Simple method for removal of cadmium ions (II) From Industrial Wastewater Using Calcinated Porcellanite

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Abstract:

A simple method is developed for the removal of cadmium ions from industrial wastewater. Batch process has been used with natural and calcinated Iraqi porcellanite as adsorbent. Experimental parameters were given, concentration cadmium ion 10-50 mg/L, pH from (2-10), time was 60 min and maximum adsorption was achieve at 30°C.The present study had indicated appositive relationship between the removal efficiency of Cadmium ions with the increasing weight of adsorbents. Adsorption process was pseudo second- order kinetics, and followed Langmuir isotherm model which gave a better fit to the experimental data in comparison with the Temkin and Freundlich equations.Thermodynamic studies of two different surfaces were also given and showed endothermic process.$\Delta H°$, $\Delta G°$ and $\Delta S°$ values were measured and showed that adsorption is spontaneous.$\Delta H°$ was positive, while $\Delta G°$ was negative. $\Delta S°$ was increased and showed activity of surface for adsorption. X-RAY and FT-IR spectroscopy were used to prove that calcinated porcellanite was more efficient than natural porcellanite.

Key words: adsorption, heavy metal, cadmium, porcellanite, Langmuir model

الخلاصة

تهدف الدراسة إلى إيجاد طريقة بسيطة جديدة لإزالةِ أيونات الكادميومِ مِنْ مخلفات المياه الصناعية باستعمال البورسلينات العراقية الطبيعية والمكلسنة بنظام الوجبة . تم دراسة الظروف التجريبية لعملية الإزالة (pH بحدود (2−10) ، درجة الحرارة = 30 C° ، زمن التماس = 60min ، والتركيز الابتدائي لايونات الكادميوم (10− 50 mg/L) . أثبتت الدراسة وجود علاقة طردية بين النسبة المئوية لإزالة ايونات الكادميوم وزيادة وزن المادة المازة.دلت دراسة حركيات التفاعل إن عملية الامتزاز تتبع المرتبة الثانية الكاذبة. أثبتت الدراسة الايزوثيرمية إن نموذج لانكماير للايزوثيرم أكثر انطباقاً من نموذجي فراندليش وتمكن في كلا السطحين. بينت الدراسات الثرموديناميكية إن العملية ماصة للحرارة من قيم $\Delta H°$ الموجبة ، وتلقائية من القيم السالبة لـــ $\Delta G°$ ، بينما دلت القيم الموجبة لـــ$\Delta S°$ على زيادة العشوائية أو اللاانتظام لعملية الإزالة. استخدمت مطيافية الأشعة تحت الحمراء وتقنية حيود الأشعة السينية لتشخيص المجاميع الفعالة على السطح الماز المستخدم.

Introduction

Heavy metals are conceded important for humans, animals and plants. Physical and chemical properties of metals such as arsenic, cadmium, lead and mercury are very toxic to millions of people in many countries such as epidemic in Bangladesh. Cadmium is conceded very toxic and induced renal damage to human and produce cancer. The famous disease ITAI which was reported in Japan was due to cadmium contamination from mine industry health (IARC, 2004). The potential sources of Cadmium in wastewaters include fertilizers, fungicides, metals used in industry, paints, pigments, and batteries (Sheela et al., 2012).Cadmium induced damage or mental defect, central nervous damage, energy loss, blood composition damage, lungs, kidneys, liver and organs damage (Zulkali et al., 2006). Removal of heavy metals from water is required to protect public health. therefore treatment at point of discharge is considered the only practical means of controlling toxic metal pollution (Manahans, 1994). Removal of these heavy metals is usually achieved by physical and chemical processes (Krishman et al., 2008).Wastewater containing toxic metals may be treated by the addition of anions that cause the precipitation of the metals(Abdel-gani, 2007).Other methods include membrane filtration (Singhk, 2005), activated carbon adsorption (Abdel-ghani et al., 2007), co-precipitation (Gardea et al., 1996) ,ion exchange (Ajmal et al., 1998) ,and adsorption (R.Zein et al., 2010) .All chemical methods have proved to be much expensive and less efficient than the adsorption process (A. Saeed, 2003). Moreover, the use of chemical to remove heavy metals increased pollution (Shah et al., 2009). Adsorption is an alternative technology for metal separation from aqueous solutions. With the selection of a proper adsorbent, the adsorption process can be a promising technique for the removal of certain types of contaminants (Rafatullah et al., 2012).different materials have been used as adsorbent for cadmium such as palm shell (Igwe et al., 2008), potato peels (Aman et al., 2008) , tea waste (Amir et al., 2005), wood ash (Malakootian, 2008), maize tassel (Zvinowanda et al., 2009), and other adsorbents (Al-Rub, 2006).all these adsorbents were used for the removal of heavy metals from water and wastewater. In present paper is attempting to use efficient and cheap readily available, natural and effective adsorbent material. There are natural and artificial porcellanite which have been used for the removal of cadmium ions from industrial wastewater.

Experimental:

Chemical and instrumentation;

Chemicals:

Stock solution; stock solution of cadmium (1000 mg/L) was prepared by dissolving (2.74 gm.) of salt (Cd $(NO_3)_2.4H_2O$) (obtained from Fluka) in 1liter of deionized water. All other chemicals are Analar. and solution of 0.1 M HCl and NaOH and both solution were standardize before used .

Natural porcellanite; natural porcellanite was obtained from the General Company of Geological Scanner, Baghdad Iraq. Calcination of porcellanite was prepared from natural porcellanite. Then washed with deionized water, and broken into many pieces into different particle size (300,500 and 700 µm) by the especial mechanical cracking.

Instrumentations:

1- Atomic absorption spectrophotometer Shimadzu AA-6200.

2- X-RAY diffraction analyzer was Shimadzu 6000.

3- FT-IR spectrophotometer – Shimadzu.

4- pH meter was Research pH meter Radiometer, Cobenhagen, Denmark .

5-Shaker was BS-11 digital, JEIO TECH, Korea.

All glasses used were clean and calibrated before use. Volumetric flasks used for preparation of solution were of polyethylene.

Procedures;

1- Preparation of natural porcellanit; Take 1.5 gm of natural porcellanitee washed with deionized water and then broken into many pieces with different particle size (300, 500, and 700um) by mechanical cracking (IKA-WERKE).

2- preparation of calcinated porcellanit ; weigh 1.5 gm of natural porcellanite and heat to 1000 c° in furnace program to increase temperature 100 °C for every 15 min. cool the calcinated porcellanit in desiccator and after that material was ready for use.

3-prepartion of spiked wastewater; prepare stock Cd solution 1000mg/L by dissolving (2.74 gm) of salt ($Cd(NO_3)_2.4H_2O$) in (1 liter) of deionized water. This Cd stock Solution was standardized against Standard disodium EDTA. Prepare series of diluted cadmium solutions(10-50mg/L) from stock solution .all measurement cadmium before and after adsorption were measured by atomic absorption spectrophotometric (Shimadzu AA 6200). Blank solution was subtracted from all measurement. Triplicate measurements were carried out.

4-batch adsorption procedure; to measure the adsorption of Cd ion on porcellanite different weights of adsorbent were used at concentration of 10-50 mg/L. all parameters were kept constant of optimum values. Measure concentration of Cd ion before and after adsorption by flame atomic absorption.

Results and Discussion:

Optimization of adsorption process; In order to obtain maximum removal of cadmium from waste water optimum condition have to be found , these are ,contact time ,pH , weigh of adsorbent , concentration of cadmium , particle size and temperature. These processes will be discussed as flowed;

1- **Effect of contact time;** Different times were taken (30, 60, 90 and 120 min.). All the parameters were fixed (,pH was 6, cadmium concentration was 50mg/L, weight was 1.5 gm. for both natural and calcinated porcellanite, temperature was 30 c°.) . The only variable in this optimization was contact time. Results are given in Fig. 4. It is shown that cadmium was removed by calcinated porcellanite better than natural porcellanite. Optimum contact time was 60 min for natural porcellanite, 90 min for calcinated porcellanite (Naya et al.,2009 ; Bulut, 2007).

2- **Effect of pH**; in order to observe the effect pH .all the parameters were fixed (amount of both adsorbents were 1.5 mg, concentration of cadmium was 50mg/L., time of adsorption was 1hour,). pH was varied from 2 to 8(pH was adjusted by using buffer solution). Results are given in fig 5. pH was optimum at 2.3 for both natural and calcinated.
3- **Effect of weight of adsorbent**; to observed the highest amounts of adsorbent that give optimum adsorption at fixed concentration of cadmium ,temperature and time of adsorption. Variable amounts of natural and calcinated (1, 2, 3, 4, and 5gm). Results are given in fig.6. Optimum adsorbent was found 1.5 for natural and calcinated porcellanite,
4- **Effect of concentration of cadmium ions**; using optimum adsorbent amount, pH, temperature, time of adsorption to measure the efficiency of cadmium removal from wastewater different concentration (10,20,30,40,and 50 mg/L).the adsorption process was carried out and results are given in fig, 7. Optimum concentration was 10mg for natural porcellanite,while 10-40 for calcinated porcellanite,
5- **Effect of particle size**; particle size was considered as important factor because is related to surface area of adsorbent, therefore it has been studied by fixing pH, time of adsorption ,temperature, weight of adsorbent, and initial concentration. Results are shown in fig8. Optimum particle size was found 300 μm for both natural and calcinated porcellanite.

6- **Effect of temperature;** the efficiency of adsorption of cadmium was affected by change temperature, therefore the effect of temperature from 20 to 50°C by fixing of all parameters .results was given in fig 9. Optimum temperature was achieved at 50°C for both natural and calcinated, but at 20°C the removal efficiency was 55% for natural and 62% for calcinated .

From above optimization conditions, summary of these study are given in table (1).

Characterization of adsorbents

In order to evaluate the adsorption properties of porcellanite, X-ray diffraction ((XRD) analysis of the solid surface was carried out and results are given in (Fig 1and 2). From the spectrum, the structure of quarts and opal were shown together with fine size silica, the figures also showed dolomite and tridymite which were appeared as peaks (tridymite is closed to quartz while dolomite was away from quartz), this indicated that adsorption activities were attributed to these mineral composition of quartz. Also the silicon oxygen groups were identified as main groups in quartz by using FT-IR spectra as shown in (Fig 3). This gave vibration at 3560 cm^{-1} for Si-OH-Si, while OH stretching vibrations were at 3421cm^{-1}. Water molecules gave absorption at 1652cm^{-1}, Si-O group absorbed at (1436cm^{-1}, and at 790cm^{-1}) and these bands were characteristic of quartz (Silverstien, 2005).

Adsorption models

Adsorption process is considered important for removal Cd ion, therefore investigation of distribution of metal ion between the liquid phase and the solid adsorbent. This adsorption is in equilibrium and can be express by one model or many other models flowing isotherm pattern (Santos et al., 2011).Three different common models of isotherm were studied (Langmuir, Freundlich and Temkin isotherms). R^2 values and slop both measured and found to be related to Langmuir isotherm model. Fig 10 and fig 11 gave linear plot, which suggested that adsorption was Langmuir isotherm for both natural and calcinated porcellanite (Langmuir, 1916).

Kinetic study

To understand the behavior of adsorption of Cd on both natural and calcinated porcellanite, The pseudo-second order rate equation was applied to fit the experimental adsorption data of cadmium (Lagregren, 1898).fig 12 and 13 proved that the adsorption was linear and flowed pseudo second order rate.

Thermodynamic Studies:

Adsorption process was found useful to calculate thermodynamic parameters such as change in free energy ΔG°, enthalpy ΔH° and entropy ΔS° were determined using the following equations (Arivoli et al., 2008 ; Arivoli, 2008).

$$\Delta G° = -RT \ln K$$

$$\text{Log } K = (\Delta S°/2.303R) - (\Delta H°/2.303\, RT)$$

$$\Delta G° = \Delta H° - T\Delta S°$$

Where K the equilibrium constant, T is the absolute temperature (K°) and R is the gas constant.

Van't Hoff equation was used to estimate the values of ΔH° and ΔS° from the intercept and slope of the plot of log K vs. 1/T (fig. 14).

These values are shown in table (2).

According to equations given above, adsorption was found endothermic (ΔH° was positive), reaction was spontaneous (ΔG° was negative), and solid solution interface was random because ΔS° was increased. The change in adsorption enthalpy was measured and found -20 to 40 $KJ.mol^{-1}$, compared to chemsorption which was in the range -400 and -80 $KJ.mol^{-1}$ (Huang et al., 2011). From values of ΔH° physisorption was the dominant mechanism.

Application

From the experimental results, it was clear that Cd ions can be removed from industrial waste using natural and calcinated porcelinate at optimum conditions. Three samples were taken from three different Iraqi factories: Babylon batteries factory, Kufa cement factory and Babylon tiers factory. From results, it was found that porcellanite natural and calcinated gave high efficiency (100%) for the removal of Cd ions at optimum conditions. Results were supported as in table 3. Therefore this method was recommended for industrial application.

Conclusions:

Many materials were used as adsorbent for the removal of cadmium ions .These materials required to be converted to carbon .this activated carbon need to be examined as adsorbent. But these materials required or needed to be available. Also it cost a lot of time and expenses. Natural and calcinated porcellanite were found for useful cadmium ions from wastewater. Optimum conditions were studied by batch method. The Langmuir adsorption isotherm models were better used to represent the experimental data on both of adsorbents. The adsorption kinetics was fit to pseudo second order models in the two adsorbents. Calcinated porcellanite was found better than natural porcellanite , therefore it is recommended as active and cheap removal of cadmium ions.

Table (1): The optimum condition for removal of Cadmium ion by natural and calcinated porcellanite

No.	Parameter	Optimum	Mechanism	Reference
1	time	60min	Proportional and constant up to 120min	(Naya et al.,2009) ; (Bulut, 2007)
2	pH	6	At acidic pH the adsorbent surface will be converted to carboxylate and phenolate which give active site on the surface of adsorbent, at alkaline medium, hydrogen ions removed by hydroxide ion, and therefore adsorption remains.	(Suleyman, 2010)
3	Amount of adsorbent	1.5gm	Increase of amount of adsorbent is proportional to removal percentage of cadmium increase in active sites but more concentration was not significant	
4	Initial concentration	10mg/L for natural , and 10-40for calcinated	At initial concentration the ratio of metal to adsorbent was reached maximum at 10mg/L and increase metal ion did not increase in adsorption sites becomes it will be saturated. but for calcinated porcellanite the capacity of active sites were higher than natural	(Zouboulis et al., 2002)
5	particle size	300um	Increase of surface area accompanied with decrease in particle size but increase particle size more than 300um will not added more active sites because a metal ion will be saturated and adsorption will be decrease due to desorption of cadmium	(Schramke et al., 1999)
6	temperature	50°C	The adsorption of Cd ion favored endothermic reaction and mobility of Cd ion was increased from 20-50°C. removal efficiency of Cd ion was optimum(90%)at 50c for both natural and calcinated ,after 50°C the Cd ion was penetrating the surface and produce swelling effect, therefore adsorption decrease and percentage removal of Cd ion was 60% which decrease about 33%	(Ennigrou et al., 2009)

Table (2): The thermodynamic parameters of removal of cadmium by natural and calcinated porcellanite

Adsorbent	Temp. (k°)	ΔH° $KJ.mol^{-1}$	ΔG° $KJ.mol^{-1}$	ΔS° $KJ.mol^{-1}.K^{-1}$
Natural porcellanite	293	22.431	-382.5	1.381
Calcinated porcellanite	293	14.640	-1473.7	5.079

Table 3: Practical applications of removal of cadmium ions from Iraqi factories wastewater by using of natural and calcinated Iraqi Porcellanite as adsorbents

Factory	Optimum conditions					Concentration before treatment (mg/L)	Concentration after treatment (mg/L)	Removal %
	pH	Contact time (min.)	Temperature (C°)	Weight of adsorbent (gm)	Particle size (μm)			
Babylon batteries	6	60	30	1.5	300	0.041	0.0	100
Kufa cement	6	60	30	1.5	300	0.112	0.0	100
Babylon tiers	6	60	30	1.5	300	0.040	0.0	100

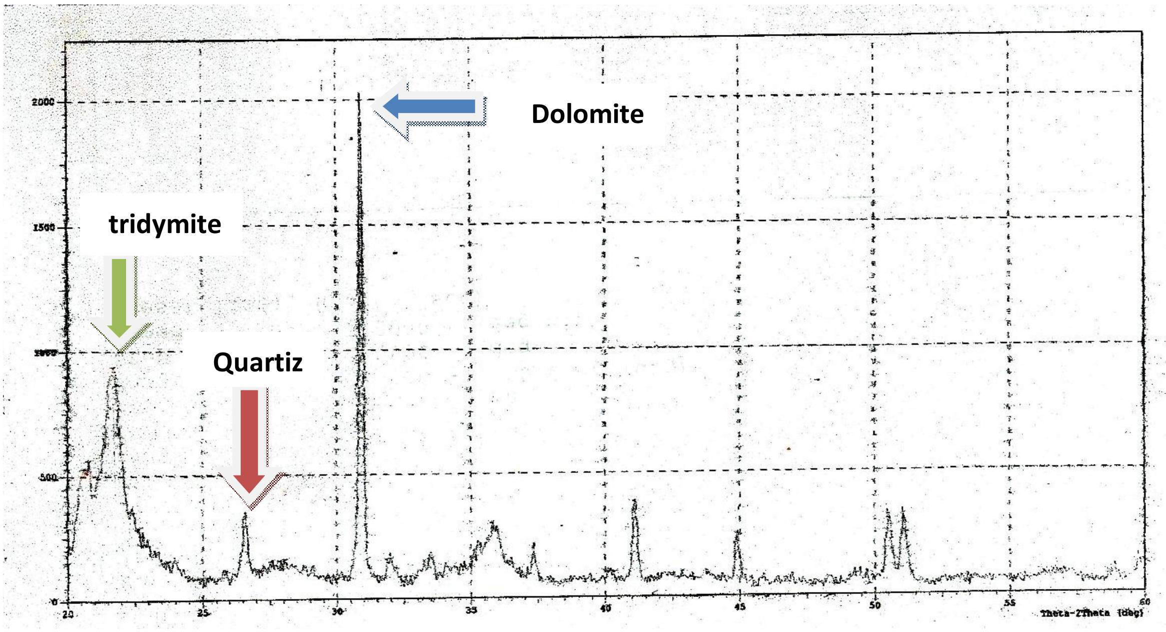

Fig.1: XRD for natural porcellanite

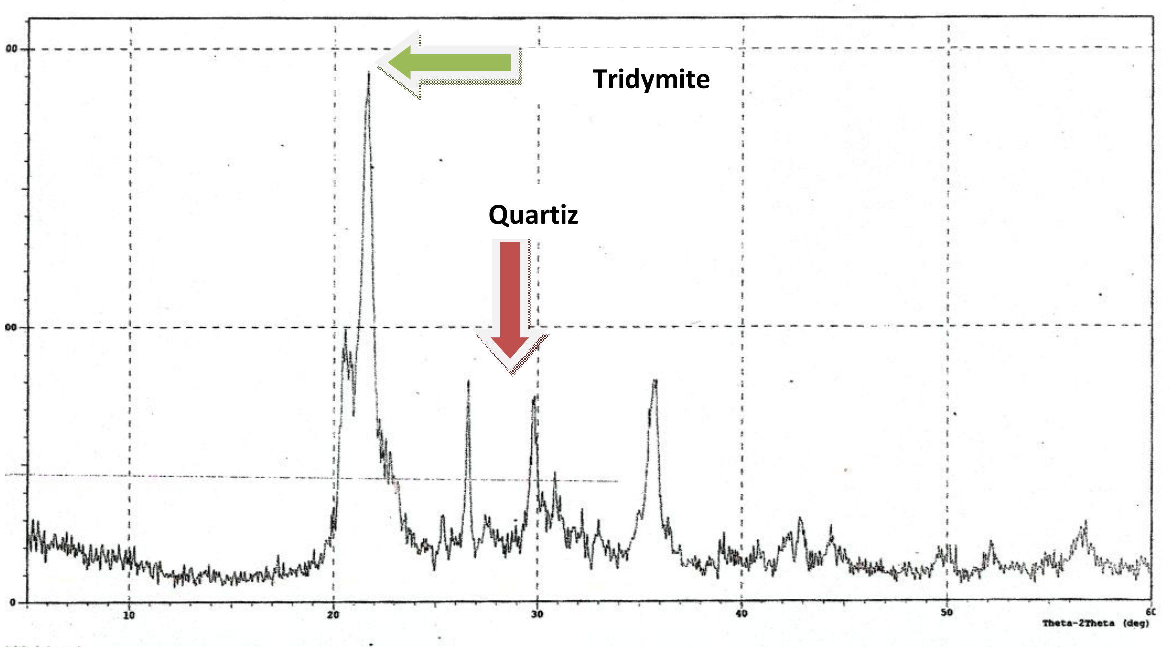

Fig.2: XRD for calcinated porcellanite

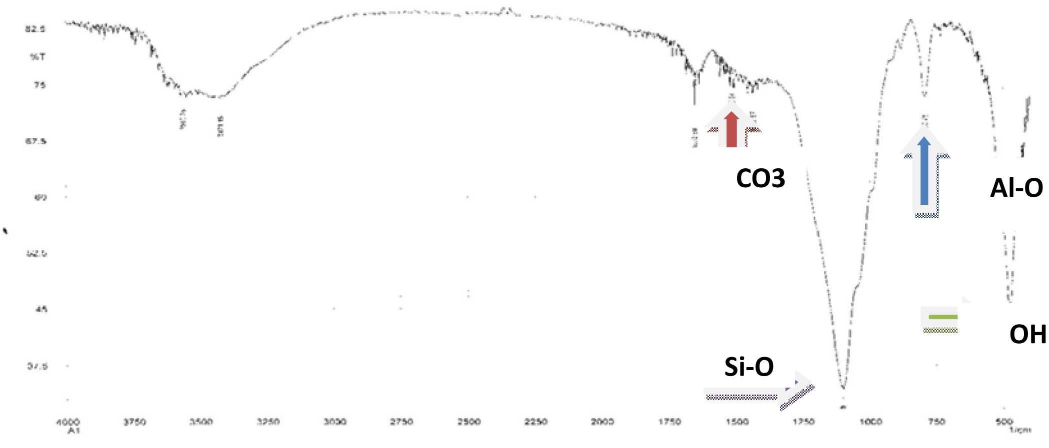

fig. 3: FT-IR for porcellanite

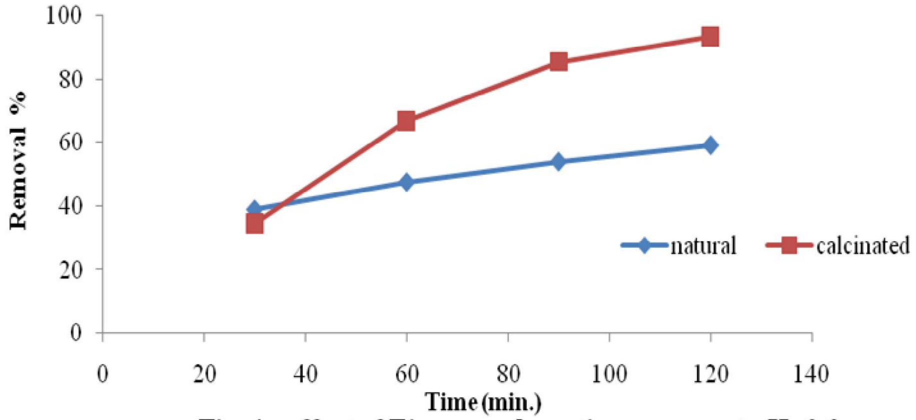

Fig. 4: effect of Time on adsorption process at pH=2.3 , temperature=30 °C, initial concentration=50 mg/l and adsorbent weight=1.5 gm

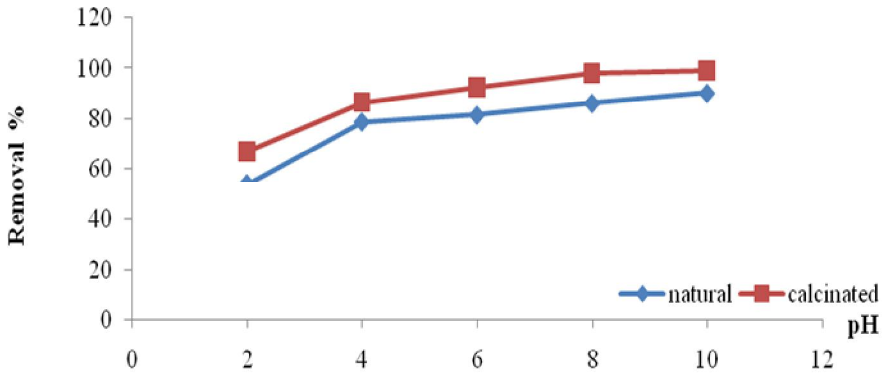

Fig. 5: effect of pH on adsorption process at temperature=30 °C ,adsorbent weight=1.5 gm, initial concentration= 50 mg/l and time= 60 min.

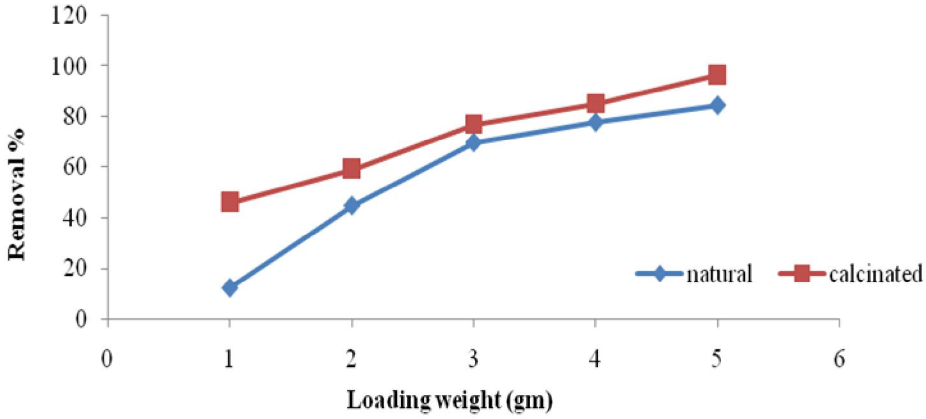

Fig . 6: effect of loading weight on adsorption process at pH=2.3,time=60 min , initial concentration=50 mg/l and temperature=30 °C

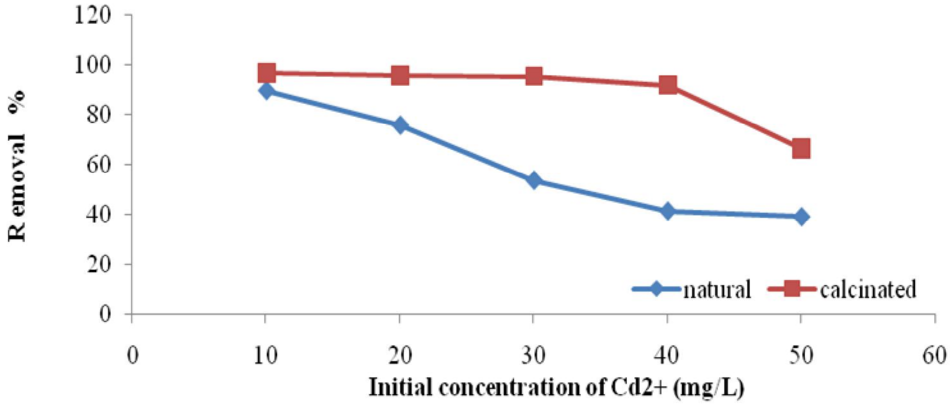

Fig. 7 effect of initial concentration of Cd2+ on adsorption process at temperature=30 °C, time=60 min, adsorbent weight=1.5 gm and pH=2.3

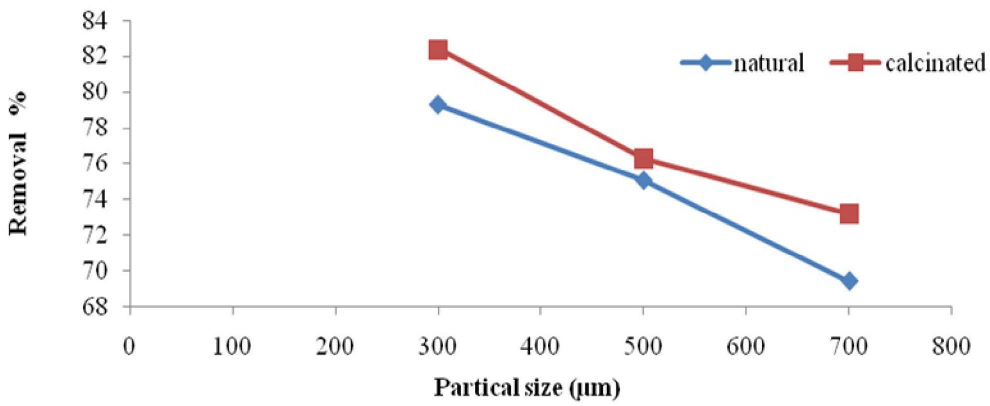

Fig 8: effect of Partical size of adsorbents on adsorption process at pH=2.3, initial concentration=50mg/l,time=60 min and temperature=30°C

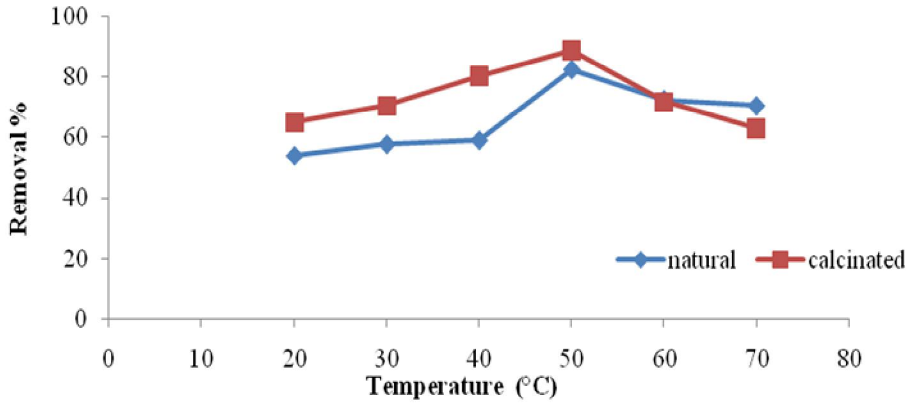

Fig. 9: effect of Temperature on adsorption process at pH=2.3,adsorbent weight=1.5 gm ,time=60 min and initial concentration=50mg/l.

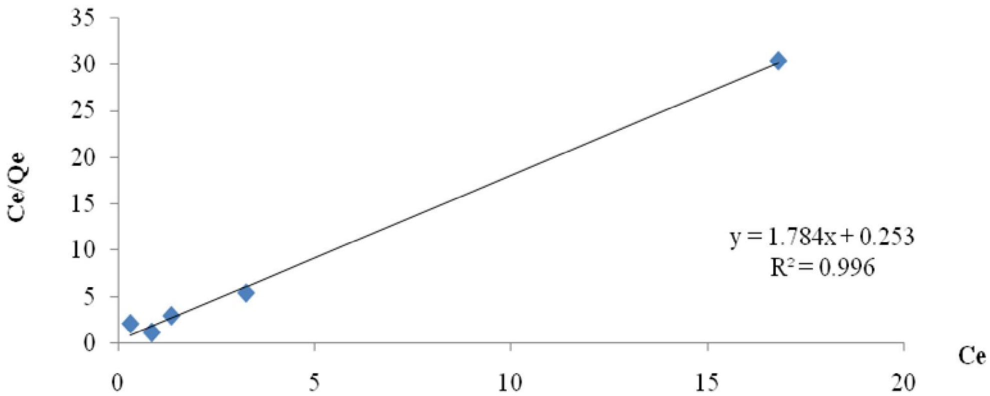

Fig. 10 : linear equation of Langmuir isotherm with calcinated porcellanite as adsorbent

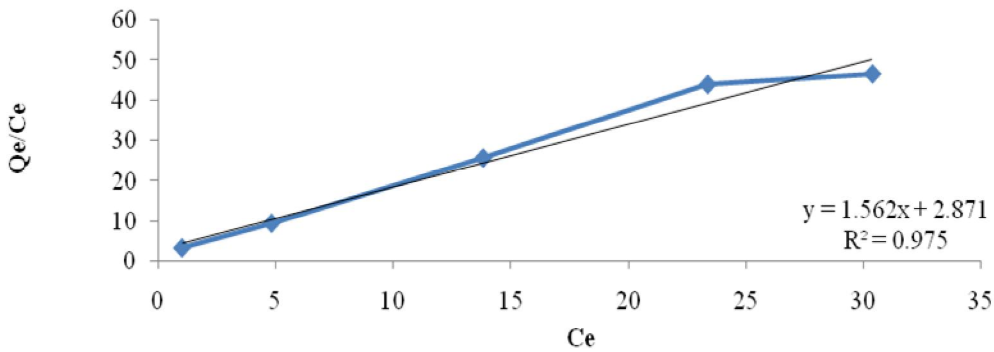

Fig. 11 : Linear equation of Langmuir isotherm with natural porcellanite as adsorbent .

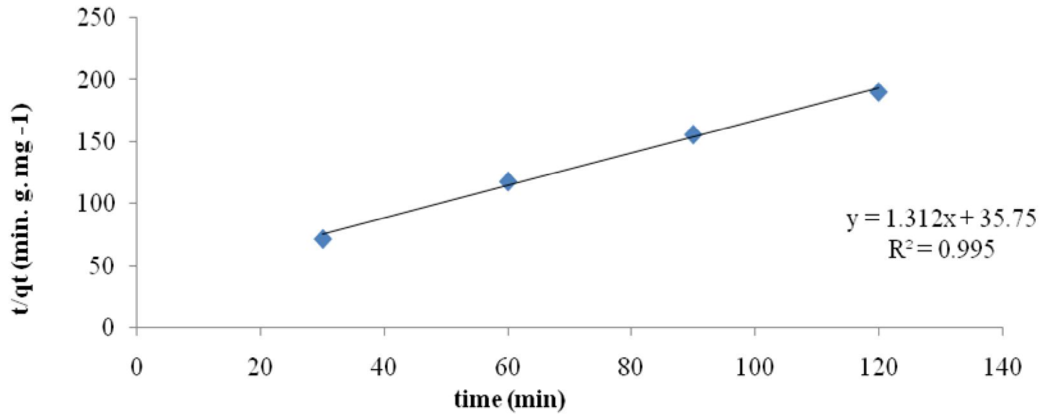

Fig. 12 :plot of pseudo-second order on natural porcellanite as adsorbent.

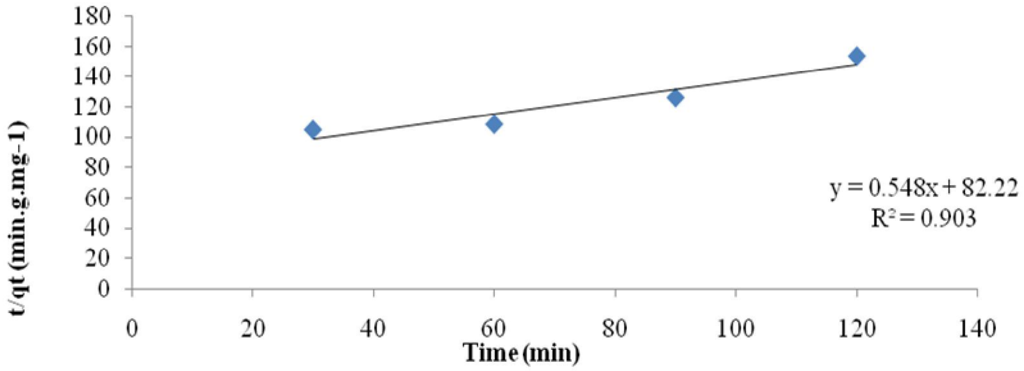

Fig. 13 : plot of pseduo-second order on calcinated porcellanite as adsorbent

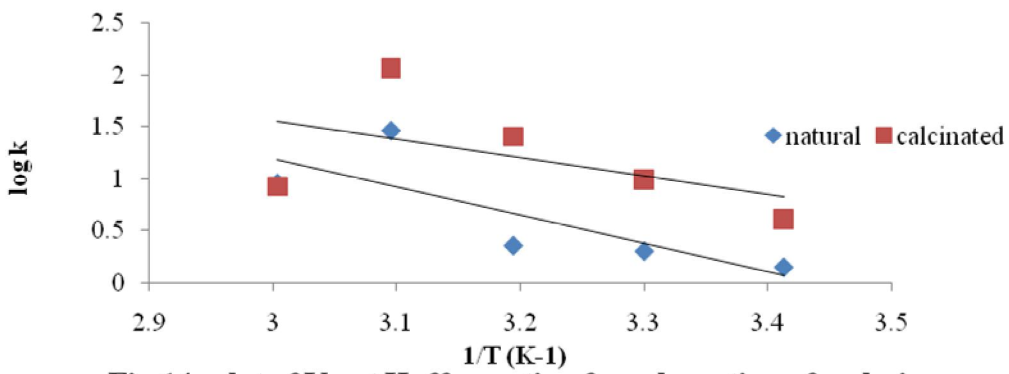

Fig.14: plot of Van,t Hoff equation for adsorption of cadmium on porcellanite

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