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Copper, Zinc and Nickel's removal by bentonite clay: Case study in mono and multicomponent systems

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ABSTRACT/RESUME

Abstract : *The main purpose of this work is the Copper, Zinc and Nickel's removal from mono and multi-metal ions aqueous solution using an Algerian bentonite without treatment. The bentonite is characterized using SEM, XRD and X-ray fluorescence. The effect of initial pH and contact time are studied.*

Under mono and multicomponent systems, the kinetic studies performed at pH 5, indicate that the adsorption follows a pseudo second order model. For both systems, the isotherm data are well correlated with Langmuir model. Whereas the maximum adsorption capacities follow the sequence's order Cu > Zn > Ni. In the case of multicomponent system, the Cu(II), Zn(II) and Ni(II) adsorptions capacities (58.82, 19.53 and 6.56 mg/g) are lower than the obtained ones for the monocomponent system (58.48, 49.02 and 31.74 mg/g). In addition to that, a mutual competitive effect is observed. Zn(II) and Ni(II) ions adsorption is also inhibited by Cu(II) ions with no change in the maximum Cu(II) adsorption capacity.

I. Introduction

The removal of heavy metals from water became an important process and is becoming more important with the increasing of industrial activities. Heavy metals such as Ni, Zn and Cu are known to be carcinogenic and highly toxic for both humans and other living form. Even at low concentration, these pollutants are not biodegradable and can accumulate along the food chain and persist in the environment [1,2]. These metals widely exist in the industrial effluents from metallurgy, mining areas, batteries, printing, electroplating, tannery and ceramic industries [3,4]. Therefore, the necessity to reduce hazardous heavy metals from wastewater effluents has become a worldwide challenge that the humanity faces today to protect public health [5]. Several technical processes have been developed over the last years for removing heavy metals. Conventional physicochemical methods including chemical precipitation, evaporation, ion exchange, oxidation/reduction and membrane filtration technologies, etc. are often ineffective and/or expensive, especially to remove heavy metal ions at low concentrations [6]. To reduce heavy metal content in wastewaters at discharge to acceptable level with low cost, efficient and environmental friendly technologies are needed to be developed. Adsorption is one alternative effective process to solve this problem [7,8]. Also, activated carbon is the most popular adsorbent. It has been widely used in wastewater treatment [9,10]. Unfortunately, it is known for its high of manufacturing and regeneration cost. Otherwise, it is necessary to find low cost and easily available adsorbents for the removal of heavy metal ions from aqueous solutions [7,10]. Natural materials, particularly clay minerals, may have potential to be used as low cost adsorbents which represent unused resource [11]. This is an economic alternative according to their high exchange capacity and high specific surface areas. It is also for their chemical and mechanical stability and layered structure, etc. Moreover, they have the advantage of being abundant and inexpensive [5,12].

In this perspective, several researchers studied the effectiveness of various type of clay in removing heavy metals from aqueous solutions including montmorillonite [13,14], Kaolin [15,16] bentonite [17,18], illite [19] and zeolite [20].

Bentonite is one of the plentiful natural clays, mainly composed of smectite, a 2:1 type of aluminosilicate. It is classified as low-cost adsorbent. Firstly, this is due to its local availability and its low-cost extraction and preparation. Secondly, its layered structure offers large retention capacity [12,21].

Several studies have been carried out on the single adsorption of heavy metal ions on bentonite [21-23]. However, industrial wastewater is a complicated mixture containing more than one metal ion. Therefore, it is necessary to extend the adsorption studies to multicomponent systems. These studies are important to obtain an accurate natural model system. Currently, there is an increasing trend for the heavy metals adsorption study in multicomponent systems i.e. competitive adsorption on bentonite or other adsorbents [24-26]. Among studies were conducted on adsorption of heavy metals in multicomponent system: Zhi-rong and Zhou [26] found that the adsorption ability of Na-bentonite for two metallic ions in a multicomponent system follows the order $Cu^{2+} > Ni^{2+}$ effect. Adebowale et al. [27] reported that the capacity of adsorption of TPP-kaolinite clay for both metal ions was decreased by simultaneous presence of both metal ions. Whereas, Yavuz et al. [28] studied the adsorption of Cu(II), Ni(II), Co(II) and Mn(II) on kaolinite. They found that kaolinite shows the following adsorption affinity order for metal ions: Cu(II) > Ni(II) > Co(II) > Mn(II). In the work of Bourliva et al. [12], it was proved that the Ca-bentonite displays a high selectivity toward one metal in a multicomponent system with an affinity order of $Cu^{2+} > Ni^{2+} > Pb^{2+} > Cd^{2+}$. Compared to single-metal system, Corami et al. [29] reveal that the competitive effects between Zn and Cu have reduced the hydroxyapatite metals adsorption. In the same point of view, Padilla-Ortega et al. [30] studied the Cd(II) and Ni(II) adsorption on bentonite and reported that the Cd(II) affinity for the bentonite was greater than that of Ni(II). However, the affinities of both metals towards the bentonite were very similar in the competitive adsorption. Eloussaief et al. [31] reported that the competitive ability of Pb(II), Zn(II) and Cd(II) followed the order Pb(II) > Zn(II) > Cd(II).

The main purpose of this work is to evaluate the Cu(II), Ni(II) and Zn(II) adsorption from aqueous solutions using Algerian bentonite without any pre-treatment. This is done in order to decrease the removal process cost. Then it is shown the effect of various experimental parameters such as solution pH, contact time, adsorbent amount and initial metal concentration. These latter were investigated under competitive and non-competitive systems.

II. Materials and methods

II.1. Instruments and reagents

All solutions are prepared from analytical reagent grade chemicals (Merck, Darmstadt, Germany). The metal ions solutions are made of metal salts of $Cu(NO_3)_2.3H_2O$ for Cu, $Zn(NO_3)_2.6H_2O$ for Zn and $Ni(NO_3)_2.6H_2O$ for Ni. The pH of the solution is adjusted with the addition of NaOH (0.1N) and HNO_3 (0.1N). Metal ion concentration is analysed by a flame atomic adsorption spectrophotometer (Perkin Elmer AAnalyst700). Whereas, the pH is measured by a standard pH-meter (HI 221, HANNA instruments, Tanneries, France).

II.2. Adsorbent

A raw bentonite from Hammam Boughrara (MAGHNIA, West Algeria) is used for these series of experiments. This bentonite is washed several times with distilled water and drieded at 70 ± 2°C before the experiments.

In first time, chemical composition is performed using Cement X-ray spectrometer Philipsx'cem.

Then the morphology of the adsorbent is investigated using JOL5510 Scanning electronic microscopy (SEM).

Finally, crystallinity is determined by powder X-ray diffraction using a diffractometer (Inel cps 120) equipped with an iron anticathode ($\lambda = 1.936$ Å) and an ethane ionisation curved detector allowing angles to be read simultaneously in the range $2\theta = 5\text{-}125°$.

II.3. Methods

The Cu, Zn and Ni adsorption by natural bentonite is studied by a batch operation at temperature (20 ± 2°C), including effects of pH, contact time, initial metal ion concentration and concentration of adsorbent in single and multicomponent systems.

The influence of the pH (1-6) and bentonite concentration (1-10 g/L) on heavy metals removal is studied. The pH is limited to value of 6.0 ± 0.2 in order to avoid the precipitation of metal ions that can occur at higher pH values. The adsorption studies of these parameters are carried out by shaking a series of bottles containing 100 mL of metal ions solution and 0.3000 ± 0.0001 g of bentonite. The samples are stirred at 300 rpm for 24 hours.

Initial metal concentration of each metal ion in multicomponent system is in the molar ratio of 2:2:2. After adsorption, the samples are centrifuged and analysed using an atomic absorption spectrophotometer. The amount of adsorbed metal per mass unit of bentonite (q_e) and adsorption percentage (R) at equilibrium are calculated by the following expressions, respectively:

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

$$R(\%) = \frac{(C_0 - C_e)}{C_0} 100 \qquad (2)$$

Where C_0 (mg/L) is the initial concentration of heavy metal ion, C_e (mg/L) is the equilibrium concentration of heavy metal ion, V (L) is the volume of aqueous solution and m (g) is the amount of the bentonite.

The kinetic experiments are performed in batch mode with 1 L of metal ion solution. These tests are carried out with initial concentration of 2 mmol/L for each metal and 3.0 g/L of bentonite under temperature of 20 ± 2°C. The solution is stirred at 300 rpm. The aqueous samples are taken and analysed at predetermined time intervals. The amount of heavy metal adsorbed per mass unit of bentonite at time t (q_t) is calculated by the following expression:

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (3)$$

Where C_0 (mg/L) is the initial concentration of heavy metal ion, V (L) is the volume of the metal ion solution, C_t (mg/L) is the concentration of heavy metal ion left in aqueous solution at time t (minutes) and m (g) is the amount of the bentonite. Pseudo-first order and pseudo-second order models are considered and fitted with the experimental data. The linear forms of these equations are expressed as:
Pseudo-first order model:

$$Ln(q_e - q_t) = Ln\, q_e - k_1 t \qquad (4)$$

Pseudo-second order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (5)$$

Where k_1 (L/min) and k_2 (g/mg.min) are the rate constant pseudo-first order and pseudo-second order respectively.

The adsorption isotherm experiments are carried out by adding 0.3 g of bentonite to 100 ml of solution with different initial concentration (10-1000 mg/L) in 250 mL Erlenmeyer flasks. The solutions are kept in a shaker at 300 rpm at 20 ± 2°C for 24 hours.

There are several isotherm equations available for analysing experimental adsorption equilibrium data including the Langmuir, the Freundlich and the Temkin models. The linear form of these equations can be written as:
Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{(q_m K_L)} + \frac{C_e}{q_m} \qquad (6)$$

Where C_e (mg/L) is the equilibrium concentration of heavy metal ion, q_m (mg/g) is the Langmuir maximum adsorption capacity of metal ion per unit mass of adsorbent, K_L (L/mg) is the Langmuir constant related to rate of adsorption.
Freundlich isotherm:

$$Lnq_e = LnK_F + (\frac{1}{n})\, LnC_e \qquad (7)$$

Where K_F ((mg/g)(L/mg)$^{1/n}$) and n are Freundlich constants that characterize the adsorption capacity and the adsorption intensity of bentonite for heavy metals,.
Temkin isotherm

$$q_e = B\, LnK_T + B\, LnC_e \qquad (8)$$

Where B = RT/b

K_T is Temkin isotherm equilibrium binding constant (L/mg), corresponding to the maximum binding energy, b is Temkin isotherm constant related to adsorption heat (J/mol). T is the absolute temperature (K) and R the universal gas constant (8.314J/mol.K).

III. Results and discussion

III.1. Characterization of bentonite

The major elements composing the investigated clay mineral are presented in **Table 1** as % oxides. The main components are SiO_2 (58.086%) and Al_2O_3 (12.169%). Whereas, we have a small percentage of Na_2O, MgO, K_2O, Fe_2O_3 and CaO. Other elements are present in minor amounts.

Table 1. *Chemical composition of raw Bentonite*

Oxides	Weight (%)
Na_2O	2.252
MgO	2.296
Al_2O_3	12.169
SiO_2	58.086
P_2O_5	0.058
SO_3	0.275
K_2O	2.139
CaO	3.518
TiO_2	0.245
Fe_2O_3	2.117
MnO	0.048
BaO	0.067

The bentonite morphology is examined by scanning electron microscope (SEM). As shown in **Fig. 1**, it seems that its surface consists of aggregates of various shapes.

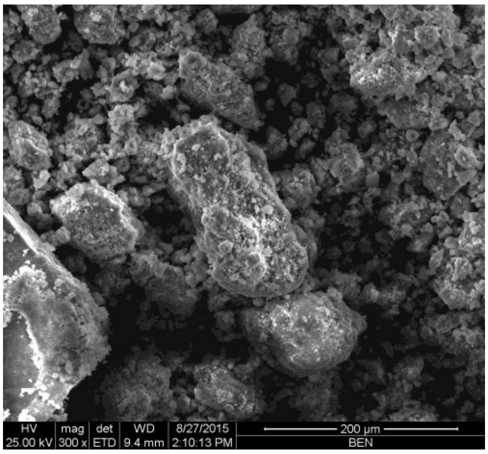

Figure 1. *SEM micrograph of raw bentonite magnification of 300x.*

The XRD pattern of the bentonite (**Fig. 2**) shows the presence of clay minerals essentially in the form of montmorillonite. It is characterized by an intense peak at 2θ = 7.0° (d = 12.704 Å) and a series of secondary peaks of varying intensity. It is also noted that there is a presence of crystalline phases in form of impurities as quartz at 2θ = 26° (d = 3.331 Å), illite at 2θ = 10° (d = 8.906 Å), calcite at 2θ = 31° (d = 2.996 Å) and dolomite at 2θ = 32.5° (d=2.754Å).

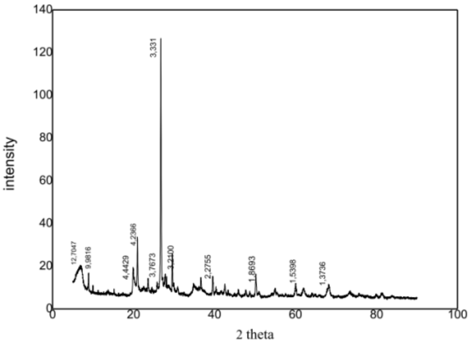

Figure 2. *Diffractograme of the raw bentonite.*

III.2. Effect of initial pH

The pH of the metal solution is an important parameter in the adsorption process because of its effect on the solubility of the metal ions, and the degree of adsorbate molecule ionisation [32] pH of removing Cu(II), Zn(II) and Ni(II) is examined in the pH range 1 to 6. The variation of these metals ion adsorption capacity as a function of pH is shown in **Fig. 3**.

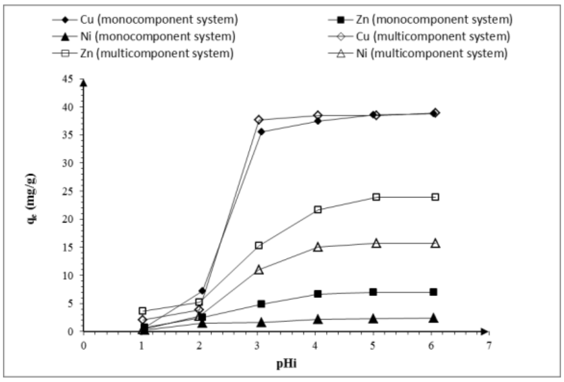

Figure 3*. Effect of pH on adsorption of Cu(II), Ni(II) and Zn(II), in monocomponent system (initial metal = 2mmol/L), and multicomponent system (molar ratio of initial metal = 2:2:2), bentonite dose = 3 g/L, 300 rpm, T = 20°C).*

It is observed, that at lower pH values, the elimination capacities of these metal ions are very low for both systems. Due to their protonation at higher H^+ concentration, a large number of active sites are less available for metals ion [24]. It is then observed a strong competitive effect between metal ions studied and the H^+ ions for the reactive sites of adsorbent. Consequently, the adsorption of metal ions was suppressed by excessive presence of H^+ [33].

As pH increased, generally, the adsorption capacity increases for all metals under mono and multicomponent systems. The maximum adsorption capacities are obtained at pH value 5 for all metal ions for both systems.

At this pH range, more H^+ ions leave the active sites of bentonite, which became more negatively charged [22]. This can favour the positively charged metal ions to be adsorbed, resulting in enhancement in the metal ions removal.

The major mechanism involved in this pH range for metal ions adsorption, may be ion exchange in addition to electronic attraction. In the case of monocomponent system, the maximum adsorption percentages are determined as 96% (38.4 mg/g), 80% (23.9 mg/g) and 43% (15.7 mg/g). Whereas, in the case of multicomponent system, these percentages are as 96% (38.9 mg/g), 25% (7 mg/g) and 7% (2.3 mg/g). These both percentages are for Cu, Zn and Ni respectively at pH value 5.

III.3. Effect of adsorbent dose

The effect of bentonite dose on copper, zinc and nickel adsorption is studied by varying the mass of bentonite from 1 to 10 g/L, with initial concentration of 2.0 mmol/L for each metal. The results are shown in **Fig. 4** and **Fig. 5**. It can be seen that the adsorption percentages of Cu^{2+}, Ni^{2+} and Zn^{2+} increase with the increase of the bentonite dose. This is due to the fact that an increase in the adsorbent dose increases the number of available vacant adsorption sites. Then a greater removal percentage of metals are obtained [26].

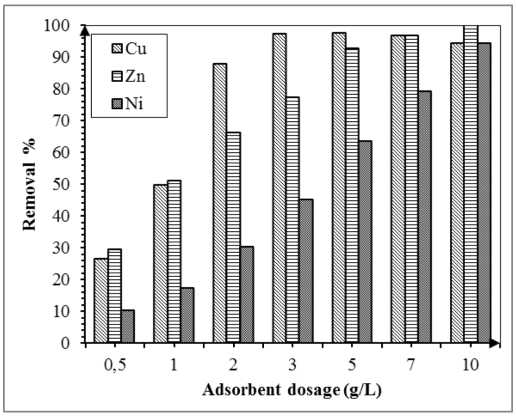

***Figure 4.** Effect of bentonite dose on adsorption of Ni(II), Cu(II) and Zn(II) in mono component system (initial metal = 2 mmol/L, contact time = 24 hours, pH = 5.0, 300 rpm, T = 20°C).*

The maximum adsorption capacity from monocomponent system is obtained at adsorbent dose of 3 g/L for Cu(II), 7 g/L for Zn(II) and 10 g/L for Ni(II), with a removal percentage of 98% for Cu and Zn, and 88% for Ni. However, in multicomponent system the same quantities of adsorbent give the same percentage of elimination for Cu(II) (98%), and much lower for Zn(II) and Ni(II) (do not exceed 50%).

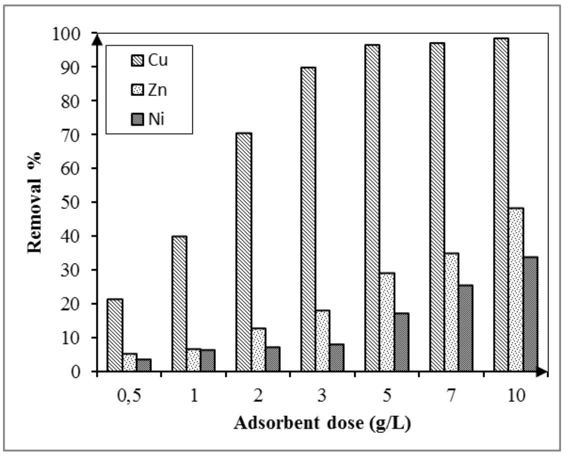

***Figure 5**. Effect of bentonite dose on adsorption of Cu(II), Zn(II) and Ni(II) in multicomponent system (molar ratio of initial metal = 2:2:2), contact time = 24 hours, pH = 5, 300 rpm, T = 20°C.*

The adsorption percentage removal of Cu(II) is larger than that of Zn(II) and Ni(II). The same observations were reported by several authors [12,26,33,34] for adsorption of metal ions by various adsorbents.

III.4. Adsorption kinetics

The evolution of the capacity of adsorbed metal ions with the contact time is shown in **Fig. 6**. It is observed that the adsorption amounts of metals have increased remarkably within the first 15-30 min contact with the bentonite. Two kinetic regions can be observed for all metals in both mono and multicomponent systems. The first one is characterized by a rapid uptake. This is due to the fact that there were a large number of vacant sites for metals on the external surface of bentonite particles in the beginning. Subsequently, the adsorption rate decreased gradually until the equilibrium because of the active sites saturation of the bentonite [35,36].

After a contact time of 300 min in monocomponent system, the removal percentages and capacities reach 95% (36 mg/g), 64% (18 mg/g) and 40% (14.5 mg/g) respectively for Cu, Zn and Ni. After the same contact time for multicomponent system, it is observed low removal efficiency respectively for Zn and Ni, 13% (6.1 mg/g) and 3% (1.4 mg/g).

In the other hand, Cu ions showed the highest removal efficiency with the removal amounts of 31.3 mg/g (85%). The low metal removal efficiency in multicomponent system as compared to the monocomponent system can be ascribed to the mutual competitively between metal ions for bentonite active sites [7,34,37].

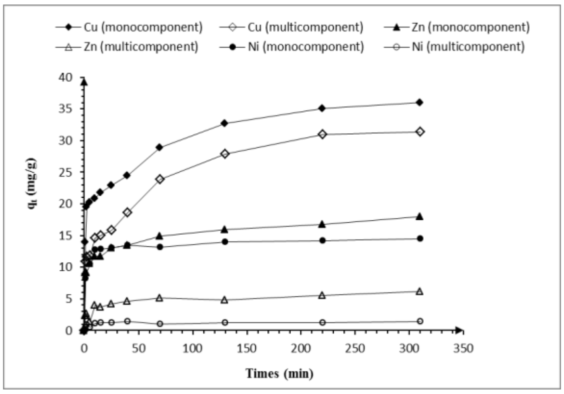

Figure 6. *Adsorption Kinetics for Cu(II), Zn(II) and Ni(II) in monocomponent system (initial metal = 2 mmol/L) and multicomponent system (molar ratio of initial metal = 2:2:2), bentonite dose = 3 g/L, pH = 5.0, 300 rpm, T = 20°C.*

The results indicate that bentonite shows the following adsorption affinity order for metal ions Cu^{2+} > Zn^{2+} > Ni^{2+} in both mono and multicomponent systems. Basing on previous findings on multi-metal sorption systems, the order of metal uptake capacities is independent of the adsorbent used but depends on the physicochemical properties of the ions under investigation [37-39].

The affinity of bentonite for Cu(II) ions over Zn(II) and Ni(II) ions can be attributed to the difference in ionic radius and hydrolysis constants solubility of these ions (**Table 2**). Cu(II) is favourably adsorbed because of its smaller ionic radius (easily access to the pores of the bentonite) and of its low solubility thus facilitating its adsorption on Bentonite. As can be seen in Table (2), $K_{Cu} < K_{Zn} < K_{Ni}$ [7,28]. This finding is in good agreement with other results reported [36,38].

Table 2. *Ionic radius and solubility product of metal ions [7,28,32]*

Metal ion	Ni	Zn	Cu
Ionic radius (A)	72	7 4	70
K of $M(OH)_2$	1,6 x10^{-16}	1,2x10^{-17}	1,6x10^{-19}

The experimental kinetics data for Cu, Zn and Ni adsorption on bentonite are fitted with pseudo-first order and pseudo-second order models (Eqs. (4-5)), they are calculated from Eq. (3).

The calculated kinetics constants of the two kinetic equations along with determination coefficients R^2 values are listed in **Table 3**.

Table 3. *Parameters of the pseudo first-order and pseudo second-order kinetic equations*

System	Heavy metal	Pseudo-first-order coefficients			Pseudo-second-order coefficients		
		q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/mg.min)	R^2
Single-component	Cu	67.660	0.074	0.570	37.037	0 .003	0.995
	Zn	7.009	0.009	0.829	17.857	0.0075	0.996
	Ni	3.448	0.012	0.618	14.492	0.0246	0.999
Multi-component	Cu	23.406	0.017	0.976	33.333	0.0018	0.991
	Zn	3.193	0.008	0.829	6.060	0.0150	0.990
	Ni	0.556	0.005	0.219	1.338	0.1270	0.985

It can be seen that the coefficients of determination for pseudo-second-order are good when compared to the pseudo-first-order model. They go beyond 99% and 98% for mono and multicomponent systems respectively. These results, suggest that the adsorption of Cu, Zn and Ni in mono and multicomponent system follows the pseudo-second order kinetic model.

The experimental values of q_e are similar to the theoretical ones. The values of the second-order rate (K_2) decrease for each metal ion from mono to multicomponent systems.

Other researchers reported the same kinetics for metals removal by hydroxyapatite [7], modified kaolinite [27], activated carbon [24], activated carbon prepared from olives stones [38], agricultural wastes [40], waste of date [34] and Iranian Bentonite [23].

III.5. Adsorption isotherms

The adsorption isotherm was obtained by plotting the mass of heavy metal adsorbed per unit mass of bentonite (q_e) against the equilibrium concentration of the adsorbate (C_e) at constant temperature (20 ± 2°C) and pH=5.0 ± 0.2. The experimental data of the mono and multicomponent adsorption isotherms for Cu, Zn and Ni are shown in **Table 4**.

Overall, it is observed that amount of Cu(II), Zn(II) and Ni(II) heavy metal ions adsorbed on natural bentonite at equilibrium increases with increasing of equilibrium concentration in aqueous solution in mono and multicomponent systems.

The results show that the capacity of bentonite to adsorb Cu(II) is higher than that of the other metal ions in both mono and multicomponent systems. Whereas for multicomponent system, they are respectively estimated to 58.82, 19.53 and 6.56 mg/g. These results indicate that the raw bentonite has a higher affinity for copper than for zinc and nickel. The maximum adsorption capacities calculated in ternary system are lower than those calculated in single solute system. This is due to the increasing competition of metal ions to be adsorbed on bentonite surface [12]. Similar observations were reported by other authors [26,40,41]. According to Jordão et al. [42], the small values of Langmuir constant related to rate of adsorption (K_L), indicate that metals ion were bind strongly to bentonite.

Under mono and multicomponent systems, the maximum adsorption capacity values of various adsorbents for Cu, Zn and Ni researches are compared to those obtained in the present paper (**Table 5**). It is found that the obtained capacities in our paper are interesting compared with ones found by other authors and suggest a good efficiency of the raw Algerian bentonite.

III.6. Competitive adsorption

Several authors evaluated the mutual effects of ions adsorption on the basis of the adsorption capacity ratio of metal ion "i" in multicomponent system (q_i^{mix}) and in mono-component system (q_i^0) such that for [26,35]:

$$\frac{q_i^{mix}}{q_i^0} \approx \frac{q_{im}^{mix}}{q_{im}^0} \qquad (9)$$

Where q_{im}^{mix} and q_{im}^0 are the maximum adsorption capacity in single and multicomponent systems respectively (mg/g).

If $\frac{q_{im}^{mix}}{q_{im}^0} > 1$: adsorption is promoted by the presence of the second metal ions;

If $\frac{q_{im}^{mix}}{q_{im}^0} = 1$: non-interaction; the mixture has no effect on the adsorption of the adsorbate;

If $\frac{q_{im}^{mix}}{q_{im}^0} < 1$: adsorption is inhibited by the presence of other metals.

As can be seen from **Table 6**, the values of the capacity ratio obtained for Ni and Zn are less than unity (0.206, 0.398) respectively. This demonstrate that Ni(II) and Zn(II) adsorption is suppressed in the presence of Cu(II). The value of the Cu(II) capacity ratio equal to unity means that the mixture had no effect on this metal adsorption. Zhirong and Zho [26] concluded that Cu(II) supress Ni(II) adsorption in binary component system. In the works of Sdiri et al. [33] and Ramech et al. [7], it was proved that Cu(II) exert a strong inhibitory effect on Zn adsorption. Similar results were also reported elsewhere [42,43].

Table 4. *Constants of isothermal adsorption for Cu^{2+}, Zn^{2+} and Ni^{2+} in single and multi-component systems.*

System	Heavy metal	Langmuir coefficients			Freundlich coefficients			Temkin coefficients		
		q_{Max} (mg/g)	K_L (L/mg)	R^2	K_f	n	R^2	K_T (L/mg)	B	R^2
Single-component	Cu	58.48	0.082	0.998	8,040	2.840	0.760	3.136	8.033	0.860
	Zn	49.02	0.043	0.979	8,015	3.248	0,830	7.163	5.358	0.894
	Ni	31.74	0.015	0.955	4,183	3.349	0.782	1.363	3.763	0.847
Multi-component	Cu	58,82	0.025	0.964	4,184	2.191	0.556	0.082	9.558	0.837
	Zn	19,53	0.006	0.882	1,548	2,958	0.869	0.354	2.720	0.746

Ni	06,56	0.011	0.954	1,952	6,978	0,716	8.448	8.448	0.648

Table 5. *Comparison of capacity of adsorption for Cu, Zn and Ni removal by various adsorbents in the literature (mg/g).*

Adsorbent	Cu	Zn	Ni	References
Na-bentonite	$18^{(1)}$ $16.5^{(2)}$		$13^{(1)}$ $10.4^{(2)}$	**[26]**
Hydroxypatite	$125^{(1)}$ $50^{(2)}$	$30.3^{(1)}$ $13.16^{(2)}$		**[7]**
$Fe(OH)_3$		$2.31^{(1)}$	$3.75^{(1)}$	**[8]**
		$0.49^{(3)}$	$0.542^{(3)}$	
Kaolinite	$10.79^{(4)}$		$1.67^{(4)}$	**[28,12]**
Natural bentonite	$32.26^{(1)}$ $9.01^{(4)}$		$26.32^{(1)}$ $7.63^{(4)}$	**[12]**
Smectite clay	$17.65^{(1)}$ $10.95^{(2)}$	$15.56^{(1)}$ $6.67^{(2)}$		**[33]**
(DETA)-functionalized PGMA	$76.25^{(1)}$ $69.9^{(5)}$	$39.23^{1)}$ $6.538^{(5)}$	$41.097^{(1)}$ $5.871^{(5)}$	**[43]**
Biomatrix from rice husk	$10.9^{(1)}$	$8.14^{(1)}$	$5.52^{(1)}$	**[44]**
Natural bentonite	$14.104^{(1)}$	$21.097^{(1)}$		**[22]**
Vermicompost		$20.3^{(1)}$		**[42]**
Activated carbon prepared from olive stones	$25.38^{(1)}$	$16.95^{(1)}$	$14.65^{(1)}$	**[38]**
Raw Algerian bentonite	$58.48^{(1)}$ $58.82^{(3)}$	$49.02^{(1)}$ $19.53^{(3)}$	$31.74^{(1)}$ $6.56^{(3)}$	**Present study**

(1) single, (2) binary, (3) tertiary, (4) quarterly, , (5) quinary

Table 6. *Aadsorption capacity ratio*

Heavy metal	$\frac{q_{lm}^{mix}}{q_{lm}^{0}}$
Cu	1.005
Zn	0.398
Ni	0.206

IV. Conclusion

The adsorption of Cu(II), Zn(II) and the Ni(II) on raw Algerian bentonite in mono and multicomponent systems are summarised in followings.

First, the adsorption capacity of heavy metal ions depends on the initial pH solution. pH = 5.0 gives high removal percentage for each metal in both mono and multicomponent systems.

Secondly, for all metal ions, the obtained results show that the adsorption kinetics can be well described by the pseudo-second order equation and the adsorption isotherm is well fitted to Langmuir model. In monocomponent system, the removal adsorption capacities of bentonite are 58.48 mg/g of Cu, 49.02 mg/g of Zn, and 31.74 mg/g of Ni. Whereas, in multicomponent system, they reach the values of 58.82, 19.53 and 6.56 mg/g of Cu(II), Zn(II) and Ni(II) respectively.

Finally, Zn(II) and Ni(II) ions can be significantly adsorbed onto bentonite from monocomponent system. However, in multicomponent system, their uptake is inhibited by Cu(II) ions. While, there was no change in the maximum adsorption capacity of the bentonite for Cu(II) in mono and multicomponent system.

According to the ratio values $\frac{q_{im}^{mix}}{q_{im}^{0}}$ (0.206 for Ni(II), 0.398 for Zn(II) and 1.005 for Cu(II)), Ni(II) and Zn(II) adsorption is inhibited by the presence of Cu(II). Elsewhere, Cu(II) adsorption is not affected by the presence of Zn(II) and Ni(II).

All results indicate that bentonite has the following adsorption affinity order Cu(II) > Zn(II) > Ni(II) for metal ions.

The adsorption capacities found in this study show a good efficiency of raw Algerian bentonite compared to the other materials adsorbent.

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