					
	Time (min)	Weight mass	C_i ppm)	Total vol	pH	TDS (ppm)	EC (µs/cm)	T (C°)	pH	TDS (ppm)	EC (µs/cm)	T (C°)	C_f (ppm)	Sorption (%)
AB10$_{min}$	10	2.0	100	50	7.0	9500	16150	23.8	7.1	3504	5957	22.9	70	30
AB20$_{min}$	20	2.0	100	50	7.0	9500	16150	23.8	7.32	3500	6160	22.8	55	45
AB30$_{min}$	30	2.0	100	50	7.0	9500	16150	23.8	7.24	4200	7224	22.7	36	64
AB40$_{min}$	40	2.0	100	50	7.0	9500	16150	23.8	6.92	3940	6698	22.7	21	79
AB50$_{min}$	50	2.0	100	50	7.0	9500	16150	23.8	7.06	3490	6142	22.8	8.7	91.3
AB60$_{min}$	60	2.0	100	50	7.0	9500	16150	23.8	6.87	2330	4008	22.7	9.3	90.7
AB70$_{min}$	70	2.0	100	50	7.0	9500	16150	23.8	6.75	4030	7214	22.3	9.6	90.4
AB80$_{min}$	80	2.0	100	50	7.0	9500	16150	23.8	7.2	3215	5754	22.2	9.4	90.6

C_i: Initial concentration; C_f: final concentration

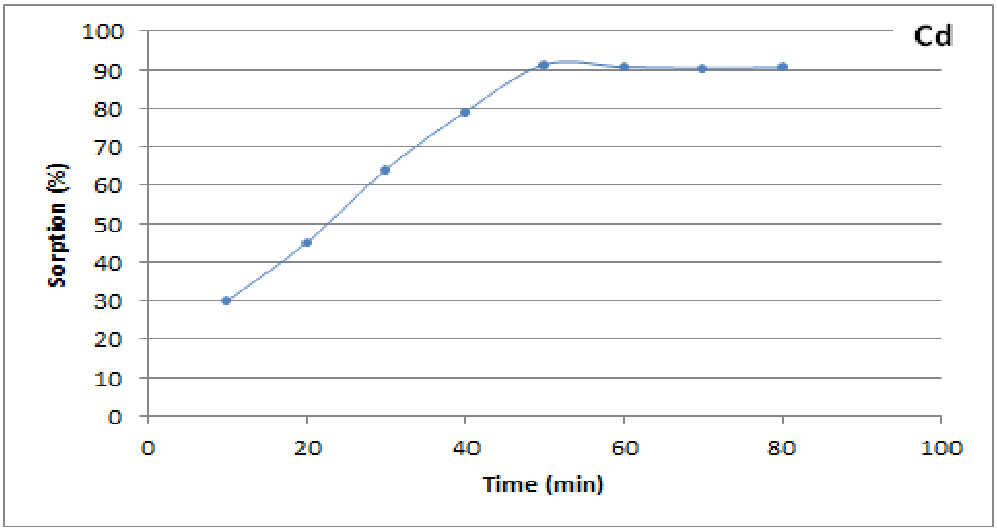

Figure 2-Relationship between Cd sorption (%) on bentonite and equilibrium reaction time.

4.2 Sorbent mass (solid to liquid ratio)

Different masses of bentonite (0.25, 0.5, 0.75 1.0, 1.25, 1.5, 1.75, 2.0 and 2.5gm) are used to test the Cd sorption (%) in total solution volume (50 ml). In these experiments, many factors are set constant; these factors are initial concentration, equilibrium reaction time, concentration and temperature. The initial concentration of Cd for each solution was 100 ppm, equilibrium reaction time was 50 min, Cd concentration was 100 ppm and temperature was15.2 °C. The results of the nine laboratory experiments. Table 4 show that the highest Cd sorption (%) is 99.1 indicating that the best weight mass of bentonite for Cd maximum removal from solution is 2 gm figure 3 in 50 ml solution.

Table 4-Results of laboratory experiments of Cd sorption on bentonite in ten solutions for different weight mass.

S. No.	Before experiment								After experiment					
	Time (min)	Weight (gm)	C_i (ppm)	Total vol	pH	TDS (mg/l)	EC (µs/cm)	T (C°)	pH	TDS (mg/l)	EC (µs/cm)	T (C°)	C_f (ppm)	Sorption (%)
AB1	50	0.25	100	50	7	9500	16150	15.2	6.85	3504	5957	15.1	68.7	31.3
AB2	50	0.50	100	50	7	9500	16150	15.2	6.67	3500	6160	15.5	64.6	35.4
AB3	50	0.75	100	50	7	9500	16150	15.2	6.8	4200	7224	15.3	60.3	39.7
AB4	50	1.00	100	50	7	9500	16150	15.2	7.01	3940	6698	15.2	52.2	47.8
AB5	50	1.25	100	50	7	9500	16150	15.2	7.05	3490	6142	15.3	39.9	60.1
AB6	50	1.50	100	50	7	9500	16150	15.2	7.01	2330	4008	15.3	24.7	75.3
AB7	50	1.75	100	50	7	9500	16150	15.2	6.96	3780	7560	15.2	8.5	91.5
AB8	50	2.00	100	50	7	9500	16150	15.2	7.07	4030	7214	15.4	0.95	99.1
AB9	50	2.50	100	50	7	9500	16150	15.2	7.03	4140	8270	15.3	3	97

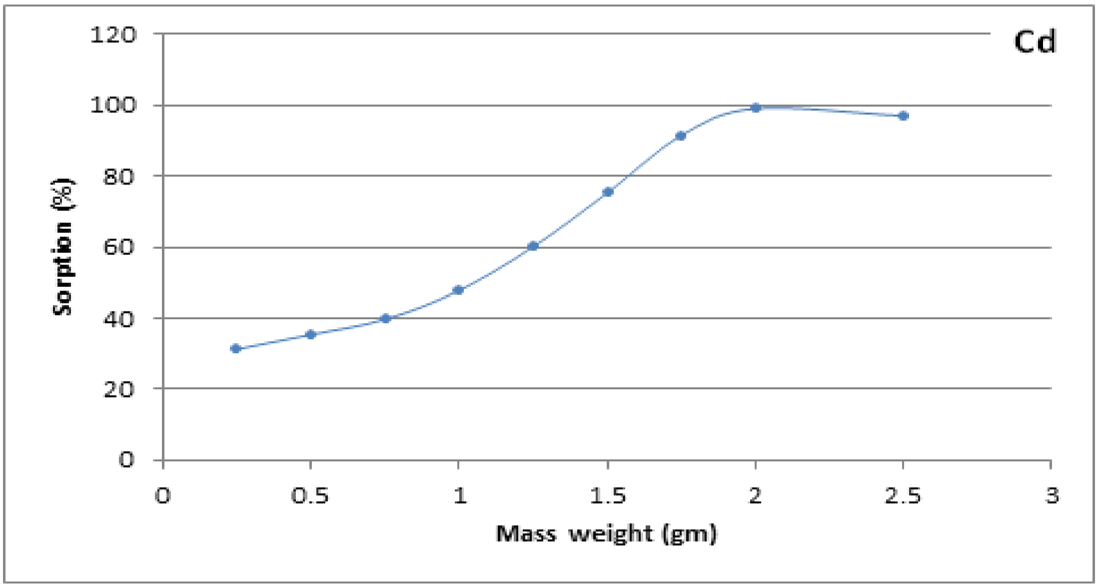

Figure 3-Relationship between Cd sorption (%) and mass weight of bentonite.

The pH effect

The effect of solution pH on M^{2+} (divalent cations) adsorption is determined for the pH range of 2.0 - 11.0 which would normally be found in an electro kinetic soil reclamation process [9].The maximum precipitation of Cd occurred at pH 8.4 with an initial concentration of 100 mg/L. Therefore, to prevent any precipitation occurring before the sorption experiments, the pH was controlled between 2.0 and 8.0 [1].The effect of pH on the sorption efficiency of bentonite is studied. For cadmium Cd (100 ppm), a wide pH range from acidic (pH 1.3) to alkali (pH 9) was tested table 4. The pH was adjusted using 1 mol/L sodium hydroxide. To accurately control the temperature, a thermometer was placed inside the reactor flask for each experiment. The minimum sorption (53.6%) was at pH (1.3), while the maximum sorption (99.6%) was at pH of 7 figure 4. But at initial pH of 5 and 9, the sorption was 96.6 and 92.5 respectively table 5.

The substitutions of Al for Si in the tetrahedral sheet and exchange of two-fold charged cations like Fe and Mg for Al in the octahedral sheets formed negative surface charge in bentonite. Thus, the charge of the basal surface is always negative and independent on pH [10].

Table 5-Results of laboratory experiments of Cd sorption on bentonite in four solutions for different pH.

S. No.	Before experiment								After experiment					
	Time (min)	Weight mass	C_i (ppm)	Total vol (ml)	pH	TDS (mg/l)	EC (µs/cm)	T (C°)	pH	TDS (mg/l)	EC (µs/cm)	T (C°)	C_f (ppm)	Sorption (%)
AB1	10	2.0	100	50	1.3	9500	16150	23.8	6.6	3504	5957	23.2	46.40	53.6
AB2	10	2.0	100	50	5	9500	16150	23.8	6.81	5300	10150	23.2	3.45	96.6
AB3	10	2.0	100	50	7	9500	16150	23.8	7.09	4800	9650	23.3	0.95	99.1
AB4	10	2.0	100	50	9	9500	16150	23.8	6.63	4650	9300	23.1	7.48	92.5

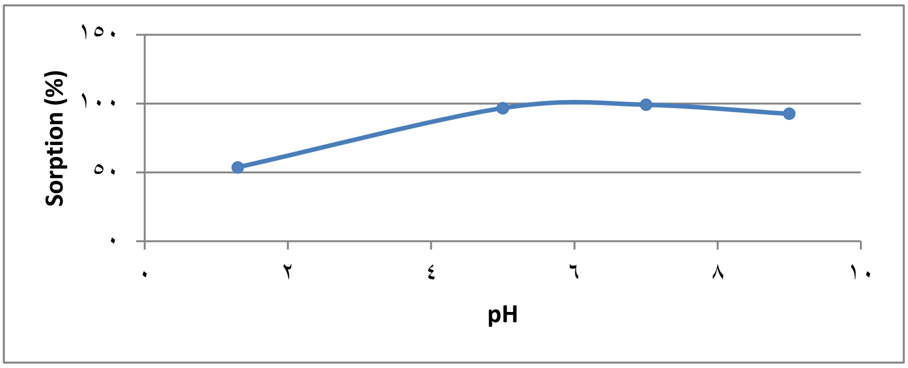

Figure 4-The relationship between sorption (%) and pH.

Effect of concentration

Ten solutions of different Cd initial concentrations (20, 40, 60, 80, 100 ppm) are treated with 2 gm weight mass of bentonite in solution of total volume 50 ml, the reaction time fixed at 50 min. Sorption (%) was found by applying the equation below:

Sorption (%) = [(Ci – Cf) / (Ci)] x 100

Where, Ci and Cf are the initial and final (equilibrium concentration) metal ion concentrations, respectively.

The results of these experiments are listed in table 6. TDS and EC were clearly decreased after the end of the experiment indicating that the Cd sorption on bentonite was done figure 5. Results of Cd sorption (%) were 61.2, 66.2, 72.66, 81.75, and 72. The highest sorption was 81.75 figure 6 confirming that the best mass weight of bentonite is 2 gm and indicating that the solid: liquid ratio is 2 gm: 50 ml.

Table 6-Experimental results of sorption (%) of bentonite with different Cd concentration at initial pH (7), reaction time (50 min) and solid: liquid ratio (2gm: 50ml)

S. No.	Before experiment						After experiment						
	Initial conc. (ppm)	Total Vol (ml)	PH	TDS (mg/l)	EC (µs/cm)	T°C	PH	TDS (mg/l)	EC (µs/cm)	T°C	Final conc. (ppm)	Sorption (ppm)	Sorption (%)
1Cd	20	50	7.0	1930	3865	23.8	6.77	820	1645	23.2	7.76	12.24	61.2
2Cd	40	50	7.0	2450	4910	23.8	6.87	1210	2420	23.3	13.5	26.5	66.2
3Cd	60	50	7.0	5780	11550	23.8	7.03	2680	5370	23.3	16.4	43.6	72.7
4Cd	80	50	7.0	7640	15280	23.8	7.11	2940	5880	23.4	14.6	65.4	81.7
5Cd	100	50	7.0	9500	16150	23.8	7.09	4800	9650	23.3	28	72	72

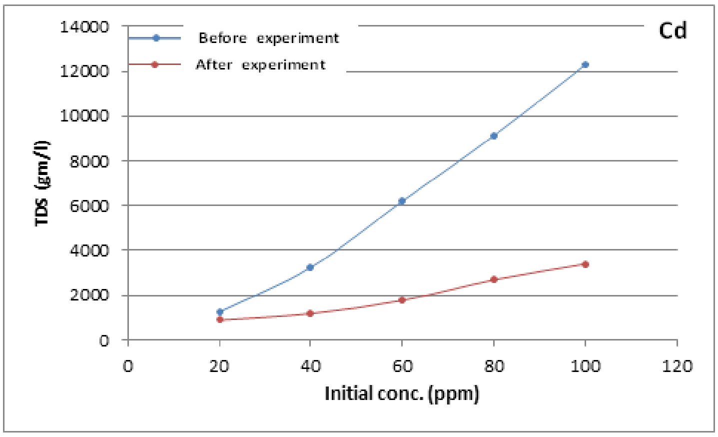

Figure 5-TDS at the initial and final experiments represents the sorption Cd on bentonite.

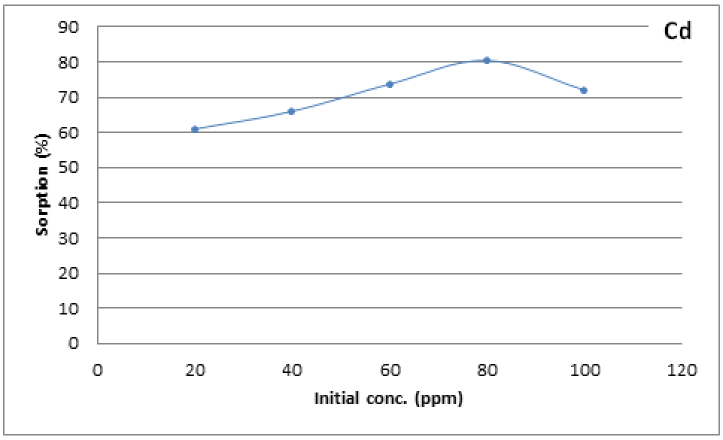

Figure 6-The effect of initial Cd concentrations on bentonite sorption (%).

Conclusions

This study demonstrated that the bentonite is a good adsorbent for removing Cd from aqueous solutions and could be useful as an agent to remove Cd from contaminated water. The optimize conditions of the laboratory experimental were determined. The pH of solution that ranges from 5 to7 can be preserved Cd as soluble ion and prevent it to precipitate. The best soild-liquid ratio is determined to be as 2 gm: 50 ml. The large number of vacant active sites and negative charges on bentonite permits to Cd ions to be adsorbed rapidly onto bentonite at early time. Accordingly, the best equilibrium reaction time is 50 min at temperature 23.8^{o}C.

The bentonite sorption efficiency for Cd from initial concentrations of 20, 40, 60, 80, and 100 ppm was 61.2, 66.2, 72.7, 81.7 and 72 respectively. The sorption efficiency was increased sequentially from 61.2% to 81.7%; then it was decreased to 72%. The decrease of sorption efficient at solutions of higher concentration (100 ppm Cd) is attributed to the strong competition between Cd2+ on the negativesites occurred on the bentonite.

References

1. Wang C. P., Wand, B. L. Liu, J. T., Yu, L., Sun, H. W and Wu. J. Z., **2012:** Adsorption of Cd (II) from acidic aqueous solutions by tourmaline as a novel material. *Environmental Chemistry*, 57 (24): 3218-3225
2. Stadler, M., and Schindler, P.W., **1993:** The effect of dissolved ligands upon the sorption of Cu(II) by Ca-montmorillonite. *Clays Clay Min.* 41:680–692.
3. Siantar, D.P., Feinberg, B.A. and Fripiat, J.J., **1994:** Interaction between organic and inorganic pollulants in the clay interlayer. *Clays Clay Min.* 42:187–196.
4. Brigatti, M.F., Campana, G., Medici, L. and Poppi, L., **1996:** The influence of layer-charge on Zn^{2+} and Pb^{2+} sorption by smectites. *Clays Clay Min.* 31:477–483.
5. Undabeytia, T., Morillo, E. and Maqueda, C., **1996:** Adsorption of Cd and Zn on montmorillonite in the presence of a cationic pesticide. *Clays Clay Min.* 31:485–490.

6. Staunton, S., and Roubaud, M., **1997:** Adsorption of Cs-137 on montmorillonite and illite: Effect of charge compensation cation, ionic strength, concentration of Cs, K and fulvic acid. *Clays Clay Min.* 45:251–260.
7. Morgan, D. J., Highley, D. E. and Bloodworth, A. J., **1993:** *Industrial Minerals laboratory Manual-Bentonite.* A report prepare for the Overseas Development Administration under the ODA/BGS Technology Development and Research Program, Project 91l1, British geological Survey, 117 p.
8. Moorlock, B. S. P. and Highley, D. E., **1991:** An appraisal of fuller's earth resources in England and Wales. Tech. Rep, Bbit. Geol. Surv. WG/91/75.
9. El-mofty, S. E. and El-Shall, H., **2008:** Adsorption mechanism of toxic metalions by clay (attapulgite). Twelfth International Water Technology Conference, IWTC12, Alexandria, Egypt, pp: 403-413.
10. Amman L., Bergaya F. and Lagaly G., **2005:** Determination of the cationexchange capacity of clays with copper complexes revisited. *Clay Minerals* 40, pp: 441-453.