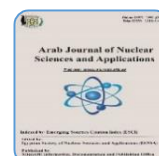




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(E S N S A)

Effect of some Organic Ligands on the Sorption of Radiocobalt on Soil

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ABSTRACT

The sorption of radiocobalt onto low cost materials (such as soil and clay) in the presence of environmentally available organic ligands (such as humic acid, phenol and gallic acid) is investigated. The organic matter was eliminated from the soil and clay and they are characterized by FT-IR, Textural analysis, X- ray diffraction (XRD) & Energy dispersive X- ray (EDX). The investigations were carried out as a function of pH, metal ion concentration and weight of sorbent, using the batch technique. The results showed that the pseudo 2nd-order equation tailored the kinetic sorption well. The sorption of Co(II) on both soil and clay is powerfully dependent on pH. A positive effect of humic acid on the sorption of Co(II) is found, whereas a negative effect is observed for phenol and gallic acid. The presence of HA, together with the other ligands, enhances the sorption in all cases. Generally, the sorption of Co(II) is higher for soil than for clay.

INTRODUCTION

The motion of heavy metals and radionuclides in soils and sediments has been broadly considered in the last decades. Although various heavy elements are required in slight amounts for the normal development of the biotic cycles, most of them become venomous at high concentrations. The great growth in the use of heavy elements over the last decades has certainly caused an enlarged fluctuation of metallic stuffs in the environment [1].

Radioelements contaminate the environment by insertion in the soil and their persistence for longer period depends on their half-life. The processes used for remediation of radio contaminated sites are possibly in-situ or ex-situ. Many practices of metal ions elimination have been already applied; though, there is still a need for innovative, effective, and non-toxic sorbents committed to heavy and radioactive metals [2].

Organic contaminants can reach the soil either intentionally, for example insecticides and other agrarian chemicals, or incidentally through a variety of provisions usually used in agricultural practices, e.g., fertilizers and developments. Once it touches the soil surface,

the organic pollutants can be partially photo decomposed and/or volatilized, and partly arrive the soil or be transported to superficial aquatic bulks by runoff and/or attrition. When pollutants reach the soil, they can undergo complete or partial chemical and/or biological decay. The original pollutant, and its decomposition products, can be absorbed by the organic and inorganic components of the soil, then absorbed by the roots of plants, and eventually reach the groundwater, and this is the source of the danger [3].

Soil has the aptitude to arrest the presented chemicals like heavy metal ions. The restriction of these chemicals is primarily due to sorption characteristics which are determined by the physicochemical properties of the soil, for instance: water content, quantity of clay and organic portion, pH, temperature of the soil and properties of the definite metal ion [4]. The solid state of the soil constitutes about 45% of soil substance in addition to mineral particles, organic matter, and mineral- organic particles [4]. They altogether show a very important role in giving the soil the ability to sorb, exchange, oxidize, reduce, catalyze and/ or precipitate chemicals and metal ions.

The inorganic colloidal portion of the soil is the most liable for the sorption process through its mineral particles. The clay minerals are negatively charged hydrous aluminum, magnesium or iron silicates [5], etc. that have a significant factor manipulating the sorption properties of the soil.

Humic substances (HS), such as humic acid (HA) and fulvic acid (FA) are recognized to have a strong effect on the sorption properties of heavy metal ions in aquifer systems. They denote an essential fraction of dissolved natural organic composites that are largely present in natural environment. The effect of HS on the sorption of heavy metal ions to natural minerals is reliant on many factors such as; the type of natural minerals, the kind of HS, nature of heavy metal ions, solution pH, etc.

Phenols are aromatic materials having hydroxyl group attached to the benzene ring. They are frailly polar Hydrophobic Ionizable Organic Contaminants (HIOCs) predominant in groundwater, because of the massive use of these compounds in agriculture and industrial processes. The toxicity of HIOCs is powerfully affected by the pH of groundwater, and the ionic species are more soluble in the aqueous phase, and thus they are more movable in the ground, although the neutral species are more poisonous, because they have a great relationship with the organic matter in the soil. Since phenolic compounds possess several degrees of toxicity, their fate in the environment is so important [6].

Gallic acid is a respectable antioxidant, antimicrobial compound and is used in many industries, such as pharmaceuticals, organic synthesis, a food- preservative, dyestuffs and cork boiling process. Propyl gallate is widely used as a component of developer in photography and printing toners, so, it could be considered as a model contaminant of the wastewater. The maximum amount acceptable in drinking water by environmental protection organizations in USA, Canada, and EU is 2 ppm [7].

^{60}Co and ^{58}Co are actually of crucial importance to waste removal and site remediation as they exist in the liquid waste released from pressurized water nuclear reactors. Also, ^{60}Co is broadly used in research and medical uses. Because of its high energy gamma radiation, large quantities of radiocobalt are disposed through shallow and interment, and in many cases it has travelled more rapidly than expected in the subsurface soil [8]. The consumption of water with high concentration of cobalt is carcinogenic and mutagenic pollutant and can lead to heart harms, asthma,

pneumonia, damage of thyroid, nausea and vomiting, hair and weight loss, that released from manufacturing and manmade sources. In current years, the control of water that has been contaminated with Cobalt has been an emergent case [9].

It is indicated by many authors that cobalt forms strong complexes by artificial organic ligands, for example EDTA, that have been used to clean the nuclear reactors. The construction of such complexes considerably affects the environmental movement of cobalt by increasing the solubility of cobalt in aqueous solutions. The likely contamination of the environment by Co is from smelting, mining and trade activities [10]. Therefore, the plan of this research was proposed to study the effect of these environmentally important organic ligands on the sorption of cobalt by the soil and clay.

Experimental

Materials

The sample of agricultural soil (200 mm surface layer) came from Al-Sharquia, Egypt. Before its use, the sample was first air-dried, then crushed in a mortar and the soil was passed through a sieve (150 micron). The particle size of the separated fractions was obtained by sedimentation-centrifugation.

Separation of clay from the soil sample

The clay fraction was separated from the soil by the sedimentation method, which includes dispersion of the soil sample, then sedimentation of the suspended soil particles by gravity or by centrifugation. Separation of the required clay size from the soil suspension is made by the pipette method.

Removal of organic matter from clay

In order to define the role of organic matter in the sorption of metal ions by soil and clay, the organic matter was removed from them by two different methods. It was removed from soil by alkali pyrophosphate and from clay by sodium hypochlorite.

A ten g sample of < 2 mm air-dried clay was mixed with 100 ml of 6% sodium hypochlorite NaOCl adjusted to pH 8 with a trace of conc. HCl. After 6 hours, the suspension was centrifuged, and the supernate is drawn off and filtered. The NaOCl-treated clay was shaken with double distilled water overnight, and then freeze-dried [11].

Characterization of soil and clay

The soil and clay were characterized by textural analysis; FT-IR, Energy dispersive X-ray (EDX) and X-ray diffraction (XRD).

Extraction of humic materials from soil

The humic materials were extracted from the soil, and purified; according to Schnitzer and, Grishina [12].

Characterization of humic materials

The humic materials are characterized by elemental analysis, UV- visible spectroscopy and Fourier transform infrared (FT-IR) spectroscopy.

Preparation of cobalt-60

The radioactive nuclide of ^{60}Co was artificially produced in Egyptian Nuclear Reactor, Inshas. The irradiated sample was dissolved in a proper volume of concentrated HCl, evaporated to dryness, and washed several times with double distilled water to eliminate excess acid. The sample was then dissolved and diluted to the desired volume, and kept as a stock solution in a stoppered vessel of dark glass and used as a mother solution for cobalt investigations.

Sorption experiments

The sorption of radioactive cobalt by soil and clay was carried out by using the batch technique. The soil and clay suspensions were equilibrated at the working pH, they were adjusted by the addition of acid or base at 25°C.

20 mL polyethylene vials with polyseal caps were used as vessels in all investigations. A suitable weight of soil or clay was shaken in the vial with the aqueous medium containing the cobalt in a thermostatic shaker at 25°C±1°C.

A tracer and carrier concentrations of the cobalt ions were used for the investigations related to the effect of metal ion concentration. Phase separation was achieved by centrifugation at 2500 rpm for 15 minutes.

The pH's of the aqueous media were measured before and after equilibration. The amount of metal retained by soil or clay is calculated by percentage of uptake.

Radioactive ^{60}Co was determined by NaI scintillation detector (Genie 2000, USA). The uptake efficiency (%R) and the amount of radionuclides retained on soil and clay samples (q_e mg/g) were calculated using the following equations respectively.

$$\text{uptake \%} = \frac{A_i - A_f}{A_i} \times 100 \quad (1)$$

$$q_e = (C_o - C_e) \frac{V}{m} \quad (2)$$

Where A_i , A_f are the initial and final radioactivity levels of the radionuclides, C_o , C_e , are the initial and equilibrium metal ion concentrations in solution (mg/L) and V , m are the volume of the solution (L) and the mass of adsorbent (g), respectively.

RESULTS AND DISCUSSION

Soil and clay characterization

Soil has a great ability to get rid of chemicals, mainly due to the sorption properties; which is determined by the physical and chemical properties of the soil such as: the amount of clay and organic residues, and pH. Solid state soils make up about 45% of the soil mass. It has mineral particles, organic- mineral particles and organic matter. All play an important role in enabling soils to absorb, exchange, oxidize, reduce, stimulate, and specifically precipitate chemicals and mineral ions.

The compositional analysis of the examined soil showed the predominance of the silt fraction (55%), followed by clay (30%), then sand (15%), and therefore the original soil is classified as alluvial silty soil. It is known that this type of soil is characterized by a high ability to retain water and minerals. The slightly alkaline pH (8.5), noted for the examined soil is usually within the range of agricultural soils. The soil also contains a low percentage of organic matter (0.1%), which is caused by the coagulation of clay and silt particles in the soil of fine texture, and therefore it cannot maintain the organic matter in the soil, SOM [13].

The IR for soil before and after removing of the organic matter is illustrated in Fig. 1. Obviously, the chemical actions caused changes in only four regions of the infrared spectra (Zimmermann et al. (2007)). The IR detection results have shown; aliphatic C-H stretch (3000-2800 cm^{-1}), carbonyl/carboxylic C = O stretch (1720-1640 cm^{-1}), aromatic C = C stretch (1620- 1525 and 1424 cm^{-1}) and aliphatic stretches of C-OH and C-C (1300-950 cm^{-1}). Infrared spectra before and after chemical reactions were used to verify the effects of the treatment on the structural properties of the investigated samples.

The intensity of the sorption bands is attributed to the amount of functional groups that were absorbed. The sorption intensities in the bands at 1735 and 1645 cm^{-1} are more significant, because the functional groups other than $\text{C}=\text{O}$ seldom has shown intense absorption bands in this region and are unaffected by the water content. The intensity of these bands in native soils and clays is not severe, which may be attributed to the low content of organic compounds in the samples.

The results showed a decrease in the intensity of the bands after interaction with both alkaline pyrophosphate and sodium hypochlorite. However, the treatment with alkaline pyrophosphate eliminates more organic matter than sodium hypochlorite. This is perhaps because pyrophosphate is predicted to extract low molecular weight components of OM, associated with Fe and Al in the complexes, and poorly crystallized minerals such as ferrihydrite, while the more organic C minerals in soils rich in amorphous minerals poorly resisted NaOCl treatment compared to soils with little FeO. This is may be due to the fact that many of the binding sites reactivity forms complexes with organic materials [14].

X-ray diffraction (XRD)

X-ray diffraction is a useful analytical technique used in testing crystalline solid materials. Based on the results

of XRD tests, poor crystallization and/or amorphous mineral phases were observed for both soil and clay, Fig. (2, 3). The results showed that the natural clay sample consist of kaolin in addition to quartz as foreign matter. As shown in Fig. (2), the diffractogram exhibits a diffraction at an angle of $2\theta = 12.4^\circ$. The latter corresponds, after conversion, to a d (001) spacing of 7.30 \AA . The second- order diffraction is at $2\theta = 25^\circ$, which corresponds to a d spacing of 3.570 \AA , and at $2\theta = 19.8^\circ$, which correspond to a d spacing of 4.47 \AA which are characteristics to kaolinite mineral. Also, the scan shows a (peak) at $2\theta = 26.6^\circ$ corresponds to the quartz minerals at a spacing of 3.338 \AA . The low signal of kaolinite as compared to quartz is explained by the smaller particle size of kaolinite, and thus the increased internal dispersion of kaolinite particles and thus the reduction of the reflected signal.

The XRD of soil sample is shown in Fig. 3. It shows that the agricultural soil is composed of montmorillonite, kaolinite, orthoclase and calcite as trace ingredients. As indicated in Fig. 3, the diffractogram shows diffraction at angles $2\theta = 19.9^\circ$ d (4.45 \AA), $2\theta = 26.8^\circ$ d (3.31 \AA), $2\theta = 12.49^\circ$ d (7.1 \AA), $2\theta = 23.8^\circ$ d (3.7 \AA) and $2\theta = 29.7^\circ$ d (3.0 \AA) for montmorillonite, quartz, kaolinite, orthoclase and calcite, respectively [15].

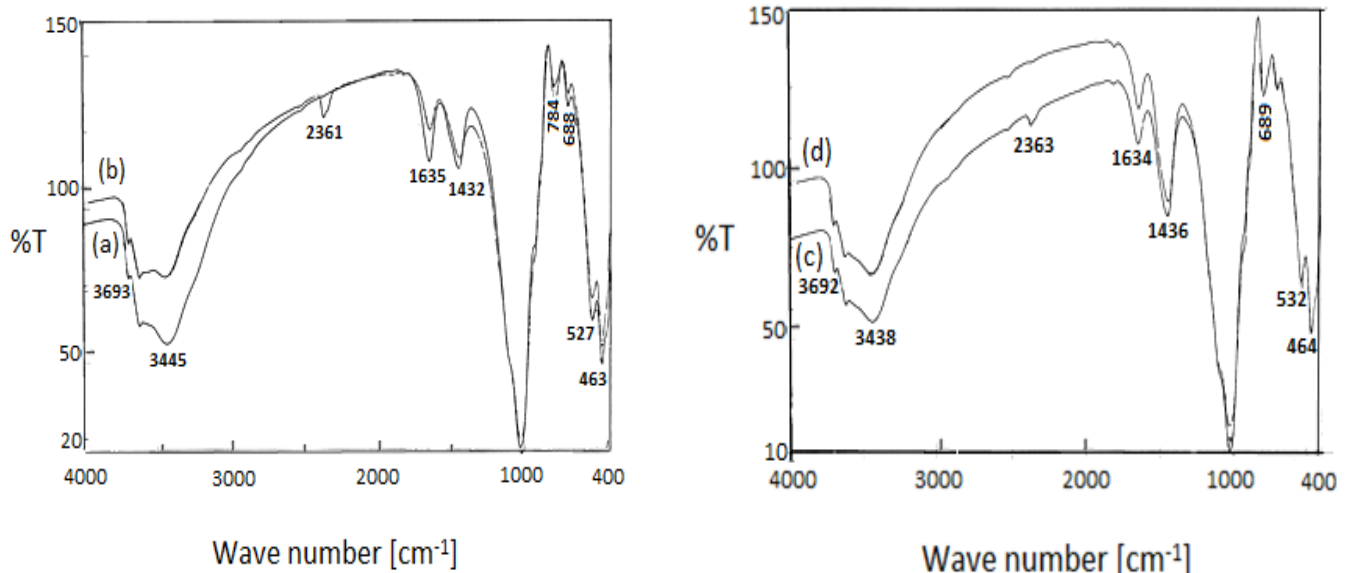


Fig. (1): IR spectra of soil: (a) before (b) after elimination of organic matter, clay: (c) before (d) after elimination of organic matter.

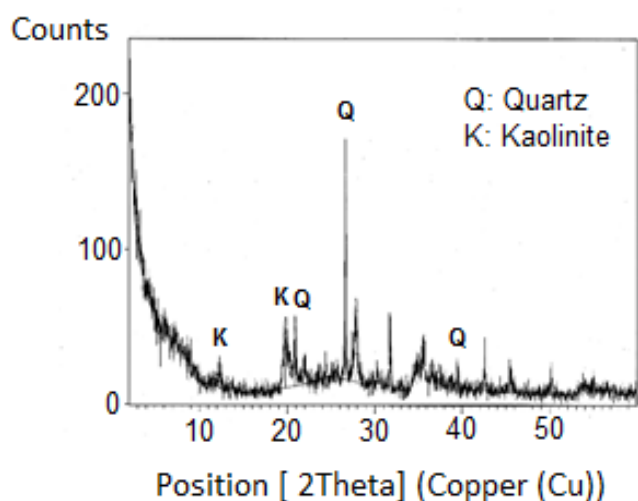


Fig. (2): XRD scan of clay

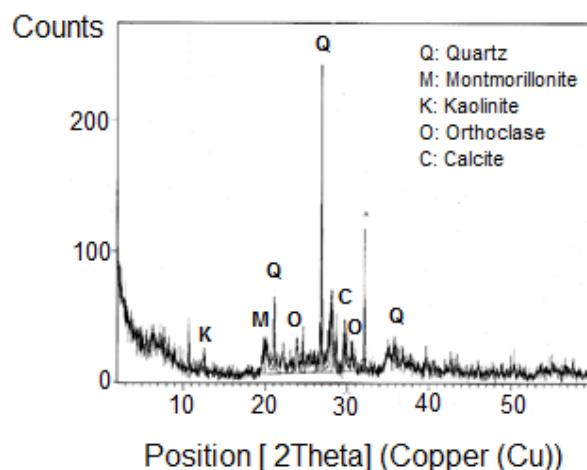


Fig. (3): XRD scan of soil

Energy dispersive X-ray (EDX):

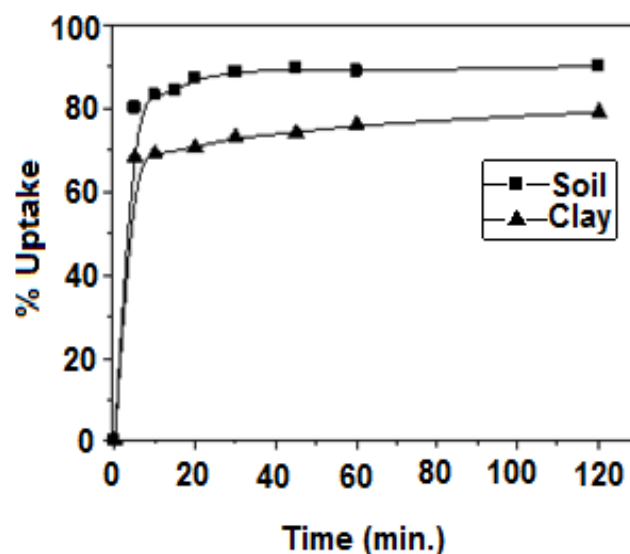
The good analytical technique; EDX, is used to determine the chemical composition, which was illustrated in a previous paper [16]. The elemental composition of kaolinite clay and soil was also determined by EDX. The results are given in Table (1); it shows that the elemental contents of kaolinite are Si, O and Al, in addition to the presence of minor contents of K, Na, Ca, and Mg. It is noted that, the amount of Si is more than that of Al. Considering that in pure kaolin the amount of Al and Si are equal, it can be concluded that the additional amount of Si is mainly originated from the quartz impurities in the natural clay [17].

Table (1): Elemental analysis of soil and clay by EDX

Soil		clay	
Element	Atomic %	Element	Atomic %
Si	19.06	Si	18.81
Mg	0.39	Mg	0.85
Al	5.45	Al	5.47
Ca	3.25	Ca	3.65
Ti	1.0	Ti	1.14
K	2.0	K	0.99
Fe	6.24	Fe	8.0
O	62.45	O	61
Mn	0.16	Na	0.09

Effect of contact time

Fig. (4) shows the effect of contact time on Co^{2+} sorption on soil and kaolinite clay. As can be understood from the figure, the sorption of Co^{2+} on both soil and clay increases rapidly at the initial contact time, then slowly, and then remains constant at 40 minutes; with increasing the contact time. The sorption on soil is higher than on clay, probably because of the presence of organic materials in the soil, in addition to the presence of other additional ingredients in the soil, other than clay.

Fig. (4): Effect of contact time on the sorption of Co^{2+} on soil and clay

The quick sorption of Co^{2+} to soil and clay demonstrates that chemical sorption in addition to physical sorption contributes to the sorption process.

According to the above results, the shaking time was set at 2.0 hours for the rest of the batch experiments to ensure the sorption equilibrium.

Effect of sorbent content

The influence of the content of the sorbent on the sorption of Co^{2+} on soil and kaolinite clay is shown in Fig. (5). As the Figure shows, the sorption increases gradually with increasing the amount of soil or clay up to 0.15g, and then accomplishes an almost constant value. The growth in sorbent dose increases the sorption sites and the surface area of the sorbent, so the % uptake is increased.

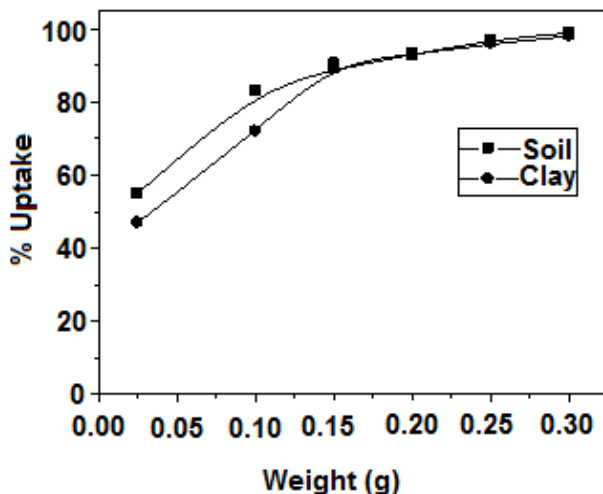


Fig. (5): Effect of sorbent weight on the sorption of Co(II) on soil and clay

Effect of pH

The pH of the soil plays a major role in the uptake of heavy metals because it directly controls the dissolution and hydrolysis of metal hydroxides, phosphates and carbonates. Moreover, it encourages ion- pair creation, solubility of organic substance, in addition to surface charging of Fe, Mn and Al – oxides, organic matter and clay edges [18]. At high pH values; metals are toughly adsorbed, mainly because a major part of the surface charge of metal and mineral oxides is pH-dependent [19].

Fig. (6) shows the pH dependence on the sorption of Co^{2+} on the investigated soil and kaolinite clay. As

expected; the pH of the solution is a main factor in affecting the sorption of Co^{2+} on both soil and clay.

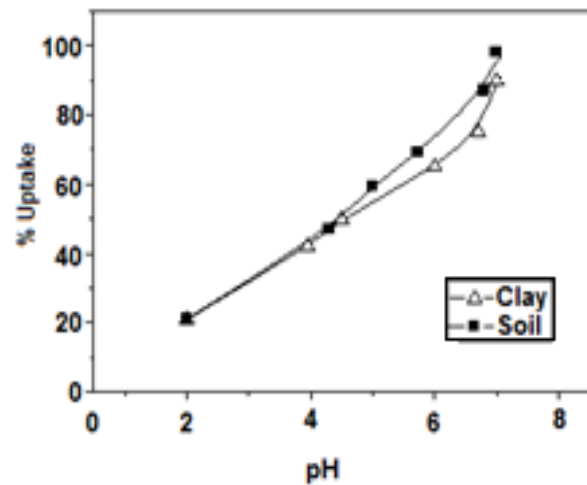


Fig. (6): Effect of pH on the sorption of Co(II) on soil and clay

The sorption of Co^{2+} rises gradually, then sharply with the increase in pH. At pH 7.0, about 99% of Co^{2+} is sorbed on soil and 95% on clay. The percent uptake is low at low pH, but increases with increasing pH. It is generally regarded that increasing pH causes a decrease in the competition between protons and metal ions for surface sites and leads to an increase in the adsorption of metal ions. Furthermore, Co^{2+} is precipitated as $\text{Co}(\text{OH})_2$, at $\text{pH} > 7.0$, as showed in Fig. (7), which displays the relative distribution of Co(II) species in solution[20].

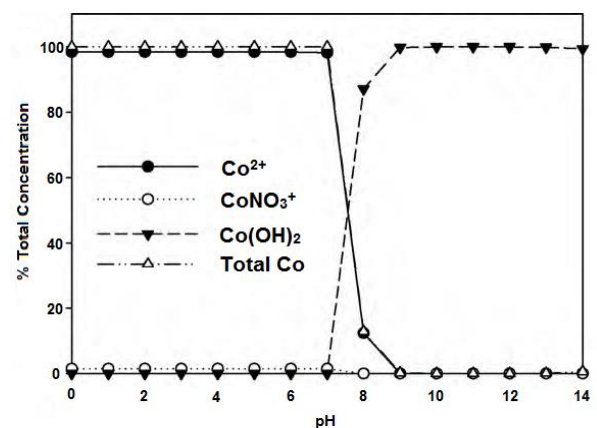


Fig. (7): The distribution of cobalt species as a function of pH [20]

As the Figure indicates; the free ion Co^{2+} is the dominant Co species at $\text{pH} < 7.0$ and $\text{Co}(\text{OH})_2$ precipitate is formed at $\text{pH} > 7.0$. A similar trend is observed by Mekhemer et al., [21] who studied the sorption of cobalt on bentonite, therefore $\text{pH} 7.0$ is chosen for this study.

Kinetic studies

The kinetic studies were accomplished to clarify the mechanism of the sorption of investigated metal ions, describe how fast the rate of chemical reaction happens and moreover to know the factors affecting the rate of reaction [22].

So as to study the sorption rate constant of Co^{2+} to soil and kaolinite clay, Lagergren first-order reaction rate model is done, equation (3). Pseudo- second order reaction model, equation (4) is used to describe the kinetics of cobalt sorption on soil and kaolinite clay[16].

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (3)$$

$$\left(\frac{t}{q_t}\right) = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t \quad (4)$$

Where, q_e and q_t are the adsorption capacity at equilibrium and at time (t), respectively (mg/g), K_1 is the rate constant of pseudo- first order adsorption (min^{-1}) and K_2 is the rate constant of pseudo- second order adsorption ($\text{gmg}^{-1} \text{min}^{-1}$).

The results are represented in Fig. (8) for Pseudo-first order model and in Fig. 9 for Pseudo- second order model, and are compared in Table (2).

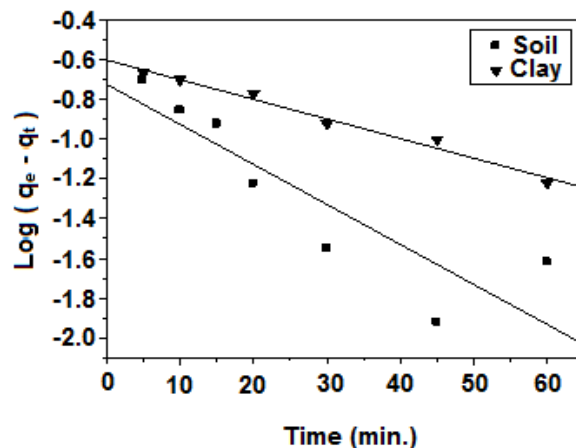


Fig. (8): First-order adsorption kinetics of Co(II) on soil and clay surfaces

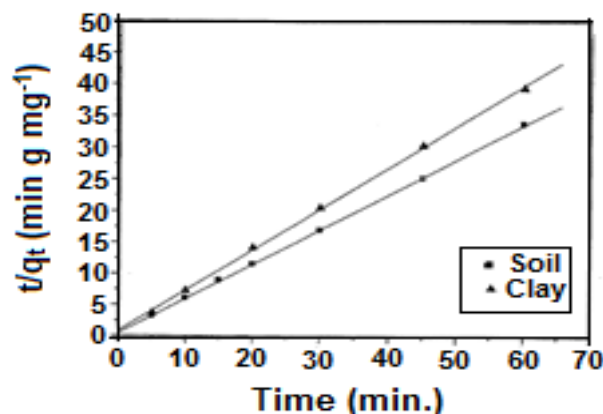


Fig. (9): Pseudo-second-order adsorption kinetics of Co(II) on soil and clay surfaces

A linear plot of t/q_t against t (in Fig. 9) was attained. The correlation coefficients (R^2) of the Pseudo- second order rate equation for the linear plot approves well with the experimental data. These results show that the kinetic sorption of Co^{2+} to soil and kaolinite clay can be well designated by the Pseudo- second order rate equation. Moreover, the K_2 value proposes that the sorption attains equilibrium quickly.

Table (2): Results of the kinetic studies of Co (II) sorbed onto soil and clay

Adsorbent	First-order kinetic parameters			Second-order kinetic parameters			$q_e, \text{exp. mg/g}$
	K_1, min^{-1}	$q_e, \text{calc. mg/g}$	R^2	$K_2, \text{g/mg.min.}$	$q_e, \text{calc. mg/g}$	R^2	
Soil	0.046	0.189	0.77	0.70	1.80	0.999	1.8
Clay	0.022	0.252	0.97	0.52	1.53	0.999	1.58

Effect of Co^{2+} ion concentration

Fig. (10) shows the effect of metal ion concentration on the sorption of Co^{2+} by both soil and kaolinite clay. The results display that the % uptake of cobalt decreases with increasing the metal ion concentration. With the increase of metal ion concentration, the Co^{2+} ions stopover in solution since the most surface groups are previously engaged and as a result, the dispersion of cobalt ions to the un- reacted functional groups is repressed [23].

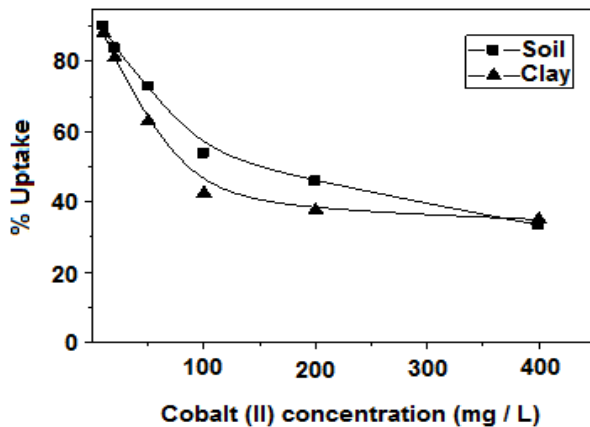


Fig. (10): Effect of metal ion concentration on the sorption of $\text{Co}(\text{II})$ by soil and clay

So as to find an association between the uptake of the metal ion and its properties, some parameters are taken into account as indicated by Mohapatra et al. [24]: mainly factors like (1) electrostatic attraction due to charge to radius ratio (2) hydroxo complex formation capabilities (3) electronegativity of the metal ion and (4) favored adsorption site on the adsorbent are liable for the favorite adsorption of one metal ion over the other.

Effect of organic ligands

The organic ingredients may cooperate with the dissolved inorganic pollutants and may affect the sorption behavior of such pollutants on the geological materials. Therefore, the radio cobalt movement in aquifers is affected. Thus, it is required to identify the effect of organic ligands, such as humic acid, gallic acid and phenol, on the sorption of the investigated radionuclide.

The occurrence of HA can affect the interaction of cobalt with soil and clay minerals, furthermore, it can cause either obstruction or release in the environment. The sorption of $\text{Co}(\text{II})$ in attendance of HA is investigated in batch experiments, by varying both the $\text{Co}(\text{II})$ and HA concentrations.

Fig. (11) indicates the results of cobalt sorption on both soil and clay, in the presence of HA. As the figure shows, the presence of HA enhances the % uptake of $\text{Co}(\text{II})$ by both soil and clay. The sorption process is governed by the construction of $\text{Co}(\text{II})$ -HA complex, which can increase the sorption of $\text{Co}(\text{II})$ apparently since HA can act as a "bridge" between the cobalt ions and the solid surface [25].

This elucidation is confirmed by changing the HA concentration, at constant cobalt ion concentration. The results are presented in Fig. (12). It is clear that, the increase in HA concentration increases the % uptake of Co^{2+} as a consequence of the formation of Co -HA complex. Once the metal is consumed, at HA concentration > 5 mg/L, the % uptake of Co^{2+} starts to be constant.

Humic substances (such as HA) may cause an improving or dropping effect on the sorption of metal ions, depending on the complex conduct of metal ions with HA in the ternary groundwater-HA-mineral surface systems. The increase of sorption is elucidated by the sorption of HA on the mineral surface followed by the interaction of metal ions with the surface adsorbed HA [26].

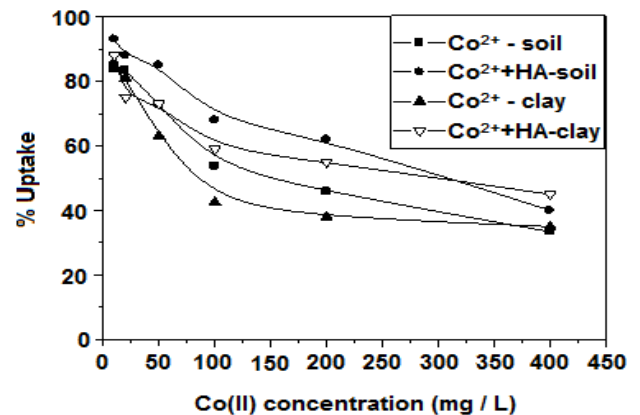


Fig. (11): Effect of humic acid on cobalt (II) sorption onto soil and clay

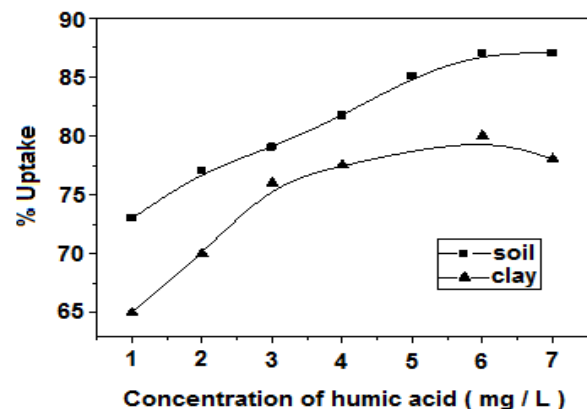


Fig. (12): Effect of HA concentration on the sorption of Co^{2+} by soil & clay

Fig. 13 displays the sorption of Co^{2+} to soil and kaolinite clay, in existence of phenol. It is clear that the sorption of cobalt is sharply decreased at low concentration of Co^{2+} , while at high concentration it is slightly decreased in case of soil, and starts to be stable in case of clay. In comparison with the single-solute adsorption of Co^{2+} , the presence of phenol in solution makes a hindrance at the soil and clay surfaces which reduces the quantities of Co^{2+} likely to interact with the sites [27].

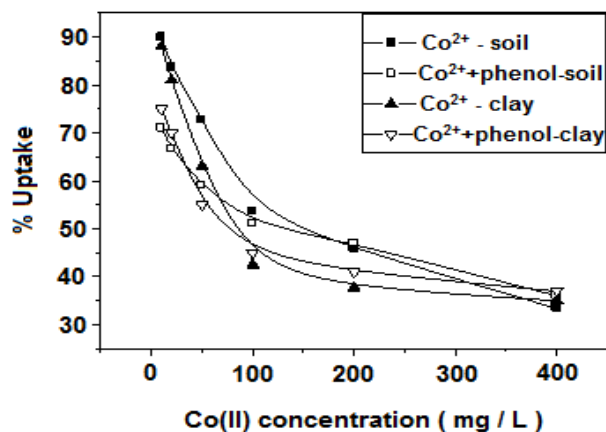


Fig. (13): Effect of phenol on the sorption of Co^{2+} on soil & clay

Fig. (14) demonstrates the sorption curves of Co^{2+} to soil and clay, in the presence of humic acid together with phenol. It is clear that the presence of HA has a supplementary effect on the sorption of Co^{2+} , in which it improved the sorption, for both soil and clay. This behavior is previously discussed in the effect of humic acid alone. The slightly highest sorption case of humic acid alone than that in case of HA with phenol, may be due to the interaction of phenol with HA via hydrophobic bond which may decrease the number of functional groups on humic acid.

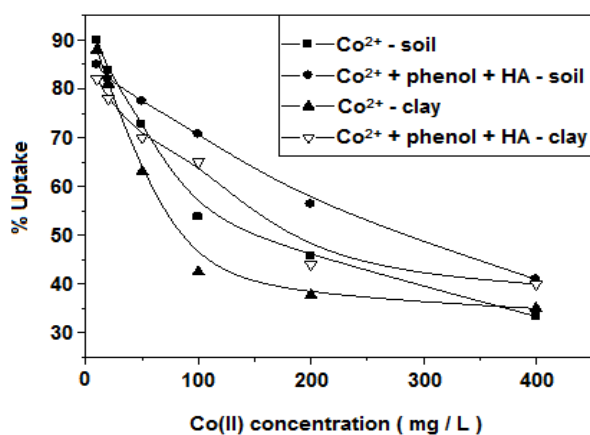


Fig. (14): Effect of phenol on the sorption of Co^{2+} on both soil & clay, in presence of HA

Fig. 15, displays the % uptake of Co^{2+} by soil and kaolinite clay in the presence of gallic acid, as a function of concentration of Co^{2+} . As the figure shows, the presence of gallic acid decreases the sorption of Co^{2+} . This may be explained as a result of complex formation between Co^{2+} and gallic acid. This complex has a low affinity to the surface sites.

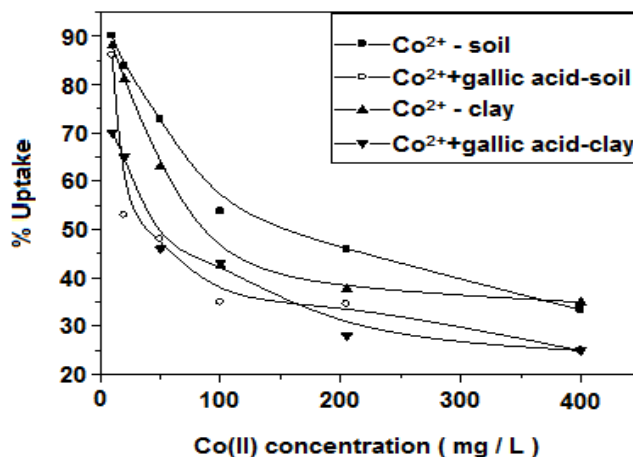


Fig. (15): Effect of gallic acid on the sorption of Co^{2+} by soil & clay

Fig. 16 illustrates the effect of gallic acid on the sorption of Co^{2+} , in the presence of HA. From the figure, it is clear that the presence of gallic acid together with humic acid increases the sorption of Co^{2+} by both soil and clay. This can be explained as previously indicated for humic acid, where HA may attract the metal to the solution.

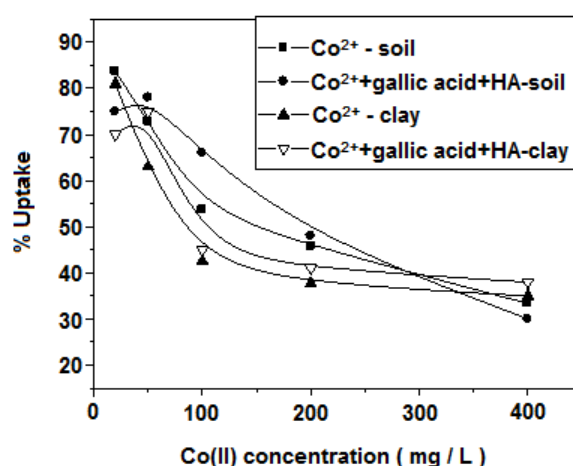


Fig. (16): Effect of gallic acid on the sorption of Co^{2+} by soil and clay, in presence of HA

A comparison of the adsorption performance of the soil and clay with other adsorbents is reported in Table (3).

Table (3): Comparison of the sorption capacities for Co(II) using various adsorbent materials

Sorbent	Q _{max} , mg/g	pH	Initial [Co], ppm	T, °C	Ref.
Magnetite clinoptilolite	2.69	8.0	25	40	[28]
CaO/Fe ₃ O ₄ Magnetic composite	217.4	2-11	5.0	25	[29]
Goethite	9.0	7.0	0.6	10-70	[30]
Fe ₃ O ₄ /bentonite	18.8	8.0	800	25	[31]
Magnetite	37.0	6.5	24.0	20	[32]
MnO ₂ -coated Zeolite	15.0	3-8	100	20	[33]
Hausmannite, Mn ₃ O ₄	0.5	4.5	20.0	25	[34]
TiO ₂	3.1	6.5	6.0	18	[35]
Natural bentonite	0.9	3-9	15-70	20-90	[36]
Montmorillonite	6.4	5.0	10.0	30	[37]
Kaolinite	0.54	3-10	6.0	10-70	[38]
Ca(II)-Montmorillonite	10.3	4.08	6.0	10-70	[39]
Saudi activated bentonite	7.3	1-10	20-210	25	[40]
Soil	1.8	7.0	20	25	This study
Clay	1.58	7.0	20	25	This study

CONCLUSIONS

Based on the experimental results of Co²⁺ sorption by soil and kaolinite clay under the investigated conditions, we can come to the following conclusions:

- (1) The sorption of cobalt is highly dependent on the pH, it increases with increasing pH; reaching 99% at pH 7.
- (2) It is controlled by ion exchange or the outer-sphere surface complexation at low pH values, and by the inner-sphere surface complexation at high pH.
- (3) The sorption of Co(II) to soil and clay is relatively fast and the kinetic sorption can be designated by the pseudo- second order model.
- (4) The sorption is affected by the presence of HA, gallic acid or phenol.

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