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Adsorption of Lead, Nickel, and Cobalt Ions onto Libyan Bentonite Clay

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In environmental studies it is important to know the adsorption process of heavy metals in clay minerals, since they are able to immobilize these metals. Knowing the cations adsorption is influenced by several factors, the objective of this research was to study the adsorption process of Lead, Nickel, and Cobalt on natural bentonite clay and to evaluate the concentration of metal ions and the influence of pH on this process. In order to quantify the adsorbed (Pb, Ni, and Co), 1 g of bentonite clay, dried at room temperature and sieved at ~200 mesh (74 μ), were equilibrated for 24 hours with 50 mL of water containing different quantities of metal ions (100, 200, 400, 600, 800, and 1000 mg / L) as background solutions of pH values 4.5 and 6.9. Maximum adsorption was obtained at pH 6-6.5. The relationship between the amounts of metal cations adsorbed was found to follow the Freundlich adsorption isotherm. Freundlich's adsorption equation in its linearized form was applied. The results showed that Freundlich equation was adequate to describe the metal ions adsorption at different pH values and concentrations.

Keyword: Adsorption, Lead, Nickel, Cobalt, Bentonite, Freundlich isotherm.

1. Introduction

Mining and industrial activities have caused extensive heavy metal contamination by introducing heavy metals directly into the surrounding environment [1-4]. Heavy metals, such as arsenic (As), lead (Pb), cadmium(Cd), zinc (Zn), nickel (Ni), and chromium (Cr) constitute one of the contaminant groups considered noxious to human health and are commonly found in several kinds of waste and landfill leachates [5-7]. Removal of heavy metals such as lead, nickel, and cadmium from aqueous solution is necessary because of the frequent appearance of these metals in waste streams from many industries. This problem has received considerable attention in recent years, primarily due to the concern that those heavy metals in waste streams can be readily adsorbed by marine animals and directly enter the human food chain, thus presenting a high health risk to consumers [8]. For environmental protection, waste solutions containing heavy metal elements need treatment systems that can remove these contaminants effectively [9]. Adsorption has been shown to be an alternative method for removing dissolved metal ions from liquid wastes [10]. The removal of heavy metal ions from industrial wastes using different adsorbents is currently of great interest. However, in order to minimize processing costs, several recent investigations have focused on the use of low cost adsorbents [e.g. agricultural by-products [11], waste materials [12], bio sorbents [13], and clay materials] [14]. Compacted clay soils are widely used as landfill liners that isolate hazardous and other waste materials from surrounding environments and to prevent the heavy metals commonly found in landfill leachates from migrating into groundwater. In which various clay minerals, oxides, and organic matters are mixed together, because the interaction among phases cannot be determined and nothing is learned about the actual partitioning of metals in various phases [15-17].In order to predict the mobility and retention

mechanism of heavy metals from a various concentration pollution source around soil and groundwater systems, the effects of pH on the adsorption of a bulk clay sample and on each constituent of the clay sample should be considered. In the present paper it is proposed to apply bentonite as sorbent of (Pb, Ni, and Co). Environmental parameters affecting the sorption process like pH and metal ion concentration, the equilibrium sorption data were evaluated by Freundlich isotherm models.

2. Materials and Methods

The bentonite ore was obtained from Umm-Ar-Razam area at north east of Libya; the upper layers of the earth crust in this area are mostly limestone, while the lower layers consist mainly of bentonite. The bentonite samples collected at depth [3-9] meters and from six different drilling sites, the samples were allowed to dry in air. The ore lumps obtained were fragmented to smaller pieces by a steel hammer, and then crushed to below 10mm particles using a Jaw-Crusher. A representation sample was obtained from the six crushed ore samples by the method of quartering [18]. Then these samples (about 5 kg) were further dried at 105-110 ^{o}C, then grounded further to obtain grain size ~200 mesh (74 μ), It is known that the broken of the large particles to smaller would lead to an increase in the surface area and causing an increase in metal ions adsorption [19]. This particle size was needed for complete chemical and x-ray analysis as well as for adsorption experiments.
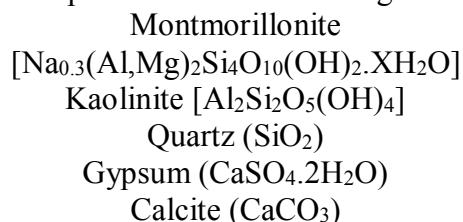
2.1. Chemical analysis of ore

One gram of the ore sample was mixed with one gram of Na_2CO_3 and the mixture was fused at 1000°C using platinum crucible, the fusion product was extracted with HCl solution (100 ml, 1:1), then filtered and washed. The filtrate and washing were completed to 500 ml measuring flask. Such solution was used for determination of Al_2O_3,CaO,MgO,Fe_2O_3,Mn,Cu, and Zn using standard methods [18]. Moisture content was determined using moisture balance. The chemical analysis results of bentonite ore are given in table1.

Table 1: Chemical Analysis of Umm-Ar-Razam bentonite ore

Component	Wt %
Al_2O_3	19.00
SiO_2	34.70
Fe_2O_3	7.35
CaO	7.98
MgO	2.35
SO_4^{2-}	0.765
P	1.5 ppm
Moisture	10.23
L.O.I	13.59
Organic Matter	0.279
Organic Carbon	0.162
K_2O	1.34
Na_2O	1.44

2.3. Characterization

The X- ray diffraction (XRD) patterns of the adsorbents were obtained using a Philips X-ray diffraction instrument with filtered Cu Kα radiation (n = 1.6418 Å) operated at 40 kV and 40 mA, The XRD pattern was recorded from 1.5 to 50° 2θ with a scanning speed of 0.02° 2θ per second. A Philip X 1.30 scanning electron microscope / EDAX was used to obtain microgram scans of mineral clay samples. X-ray diffraction analysis of powdered bentonite sample showed the presence of the following minerals:

Montmorillonite
[$Na_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2.XH_2O$]
Kaolinite [$Al_2Si_2O_5(OH)_4$]
Quartz (SiO_2)
Gypsum ($CaSO_4.2H_2O$)
Calcite ($CaCO_3$)

2.4. Adsorption experiments

Adsorption experiments were carried out at room temperature and conducted by mixing 1 g

bentonite sample 74 μ with standard solutions of Pb^{2+}, Ni^{2+}, and Co^{2+}.

2.5. Preparation of standard solutions
All reagents used were Analar grade and were used as sourced without further purification. Stock solutions of 1000 mg L^{-1} Pb(II) ,Ni(II),and Co(II) ions were prepared from Pb $(NO_3)_2$, Ni $(NO_3)_2$, and Co $(NO_3)_2$ respectively, by dissolving appropriate amounts of solid salt in double distilled water [20] in a measuring flask to give a standard solution of 1000 ppm of the metal ion, from this solution concentration 200, 400, 600 and 800 ppm were prepared. Determination of Pb^{2+}, Ni^{2+}, and Co^{2+} concentrations were done by atomic absorption spectrometer (AAS). Measurements showed that best sensitivity and accuracy of the spectrophotometer was in the range up to 5 ppm and hence all solutions were diluted to be within that range.

2.6. Technique of adsorption experiments
Duplicate 1 g samples of bentonite (74 μ) were equilibrated for 24 hrs including an initial conditioning for 2 hrs on a reciprocating shaker at 25°C with 50 ml of different metal cation solutions. The metal cation concentrations of Pb^{2+},Ni^{2+}, and Co^{2+} were 200, 400, 600, 800,and 1000 ppm, as nitrates. The samples were then centrifuged and the centrifugates were analyzed for the respective cation concentration by atomic absorption spectrophotometer, the adsorption densities for each cation were calculated.

2.7. PH adjustment
When 1 g bentonite is well mixed with double distilled water (50 ml), the pH of the emulsion is 7.9-8.1, that may be due to the presence of some alkaline cations such as K^+, Na^+, Ca^{2+}, and Mg^{2+}. When adding the metal cation solution of pH 2.5 to bentonite the pH of the mixture becomes ~5.5. To adjust the pH of the mixture to the required value few drops of either 1 M NaOH or HNO_3 were added.

3. Results and Discussion
3.1 Adsorption of Pb^{2+}, Ni^{2+}, and Co^{2+} ions on the bentonite
Effect of pH of the medium on adsorption
The process of cation exchange between solid surface and the solution containing the heavy metal cations is highly dependent on the pH value of the medium. Accordingly, the adsorption of Pb^{2+},Ni^{2+} and Co^{2+} was studied at different pH values ranging from highly acidic (pH= 0.5-1.0) to slightly acidic (pH= 6.0 - 6.5). When 1 g of bentonite ore is mixed with 50 ml of double distilled water, the pH of the emulsion is 7.9-8.1. The alkalinity of the emulsion is most probably due to the predominance of the cations Ca, Mg, Na and K on the surface of clay crystals which gives rise to the formation of the Corresponding hydroxides. On the other hand when 1 g of the bentonite ore is mixed with 50 ml of the metal cation solution (pH=2.5) the pH of the mixture becomes about ~ 5.5. The pH value is varied by adding few drops of 1M NaOH or HNO_3. The results of adsorption experiments are given in tables 2, 3 and 4.

Table 2: Adsorption of Pb^{2+} ions on bentonite at different pH values

Original Conc. of Pb^{2+} (ppm)	pH	Pb^{2+} remaining in solution (ppm)	Pb^{2+} adsorbed (ppm)	Remarks
200	1.0	189.70	50.30	Normal samples
200	2.8	167.28	82.72	" "
200	4.9	120.50	129.50	" "
200	5.5	98.65	157.35	" "
200	6.0	70.45	179.55	" "
200	6.5	55.89	184.11	" "
200	7.0	89.59	165.41	" "
400	1.0	383.38	16.62	" "

400	2.9	317.50	82.50	"	"
400	4.5	260.34	139.66	"	"
400	5.0	214.20	185.80	"	"
400	5.5	174.77	225.23	"	"
400	6.0	109.46	290.54	"	"
400	6.5	85.20	314.80	"	"
600	1.0	570.44	29.56	"	"
600	4.1	480.40	119.60	"	"
600	5.0	418.34	181.66	"	"
600	5.5	363.19	236.81	"	"
600	6.0	309.30	290.70	Normal samples	
600	6.5	243.45	356.55	"	"
800	1.0	758.90	41.10	"	"
800	3.0	685.37	114.63	"	"
800	5.0	447.98	352.02	"	"
800	6.0	376.77	423.23	"	"
800	6.5	327.40	472.60	"	"
1000	1.0	926.80	73.20	"	"
1000	2.5	877.70	122.30	"	"
1000	4.5	740.30	259.70	"	"
1000	5.5	689.20	310.80	"	"
1000	6.0	625.70	374.30	"	"
1000	6.5	351.40	648.60	"	"

Table 3: Adsorption of Ni^{2+} ions on bentonite at different pH values

Original Conc. of Ni^{2+} (ppm)	pH	Ni^{2+} remaining in solution (ppm)	Ni^{2+} adsorbed (ppm)	Remarks
200	1.0	180.70	19.30	Normal samples
200	2.8	160.40	39.60	" "
200	4.9	144.50	55.50	" "
200	5.5	125.35	74.65	" "
200	6.0	112.70	87.30	" "
200	6.5	24.60	175.40	" "
200	7.0	60.40	159.60	" "
400	1.0	387.58	12.42	" "
400	2.9	365.50	34.50	" "
400	4.5	327.34	72.66	" "
400	5.0	292.77	117.23	" "
400	5.5	255.90	144.10	" "
400	6.5	195.89	204.11	"

				"
400	7.0	190.60	209.40	"
600	1.0	579.20	20.80	"
600	4.0	456.40	143.60	"
600	5.0	397.60	202.40	"
600	5.5	344.19	255.81	"
600	6.0	299.30	300.70	Normal samples
600	6.5	257.45	342.55	"
800	1.0	769.90	30.10	"
800	4.0	735.37	64.63	"
800	5.0	687.5	112.50	"
800	6.0	597.5	202.50	"
800	6.5	372.9	427.10	"
1000	1.0	946.80	53.20	"
1000	2.5	917.70	82.30	"
1000	4.5	890.30	109.70	"
1000	5.5	840.20	159.80	"
1000	6.0	797.70	202.30	"
1000	6.5	455.40	544.60	"

Table 4: Adsorption of Co^{2+} ions on bentonite at different pH values

Original Conc. of Co^{2+} (ppm)	pH	Co^{2+} remaining in solution (ppm)	Co^{2+} adsorbed (ppm)	Remarks
200	1.0	194.50	05.50	Normal samples
200	2.8	177.40	22.60	" "
200	5.0	152.50	47.50	" "
200	5.5	85.35	114.65	" "
200	6.0	50.70	149.30	" "

200	6.5	35.99	164.01	"	"
200	7.0	54.99	145.01	"	"
400	1.0	389.60	10.40	"	"
400	2.9	375.50	24.50	"	"
400	4.5	357.34	42.66	"	"
400	5.0	312.77	87.23	"	"
400	5.5	285.90	114.10	"	"
400	6.5	245.89	154.11	"	"
400	7.0	284.60	115.40	"	"
600	1.0	564.20	35.80	"	"
600	4.0	526.40	73.60	"	"
600	5.0	487.60	112.40	"	"
600	5.5	444.19	155.81	"	"
600	6.0	399.30	200.70	Normal samples	
600	6.5	360.45	239.55	"	"
800	1.0	750.90	49.10	"	"
800	4.0	725.37	74.63	"	"
800	5.0	697.98	142.02	"	"
800	6.0	657.50	192.50	"	"
800	6.5	422.90	377.10	"	"
1000	1.0	936.80	63.20	"	"
1000	2.5	917.70	82.30	"	"
1000	4.5	870.30	129.70	"	"
1000	5.5	830.20	169.80	"	"
1000	6.0	792.70	207.30	"	"
1000	6.5	565.40	434.60	"	"

It can be observed from the results that the adsorption of Pb^{2+}, Ni^{2+}, and Co^{2+} ions on bentonite is very sensitive to the pH value of the medium, the adsorption of Pb(II) increases with an increase in pH of the mixture to a maximum around pH 6.0 to 6.5, and then decreases as the pH becomes more basic, because the metal cations begin to hydrolyze and precipitate and

hence become not available for adsorption. This is true regardless of the concentration of the solution investigated, from the table 3 that the adsorption of Ni(II) ions increases with pH increases from 3 to 6.5. For all cases, the greatest increase occurred at the lower Ni(II) concentrations. However, the results of Ni(II) ions adsorption onto clay are in agreement with those found by DEMIRBA, E and etal [21], which indicated that adsorption of Ni(II) from aqueous solution onto hazelnut shell activated carbon increases with increasing pH. Bentonite clay is a 2:1 mineral with one octahedral sheet and two silica sheets, which forms a layer. It carries a net negative charge due to the broken bonds around the edges of the silica–alumina units. This would give rise to unsatisfied charges, which would be balanced by the exchanging cations [22]. Clays are known to possess a negative surface charge in solution. As pH changes, surface charge also changes, and the sorption of charged species are affected (attraction between the positively charged metal ion and the negatively charged clay surface). It is conceivable that at low pH values, where there is an excess of H_3O^+ ions in solution, a competition exists between the positively charged hydrogen ions and metal ions for the available adsorption sites on the negatively charged clay surface. As the pH increases and the balance between H_3O^+ and OH^- are more equal. Generally, the specific adsorption of these metals at low concentrations ($< 10^{-3}$ M) was found to increase with pH and was virtually complete at pH values less than the corresponding pK (the first hydrolysis constant of the metal, thus the cation which is most readily hydrolyzed in solution also has the highest affinity to be adsorbed) [23]. However, the present results agree with such conclusions.

3.2. Adsorption Studies

The relationship between the equilibrium concentrations (C) of the metal cations Pb^{2+}, Ni^{2+} and Co^{2+}, the amounts of cations adsorbed on bentonite surface (x/m) was studied at pH= 6.5. The results are given in tables 5,6, and 7.

Table 5: Amounts of Pb^{2+} ions adsorbed onto bentonite at pH = 6.5

Equilibrium Conc. of Pb^{2+} (C)			Amounts of Pb^{2+} adsorbed per 1 g bentonite (x/m)		
ppm	meq/L	log C	ppm	meq/g	log x/m
200	0.965	-0.015	145	0.700	- 0.155
400	1.931	0.286	298	1.438	0.138
600	2.896	0.462	398	1.921	0.283
800	3.861	0.587	477	2.302	0.400
1000	4.826	0.684	622	3.002	0.477

Each reading is the average of four measurements.

Table 6: Amounts of Ni^{2+} ions adsorbed onto bentonite at pH = 6.5

Equilibrium Conc. of Ni^{2+} (C)			Amounts of Ni^{2+} adsorbed per 1 g bentonite (x/m)		
ppm	meq/L	log C	ppm	meq/g	log x/m
200	3.407	0.532	68	1.158	0.064
400	6.813	0.833	113	1.933	0.286
600	10.220	1.009	136	2.322	0.366

| 800 | 13.626 | 1.134 | 147 | 2.510 | 0.400 |
| 1000 | 17.033 | 1.231 | 170 | 2.897 | 0.462 |

Each reading is the average of four measurements.

Table 7: Amounts of Co^{2+} ions adsorbed onto bentonite at pH = 6.5

Equilibrium Conc. of Co^{2+} (C)			Amounts of Co^{2+} adsorbed per 1 g bentonite (x/m)		
ppm	meq/L	log C	ppm	meq/g	log x/m
200	1.78	0.250	38	0.338	-0.461
400	3.560	0.551	69	0.617	-0.210
600	5.338	0.727	136	1.213	-0.084
800	7.117	0.852	133	1.180	0.072
1000	8.896	0.949	162	1.439	0.158

The results of this study indicate that bentonite can be successfully used for the metal ions removal from aqueous solutions. It is obvious that the amount of Pb^{2+}, Ni^{2+}, and Co^{2+} ions adsorbed increase with increase in the equilibrium concentration of the cation in the bulk solution, but the increase becomes less for higher concentrations. However adsorption seems to reach a maximum value when all adsorption sites are occupied with ions.The effect of pH on the metal adsorption by the bentonite was studied in the pH region between 2 – 6.5, The pH was limited to values less or equal to 6.5 because of precipitation at higher pH [24]. The available adsorption sites are preferentially distributed between all cations depending on the strength of link of each cation. Applying the Freundlich adsorption isotherm equation shown below to the experimental data, it satisfactorily fits and give a straight line relationship between log x/m and log C for the Pb^{2+}, Ni^{2+}, and Co^{2+} ions (Figure 1,2, and 3).
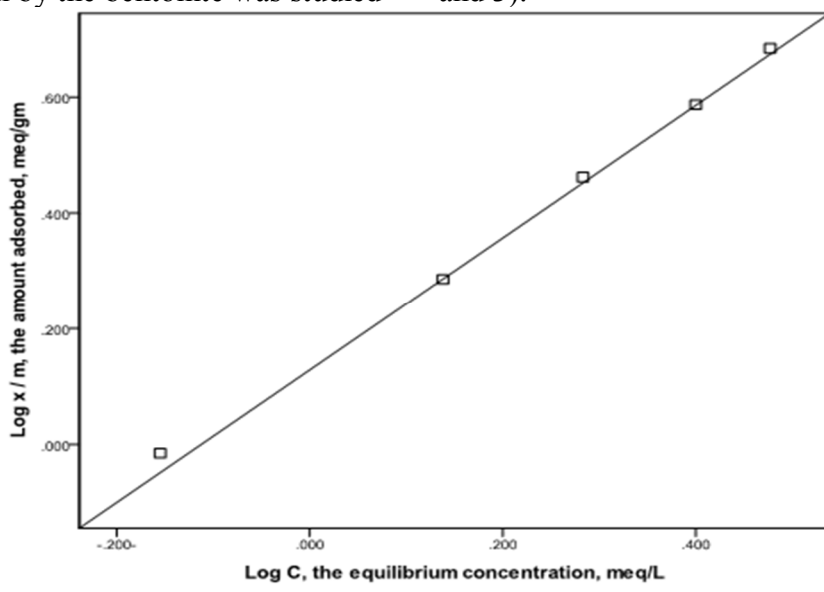

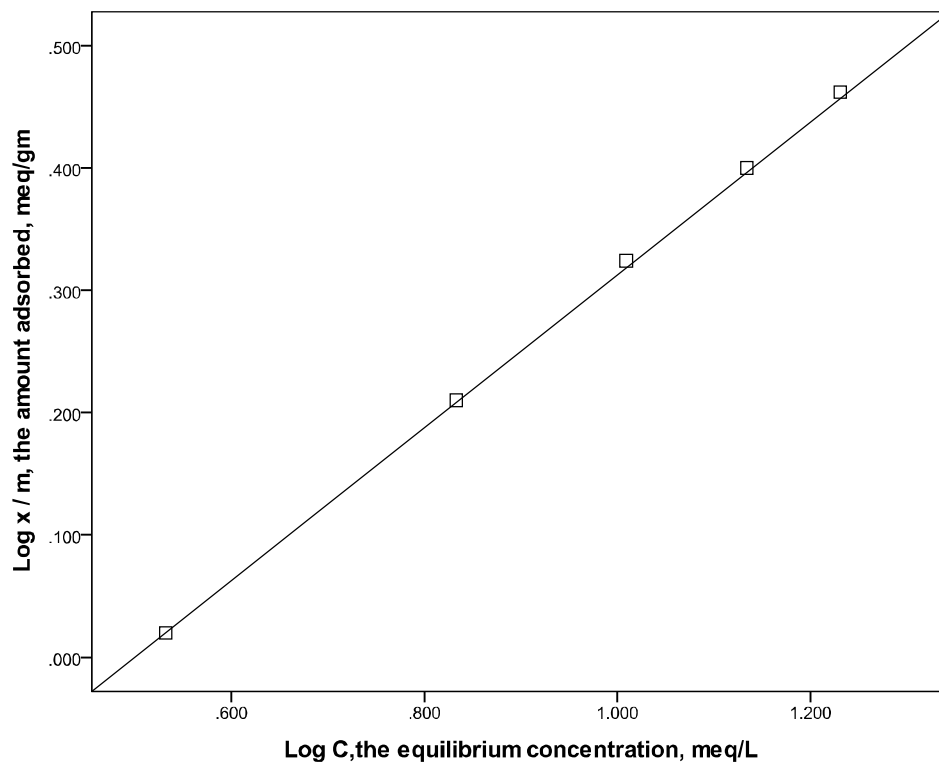**Fig 1:** Freundlich adsorption isotherms for Pb^{+2} at pH 6.5

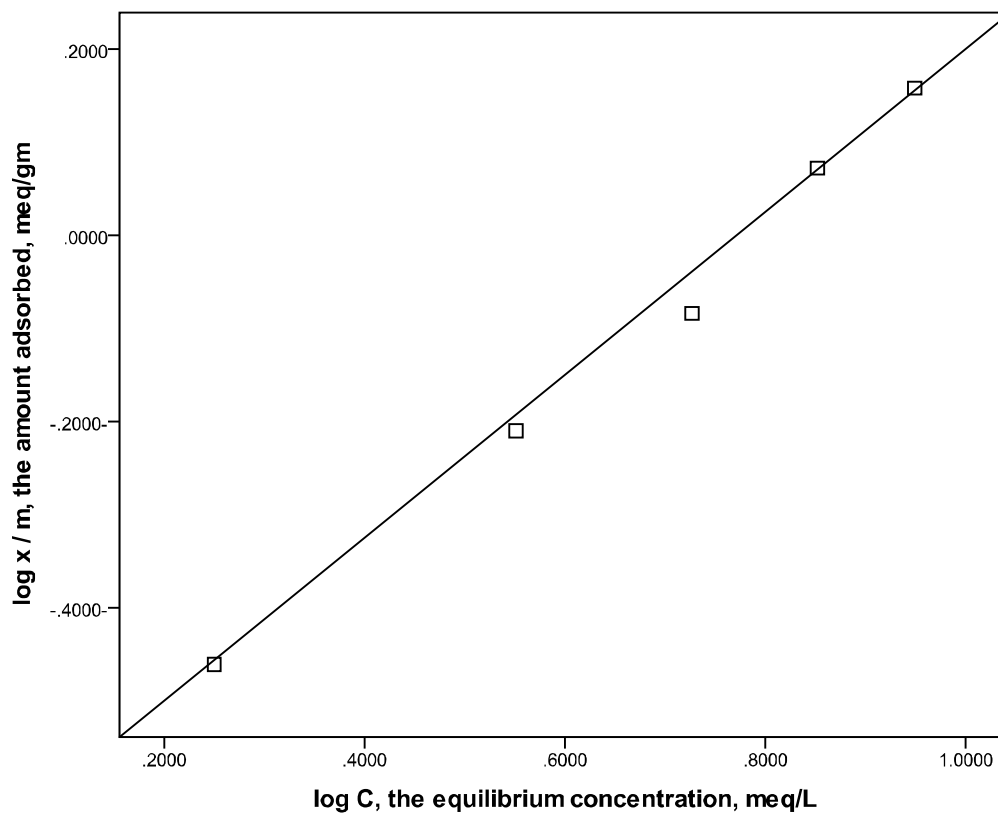**Fig 2:** Freundlich adsorption isotherms for Ni^{+2} at pH 6.5

Fig 3: Freundlich adsorption isotherms for Co^{+2} at pH 6.5

log x/m = l/n log C + log K

Where x = the amount of heavy metal cation absorbed

m = weight of adsorbate

Thus x/m = amount absorbed per unit weight

l/n = constant

C = equilibrium concentration of metal cation

K = constant

The linear trend of the plots log c vs log x / m for Pb. Ni, and Co confirm that their adsorption on clay also follows the Freundlich adsorption model. However, the Freundlich isotherm model is usually adopted for heterogeneous adsorption [25].

The removal capacity of clay mineral for heavy metals in aqueous solutions is related to their (metals') potential towards hydrolysis. Though ordinary clay adsorbs only a small amount of heavy metals yet it can be used as a low cost adsorbent for their removal from wastewaters (containing low conc. of such metals). especially in the developing countries.

4. References

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