

## **Dynamic removal of cumulative toxic heavy metals Pb(II) and Cd(II) from aqueous solutions via Activated Nano-sized bentonite adsorbents**

**Hend H. Ghounam<sup>1</sup>, Somia B. Ahmed<sup>2</sup>, Mohamed A.Okbah<sup>2</sup>, Saeda A. El-Enein<sup>1</sup>, Eman R. Sallam<sup>2</sup>**

<sup>1</sup>Chemistry Department, Faculty of Science, Menoufia University,

<sup>2</sup>National Institute of Oceanography and Fisheries, Alexandria, Egypt

**\*Corresponding author: m\_okbah@yahoo.com**

### **Abstract**

The ability of three prepared nanobentonite adsorbents to remove Pb(II) and Cd(II) from aqueous solutions and real filed samples has been studied at different optimized conditions of concentrations, amount of adsorbent, temperature, contact time and pH. Maximum adsorption of Pb (II) and Cd (II) approximately 70% has been achieved in pH 7-8 at 30 min. The adsorption increased by increasing dosage of adsorbents amount. Isotherm analysis of adsorption data obtained at 25°C showed that the adsorption pattern of Pb (II) and Cd (II) on different types of nanobentonite adsorbents followed the Langmuir and Freundlich isotherm, respectively. The applicability of studied nano-adsorbents in filed was found successfully remove both metal ions in range ~ 90%.

**Keywords:** nanobentonite, adsorbents, lead, cadmium

## 1. Introduction

Water resources pollution is the major concern, as a result of the degree of the problems caused by heavy metals pollution, removal of heavy metals from wastewater is important. Increasing contamination of aquatic sources with large number of pollutants is not only threat for aquatic biota but creating a worldwide shortage of recreational waters. The water of aquatic systems contaminated by domestic activities, mining activities, municipal wastes, modern agricultural practices, marine dumping, radioactive wastes, oil spillage and industries (Ahalya et al. 2003; Das et al. 2008). The noncontrolling discharge of toxic chemicals through effluents from a wide range of industries (i.e. textile, steel, oil, tanneries, canneries, refineries, mines, fertilizers production units, detergent production units, electroplating units and sugar mills) into water bodies pollutes, these resources and causes hazardous effects on flora and fauna. Millions of gallons of water with toxic heavy metals are produced every year from several metal processing industries and discharged into the water bodies which are creating large impact on the environment and public health (IJSR 2013; Mahmoud et al. 2012). The heavy metal pollution researchers have used too many methods to obtain the most optimum and cost applicable method to remove toxic heavy metals from water. The most abundant metal existing in wastewater are Chromium, Mercury, Lead, Zinc, Nickel, Arsenic, Copper, Magnesium. Some of the methods applied, or studied, include precipitation, filtration, coagulation, ion-exchange, magnetic fields, fluidized bed reactor, ion flotation, reverse osmosis and adsorption. Hence, the disadvantages like incomplete metal removal, high reagent and energy requirement, generation of toxic sludge or other wastewaters that require careful disposal has made it imperative for a cost effective treatment method that is capable of removing heavy metals from aqueous effluent (Parham et al. 2012; Mohamed et al. 2015). Now a day's many novel materials may be used as adsorbents which collect, or adsorb, the heavy metals from the wastewater such as nano-sized particles. Various nano-sized materials using in the purification of surface water, groundwater and industrial wastewater streams is a matter of continuing concern. Nano-particles can be designed and synthesized to act as either separation or reaction media for pollutants. The high surface area to mass ratios of nanoparticles can greatly enhance the adsorption capacities of sorbent materials. They are good building blocks for developing good capability as adsorbents materials with modification ability to enhance their affinity and selectivity for purification of contaminated waters. Application of nanoparticles (NPs)

as novel adsorbents for removal of pollutants is gaining research interest. Recently, magnetic iron oxide nanoparticles, titanium oxide, silver nanoparticles have shown widespread applications as solid phase adsorbent for removal of different types of pollutants such as dyes and heavy metals (Sharma et al. 2009; Parham et al. 2012; Mohamed et al. 2015; Ahmed et al. 2014; Engates and Shipley 2011; Gong et al. 2012; Hua et al. 2012; Mohamed et al. 2016).

Bentonite is an aluminum phyllosilicate and generally impure clay consisting mostly of montmorillonite. There are a few types of bentonite and their names depend on the dominant elements, such as K, Na, Ca, and Al. Industry bentonite is a very rich clay mineral, consists of layers of two tetrahedral silica sheets sandwiching one octahedral alumina sheet (Kahr et al. 1990). Bentonite was used for adsorption of radioactive wastes and their sorption properties were investigated by Galamboš et al. (2009), the magnetic clays and bentonite were also investigated for adsorption of cadmium (II) and nickel from aqueous solution. The removal of Co(II) from aqueous solutions was studied by adsorption on natural clinoptilolite, kaolinite, activated carbon prepared from apricot stone, and sepiolite (Galamboš et al. 2009; Vereš, et al. 2010; Smiciklas et al. 2007; Saeedeh et al. 2015; Kobya, et al. 2005; Kara, et al. 2003; Akcay 2004).

The present work aim to investigate the adsorption of lead and cadmium ions on activated Nanobentonite from water solution in a short time via an easy procedure and lowers the concentration of this ion, close to the standard healthy levels announced by the World Health Organization.

## **2. Material and methods**

### *2.1 Chemicals and solutions:*

Powder commercial Bentonite was purchased from El-Sadat Bricks factory, El-Sadat city, Egypt. Nitric acid, hydrochloric acid, ethanol, sodium acetate anhydrite purchased from El-Nasr chemical company Alexandria,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Cd}(\text{NO}_3)_2$  purchased from CPA Chem. Buffer solutions (3.0, 4.0, 5.0, 6.0, 7.0 and 8.0) were prepared from 1.0 M hydrochloric acid and 1.0 M sodium acetate anhydrite solution by mixing the appropriate volumes of the two solutions and diluting to 1.0 L. The pH-value of resulting solution

was adjusted by a pH meter .The metal ion solutions were prepared from deionized doubly distilled water (DDW).

## 2.2 Instrumentation:

FTIR Spectrum (Bx –TENSOR- 37) used in the range 400-4000  $\text{cm}^{-1}$  to acquire the FTIR spectra of all chemically treated nanobentonite sorbents. These sorbents were also imaged using scanning electron microscope (JSM-5300, JEOL Ltd.). An ion sputtering coating device (JEOL-JFC-1100E) was used to coat the SEM specimens with gold to increase the conductivity (Figure 2). The pH measurements of buffer and metal ion solutions were carried out by using Digital pH meter (3505-Jenway ) calibrated against standard buffer solutions of pH ( from 3.0 to 8.0). All metal concentration in various samples was determined by Shimadzu model AA-6650 atomic absorption spectrophotometer at the specified wavelength.

## 2.3 Nanobentonite sorbets Synthesis:

Each 0.25 gm of bentonite was weighted and transferred to 250mL beaker. The 200ml of ethanol was added then the mixture sonicated for 4h at 25°C, the mixture dried at 120°C in vacuum oven. The dried phase was grinded in manual mortar to get fine particles of (Native–NBent.). 4.0 gm of (Native–NBent.) was add to 1L of 1.0M NaOH and stirred for 4h. Base treated nanobentonite was filtrated, washed with D.W and dried at 120°C to produce (B-NBent.) sorbent. Acid treated nanobentonite was prepared by the same way, a sample of 4.0 gm of (Nativ–NBent.) was weight and add to 1L of HCl solution (1:1, v/v ratio) the reaction mixture stirred for 4h, then filtrated, washed with distilled water and dried at 120°C to produce that sorbent (A-NBent.). All nano-adsorbents were listed in Table 1.

**Table (1): Nanobintonite adsorbents.**

No.	Adsorbents	Abbreviation
1	Native nanobentonite adsorbents	Native–NBnt.
2	Basic activated nanobentonite adsorbents	B–NBnt.
3	Acidic activated nanobentonite adsorbents	A–NBnt.

## 2.4 Adsorption experiments:

### 2.4.1 Batch adsorption experiments:

Batch adsorption experiments were conducted by adding  $25 \pm 1$  mg of the nano-adsorbent mass to 50 mL of different Pb(II) and Cd(II) test solutions at different pH (3-8) in an Erlenmeyer flask (100 mL capacity). The initial solution pH was adjusted using 0.1M HCl and sodium acetate. The flasks were agitated at speed (150 rpm) in a rotary shaker for different contact time (5-60 min). The nano-adsorbent mass was separated from the test solution by filtration using Whitman filter paper. All experiments were carried out at ambient temperature (25°C). The amount of metal adsorbed was calculated from the difference between its concentration in test solution and in the supernatant liquid. The initial and final concentrations of metal were analyzed by atomic absorption (Gupta et al. 2011)

#### *2.4.2 Applications of Nanobentonite adsorbents for removal of toxic heavy metal from real water samples.*

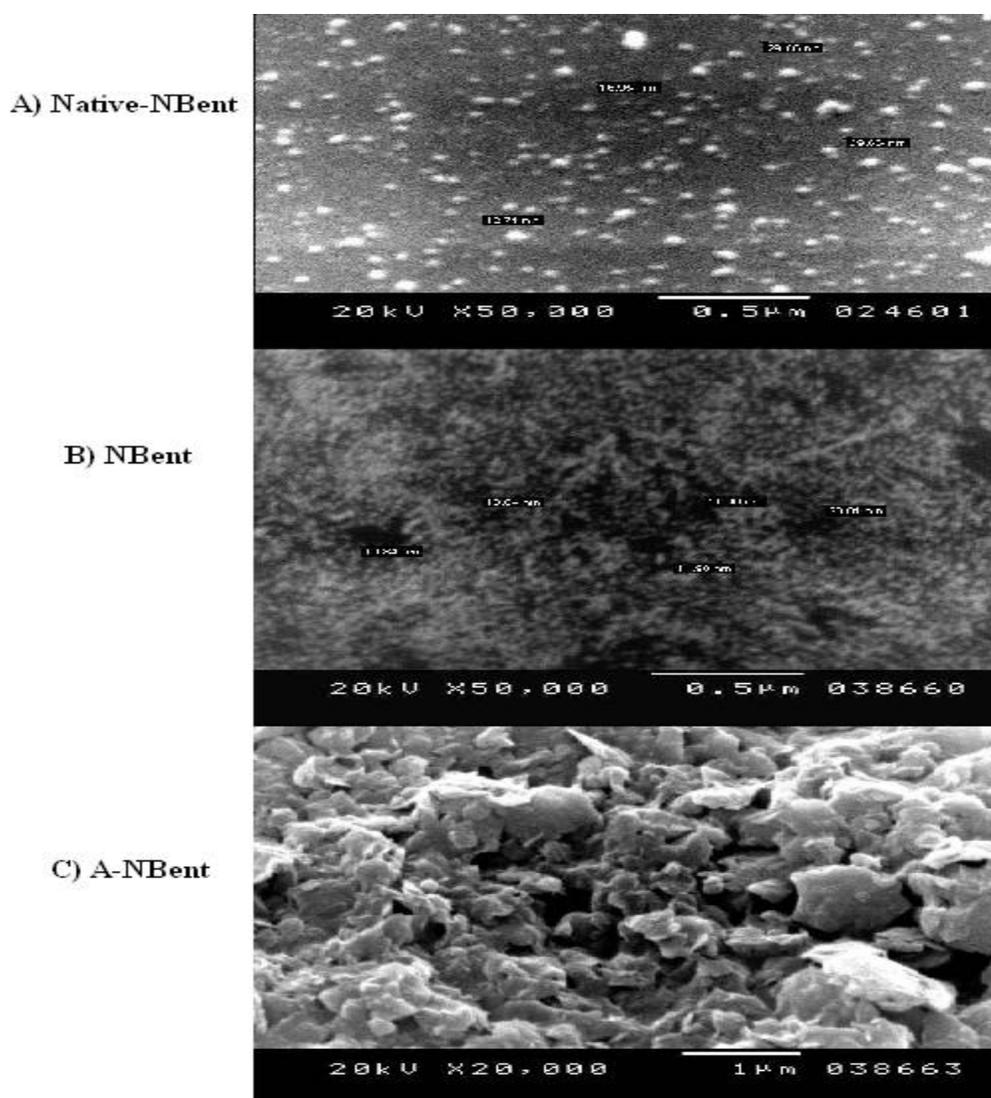
Removal and extraction of cadmium and lead from various water samples were performed according to the following procedure. Raw water samples (Shibin domestic waste water station) were collected and a 1.0 L of each sample was spiked with 1–2 ppm of each metal ion. Batch equilibrium technique was used and applied to evaluate the efficiency of Nanobentonite adsorbents by add  $100 \pm 1$  mg of each nanobentonite adsorbents to 1L  $\pm 1$  mg of real sample with starring for 1h then the unbounded metal detected by atomic absorption spectrophotometric analysis (Tarek et al. 2014).

### **3. Results and discussion**

#### *3.1 Surface characterization:*

The surface functional groups of the studied nano-adsorption systems were characterized by using the FTIR analysis for activated acidic and basic nanobentonite. As the bentonite is absorbent aluminum phyllosilicate clay consisting mostly of montmorillonite, the most characteristics related peaks for both adsorbent were found the OH bending band at  $915 \text{ cm}^{-1}$  was readily assigned to Al–OH. The strong band centered at  $1029 \text{ cm}^{-1}$  was the Si–O stretching vibration together with those at  $524$  and  $463 \text{ cm}^{-1}$  which indicated the Si–O–Al and Si–O–Si bending vibrations, respectively that were typical of the tetrahedral Si–O. Bands at  $3426$  and  $1637 \text{ cm}^{-1}$  were attributed to the OH stretching and bending vibrations of molecular water, respectively (Zagorka and AleksandrEur

2007, Fenandes et al. 2007). Band at  $1475\text{ cm}^{-1}$  was assigned to the presence of carbonate (Chattopadhyay et al. 2006). The morphologies of three prepared nanobentonite adsorbents were obtained by SEM. Figure 1 (A, B and C) showed the SEM images of Native-NBent., B-NBent. and A-N.Bent., respectively. SEM image (Figure 1B) of B-NBent showed more uniform and less Nanoparticles size ( $\sim 11\text{-}23\text{nm}$ ) than the native one which have particles size in around  $\sim 12\text{-}29\text{nm}$ . On the other hand, the acidic activation seems to be non effective process over nanobentonite surface, where the particles size of A-NBent was found more compact and less uniform than N-Bent adsorbent surface (Figure 1C).



**Figure (1): SEM of Nano-bentonite adsorbents**

### 3.2 Adsorption results:

#### 3.2.1 Effect of contact time:

The effect of contact time on the adsorption capacity removal percent of different prepared nano-adsorbent (Native–NBent., B-NBent. and A-NBent.) is depicted in Table 2. The results showed a good ability to remove Cd (II) from aqueous solution. Both Nativ–N.Bnt. and B-N.Bnt. showed a greater ability from first 5min. approximately 45%, 46%, respectively. Adsorption increased gradually to reach maximum (69%, 77%) after 30 min contact time. In the other side the percentage removal of A-N.Bnt. showed slow start with 16% after 5 min. also, the percentage increased quickly to 71% at 30min. The percentage of removal of all Nano-adsorbents was decreasing after 30 min. gradually. The same manner was also observed when Pb (II) removal tested by the same three nanosorbents. The removal percentage of lead ion was increased gradually from approximately 52, 39 and 45% for Native–NBent., B-NBent. and A-NBent., respectively. These ratios were also increased gradually to a maximum at 30 min. to reach 72.7, 72.5 and 70.3, respectively. The present study can be concluded that the contact time between the nanobentonite and the metal ions shouldn't continue after 30 min.

**Table (2): Effect of contact time on the adsorption capacity removal percent of Pb (II) and Cd (II), using different prepared nano-adsorbent (Native–NBent., B-NBent. and A-NBent.)**

		Time(min.)						
		5 min	15 min	20 min	30 min	35 min	40 min	60 min
<b>Pb (II) removal %</b>	<b>Acidic-N.Bent.</b>	<b>47.02</b>	<b>51.08</b>	<b>59.28</b>	<b>70.34</b>	<b>60.62</b>	<b>49.46</b>	<b>47.02</b>
	<b>Basic-N.Bent.</b>	<b>39.5</b>	<b>50.86</b>	<b>63.03</b>	<b>72.58</b>	<b>59.85</b>	<b>45.16</b>	<b>40.42</b>
	<b>Native-N.Bent.</b>	<b>52.02</b>	<b>52.4</b>	<b>59.54</b>	<b>72.75</b>	<b>71.5</b>	<b>61.81</b>	<b>59.44</b>
<b>Cd (II) removal %</b>	<b>Acidic-N.Bent.</b>	<b>16.52</b>	<b>38.38</b>	<b>53.5</b>	<b>71.28</b>	<b>55.47</b>	<b>43.88</b>	<b>29.1</b>
	<b>Basic-N.Bent.</b>	<b>46.54</b>	<b>46.83</b>	<b>54.59</b>	<b>77.3</b>	<b>58.91</b>	<b>41.09</b>	<b>40.48</b>
	<b>Native-N.Bent.</b>	<b>45.1</b>	<b>48.94</b>	<b>54.7</b>	<b>69.21</b>	<b>43.7</b>	<b>43.81</b>	<b>42.28</b>

#### 3.2.2 Effect of pH:

The pH effect on the adsorption of Cd (II) and Pb (II) onto the prepared nanobentonite was studied by evaluating the adsorption at different pH values of 3, 4, 5, 6, 7 and 8 (Table 3). It was

found that the nanobentonite effective for the adsorption of both tested metal ions above pH 3 and below pH 8, since Pb (II) at strongly acidic media did not adsorb well to the nanobentonit with percentage removal in range 15-20%. The adsorption of Cd (II) in acidic medium showed more percentage reached to 48, 40 and 33% for Native–NBent, B-NBent and A-NBent, respectively. The data illustrates that the maximum adsorption removal was at pH 7 to 8. The natural and slight basic medium raises the removal adsorption of Cd (II) reach 87.5, 87.9 and 84.5% at pH 8 for Native-NBent, B-NBent and A-NBent, respectively. The three nanobentonite ability to uptake metal ions found more selective to Pb (II) than Cd (II) to reach approximately 90% at pH 8. The result could be explained that, at low pH values, nanobentonite surfaces are protonated such that the net surface charge is positive, which not enhancing the adsorption of the positively charged of Cd (II) and Pb (II). As the pH increases, the nanobentonit surface is increasingly deprotonated such that the net surface’s positive charge decreased, leading to a high in metal ions adsorption (Mohamed et al. 2015). Thus, the pH dependent behavior of both metal ions sorption onto nanobentonite adsorbents suggests that Cd (II) and Pb (II) sorption is physical adsorption one.

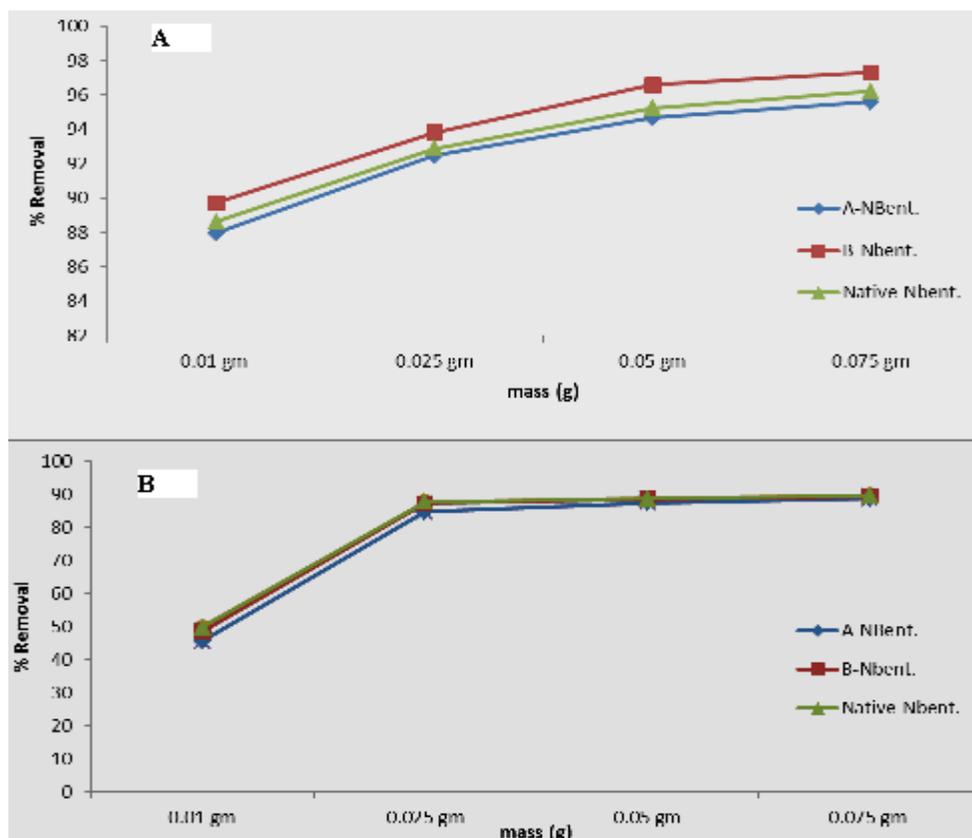
**Table (3): Effect of pH on the adsorption capacity removal percent of Pb (II) and Cd (II), using different prepared nano-adsorbent (Native–NBent, B-NBent and A-NBent)**

		pH					
		3	4	5	6	7	8
<b>Pb (II) removal %</b>	<b>Acidic-N.Bent.</b>	<b>15.89</b>	<b>35.14</b>	<b>41.79</b>	<b>56.68</b>	<b>70.62</b>	<b>92.59</b>
	<b>Basic-N.Bent.</b>	<b>19.58</b>	<b>36.6</b>	<b>40.47</b>	<b>59.22</b>	<b>72.24</b>	<b>93.24</b>
	<b>Native-N.Bent.</b>	<b>20.05</b>	<b>37.83</b>	<b>40.86</b>	<b>55.6</b>	<b>71.65</b>	<b>92.92</b>
<b>Cd (II) removal %</b>	<b>Acidic-N.Bent.</b>	<b>33.95</b>	<b>50.92</b>	<b>67.87</b>	<b>65.16</b>	<b>71.01</b>	<b>84.55</b>
	<b>Basic-N.Bent.</b>	<b>40.07</b>	<b>51.07</b>	<b>69.24</b>	<b>65.43</b>	<b>77.39</b>	<b>87.9</b>
	<b>Native-N.Bent.</b>	<b>48.94</b>	<b>65.13</b>	<b>72.57</b>	<b>66.81</b>	<b>77.79</b>	<b>87.54</b>

### 3.2.3 Effect of dosage of adsorbent:

Various amounts of adsorbent ranged from 10 mg to 75 mg were used. The percentage removal of the tested metal ions varied linearly with the amount of the adsorbent as shown in Figure 2. The increasing in dose of nanobentonit adsorbents enhances the percentage removal of Pb (II) to above 95% at 75 mg only. That removal percentage was below 90% for Cd (II) via B-NBent and A-

NBent, while it was below 50% for Cd (II) by Native-NBent, which excluded it from the previous trend. That behavior explained by the favorability of nano-sorbents to aggregate together at high dosage more than uptake the metal ions (Mohamed et al. 2015).one can easily observed that the activation of Native nanobentonit by acid or base overcome the aggregation problem which happen at high dosage of nano-sorbents.

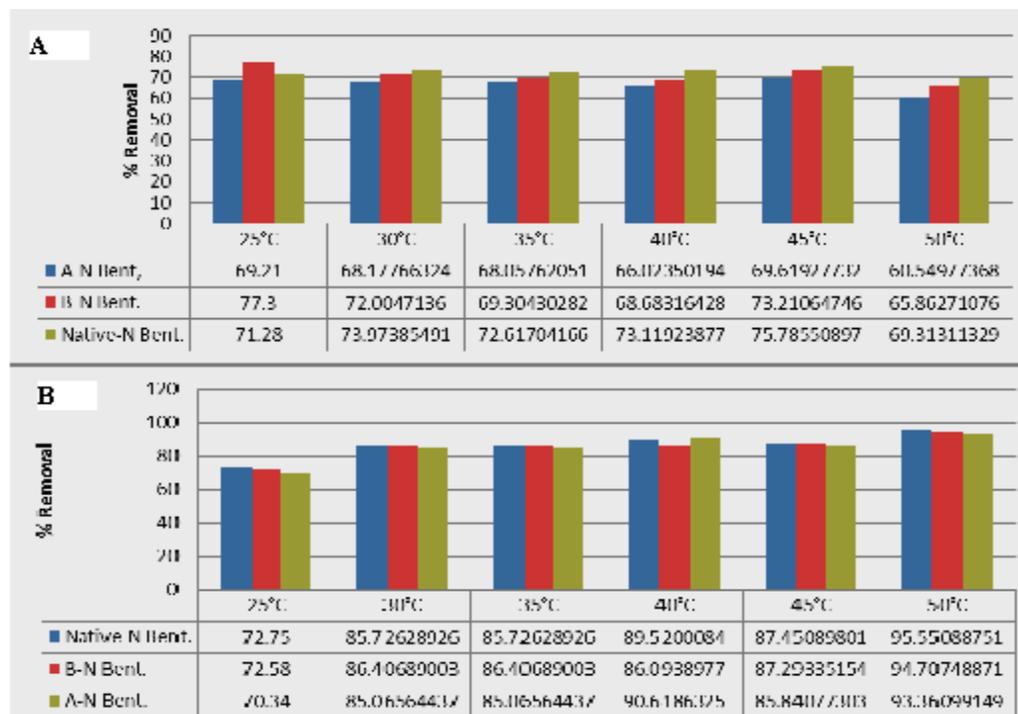


**Figure (2): Effect of mass dosage on A) Pb (II) and B) Cd (II) adsorptions**

### 3.2.4 Effect of temperature on both metal adsorptions:

Figure 3 showed the effect of temperature on both metal adsorptions. The percentage removal of Pb (II) was found increasing with temperature for three nano-adsorbents to maximum at 50°C, above 90%. That trend wasn't observed at all in case of Cd (II) adsorption. The three nano-adsorbents show no obvious variation with change in temperature. That result was compatible with

results from pervious sections which reflected more adsorption selectivity for Pb (II) via those three nanobentonite adsorbents.

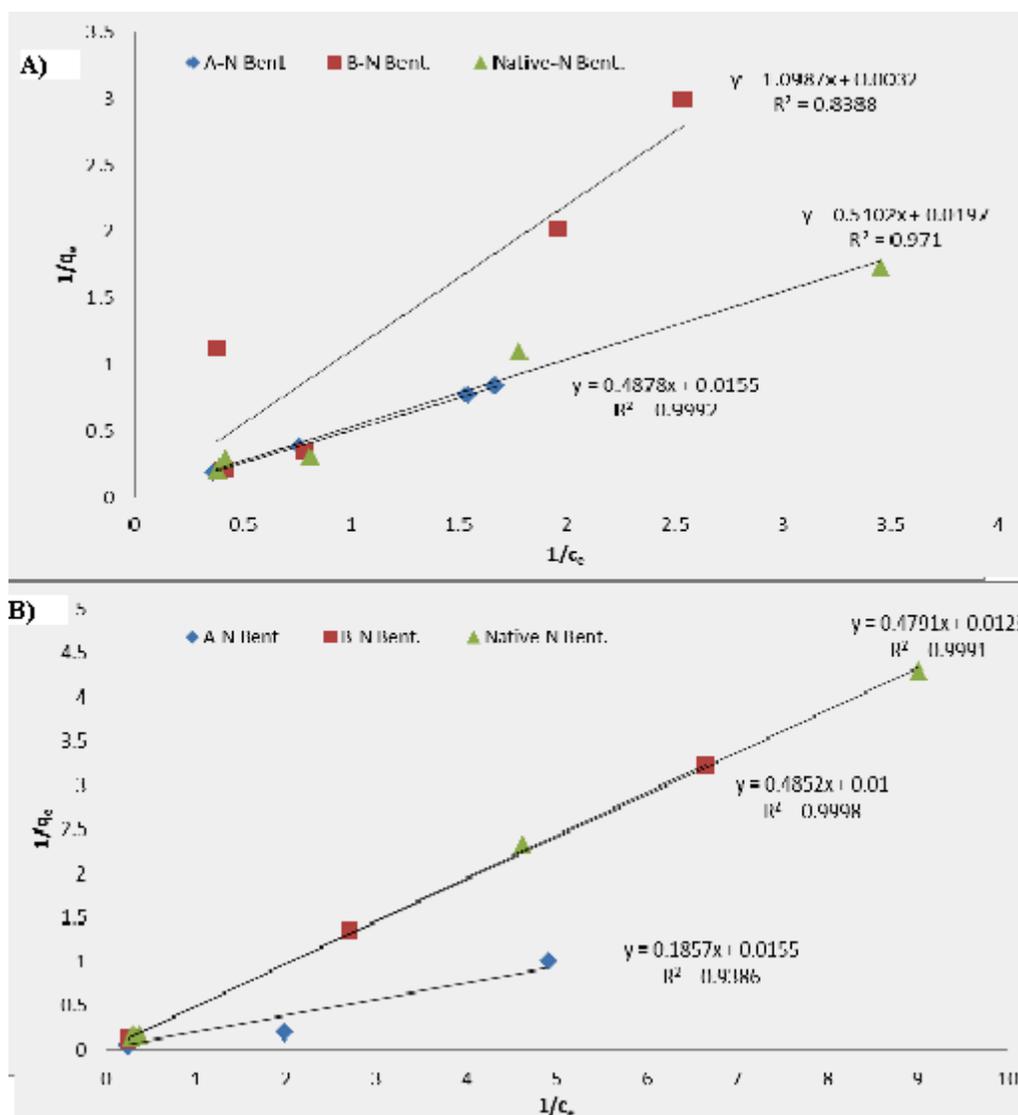


**Figure (3): Effect of temperature on A) Pb (II) and B) Cd (II) adsorptions**

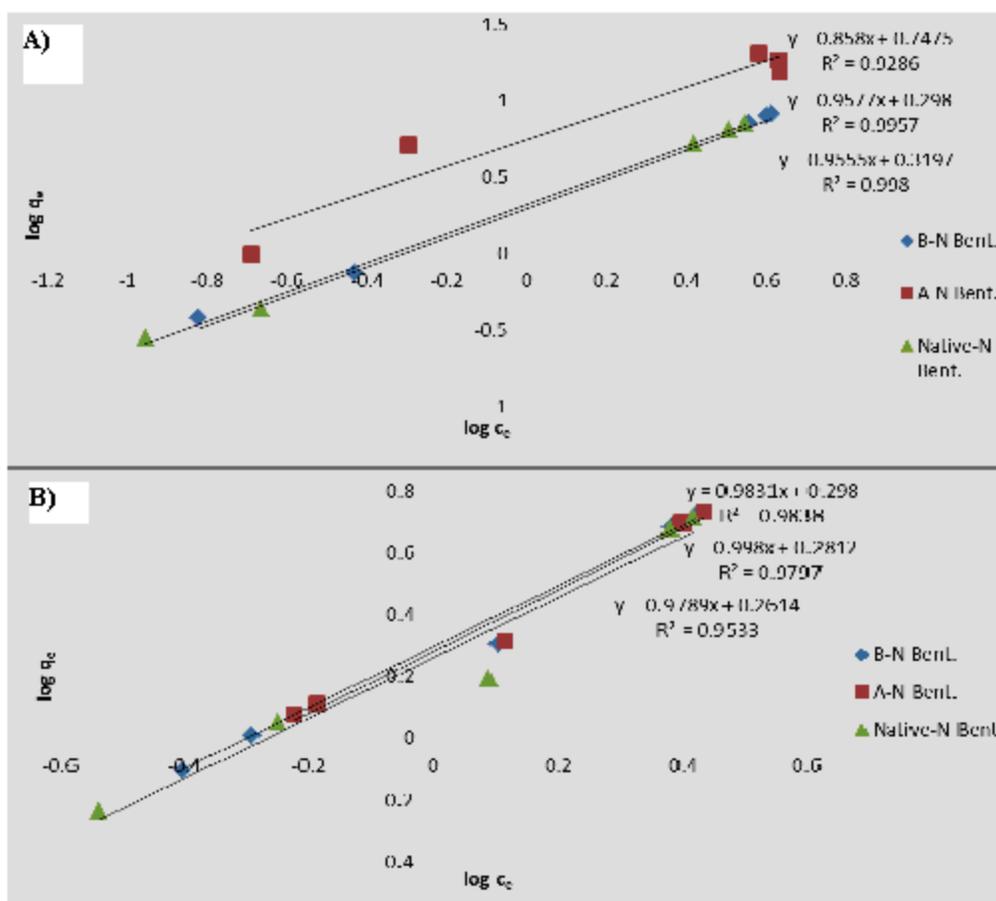
### 3.2.5 Effect of initial concentration of metal ions:

The results of tested metal ions equilibrium experiments for Native-NBent., B-NBent. and A-NBent such as effective adsorbents are given in Figures 4–5. Two isotherm models were used here to describe the relationship between metal ions and sorbents' surface. The first is the Langmuir model, which is mainly based on the adsorption of the target species by assuming that the adsorptive forces are similar to those characterized in chemical interaction. The isotherm constants for the two models were obtained by linear regression method and were listed in Table 6. In case of the two applied models, Langmuir adsorption model, high correlation of the experimental and model data was obtained ( $R^2$ , were almost above 0.9). The values of the Nano-adsorption capacity  $q_{max}$  and Langmuir constant  $k_1$  were calculated by linear regression. The  $q_{max}$  values were around 52,333, 66 mg/g for Pb (II) in the presence Native NBent., B-NBent. and A-NBent., respectively and for Cd (II) were around 83. 100 and 66, in respectively. All  $K_L$  values obtained are greater than zero and less than unity indicates the favorable adsorption of both Pb (II) and Cd (II) by the different nanobentonite adsorbents. The matching of results to Langmuir equilibrium isotherm well

describes the metal adsorption process as the monolayer formation of metal ions onto the nano-adsorbent surface with finite number of identical sites, which are homogeneously distributed over the nano-adsorbents surface. Freundlich model provides two parameters:  $k_f$  and  $n$ .  $k_f$  is related to the adsorption capacity and adsorption intensity of the metal ions on the different nano-adsorbents, and represents the quantity of metal ions adsorbed onto three nanobentonite adsorbent at equilibrium concentration.  $n$  represents the strength of metal ions adsorption with value from 1 to 10 indicates relatively strong adsorption. The obtained  $n$  values in that studied were more than 1, which indicates relatively strong adsorption of the metal ions on the nano-adsorbents surface (Kiran and Kaushik, 2008; Sadeek et al. 2015).



**Figure (4): Langmuir isotherm model of A) Pb (II) and B) Cd (II)**



**Figure (5): Freundlich isotherm model of A) Pb (II) and B) Cd (II)**

### 3.3 Applications of Nanobentonite adsorbents for removal of Pb (II) and Cd (II) from real water samples

The capacity removal of the nanobentonite adsorbents for Cd (II) and Pb (II) from raw samples (Shibin domestic wastewater station) were evaluated as the final step in determination of those adsorbents validity. That raw water sample collected was found containing a traces concentration of some heavy metals beside the target metal ions (Pb (II) and Cd (II)) which effect on the validity of the three nano-adsorbent in real application (Table 4).

**Table (4): Langmuir parameter**

Adsorbents	Pb (II)		Cd (II)	
	$q_{max}$	$K_L$	$q_{max}$	$K_L$
Native-NBent.	66.666	0.037255	83.33333	0.025052
Basic-NBent.	333.3333	0.002732	100	0.020619
Acidic-N.Bent	52.63158	0.030801	66.66667	0.081081

Table 5 lists the results of metal extraction removal percent by three prepared nanobentonite adsorbents. The extraction percentages of Cd(III) from waste water by three nano-adsorbents were found to be about 43,41 and 42% in first stage and that percentage raises massively to be around 84,82 and 81% in second stage, for Native-NBent, B-NBent and A-NBent, respectively. On the other hand the percentages of removal of Pb (II) show very low start at first stage by percent around 12-15%. That percentage was jump to be approximately 90% for all three nano-adsorbents after 2<sup>nd</sup> stage. That trend of removal totally different from the removal of both metal ions in absence of other traces heavy metal, especially with Pb (II) extraction. Which lead us to assume that the competitive action, in first stage, between the different metal ions in solution slow down the selectivity of removal of nanobentonit adsorbents toward target metal ions (Pb (II) and Cd (II)), especially in case of Pb (II). In second stage, the competition was found less or ended which increase the adsorbativity of three nano-adsorbents of target metal ions.

Pb(II)				Cd(II)			
Conc. 1.7466 (ppm)	After 1 <sup>st</sup> stage			Conc. 2.3048 (ppm)	After 1 <sup>st</sup> stage		
	Native-NBent.	Basic-NBent.	Acidic-NBent.		Native-NBent.	Basic-NBent.	Acidic-NBent.
	1.5210 (12.91%)	1.4690 (15.89%)	1.4807 (15.22%)		1.2991 (43.60%)	1.3105 (43.14%)	1.3236 (42.57 %)
	After 2 <sup>nd</sup> stage				After 2 <sup>nd</sup> stage		
0.5200 (92.87%)	0.4490 (91.36%)	0.4661 (90.36%)	0.5579 (82.60 %)	0.6098 (84.68%)	0.6895 (81.46%)		

**Table (5): Removal percentage of Pb (II) and Cd (II) from Shibin domestic wastewater station.**

#### 4. Conclusion

The nanobentonite adsorbent was prepared and activated by both acid and base treated. Characterization using SEM image shows more uniform and more surface area for B-NBent adsorbent than other two nanobintonite adsorbents. The adsorbents show good adsorption percentage removal for both metal ions Pb (II) and Cd (II). In the batch mode, it was found that the adsorption removal is increased by increasing the contact time till 30 min and change pH from acidic medium to natural and slight basic one. The three nanobentonite adsorbents was obeyed both Langmuir and Freudlich model of isotherm with  $K_1$  less than unit. Our results demonstrate that the nanobentonite adsorbent, whose activated by base, are very promising materials as

adsorbent for both tested metal ions while the acidic activation show as a non-effective one comparing to other nanobentonite adsorbents. Also the three adsorbent show high selectivity to Pb (II) removal under almost tested parameters. The highly performance of three nano-adsorbents in removal of contaminants in real water here could be used as a base for nano-filtration unit systems. We believe it is required to have a small material with large surface area and good ability to remove pollutants, especially for compact columns used in water filtration units.

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