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# Sorption of Pb(II), Cd(II) and Zn(II) ions from aqueous solution using Jordanian kaolinite modified by the amino acids methionine or cysteine

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## ABSTRACT

Modification of kaolinite clay with amino acids methionine or cysteine and the adsorption of Pb(II), Cd(II) and Zn(II) ions from aqueous solutions were studied. The modified kaolinite (K-Meth or K-Cyst) was characterized by FTIR, TGA, SEM, and XRD. The sorption behavior and adsorption isotherms of the K-Meth or K-Cyst toward Pb(II), Cd(II), and Zn(II) was studied by batch equilibrium technique as a function of K-Meth or K-Cyst mass, pH, temperature and contact time. The column experiment was effectively used for the determination of metal ions loading capacity as well as for desorption studies. The K-Meth or K-Cyst showed high metal-ion uptake capacity towards Pb(II) more than Cd(II) and Zn(II). The adsorption isotherm data shows fittings for Langmuir's more than Freundlich and Dubinin-Radushkevich equations. The adsorption reaction was found to have positive values for $\Delta H°$ and $\Delta S°$, this suggest an increase in randomness at the solid-liquid interface during the adsorption process. The interactions are thermodynamically favorable and are accompanied by a decrease in Gibbs energy with temperature. The column loaded K-Meth or K-Cyst was regenerated by 0.1 M $HNO_3$ and therefore can be employed for the removal of heavy metal pollutants in environmental and industrial applications.

*Keywords:* Modification; Kaolinite; Methionine; Cysteine; Sorption; Heavy metals

## 1. Introduction

Heavy metals, such as Pb(II), Zn(II) and Cd(II), pollution represents a serious problem for human health and life. The disposal of heavy metals is a consequence of several activities like chemical manufacturing, painting, coating, mining, extractive metallurgy, nuclear and other industries. Those metals exert a deleterious effect on fauna and flora of lakes and streams [1]. Thus, metals cause environmental pollution, threats to human health and ecosystems, such as acute lead poisoning has been known to affect gastrointestinal track, or nervous system and sometimes both, cadmium ions cause serious cases of acute toxicity and diseases such as lung cancer and kidney failure and zinc may cause gross lack of coordination of the human muscle movements [2]. Several techniques were used for the removal of such contaminants from water including filtration, flocculation, ion-exchange resins, adsorption, reverse osmosis, and precipitation [3]. However, techniques like ion exchange, membrane technologies and activated carbon adsorption process are extremely expensive when treating large amount of wastewater containing heavy metal ions in low concentration. Adsorption technique has advantages of applicability at very low concentration, suitability for using batch and continuous processes, ease of operation, little sludge formation, possibility of reusing, and low operational cost [4]. Several adsorbents have been studied to remove targeted heavy metal ions as shown in Table 1.

Kaolinite has a 1:1 layer structure, with the basic unit consisting of a tetrahedral sheet of $SiO_4$ and an octahedral sheet with $Al^{3+}$ as the octahedral cation. Both sheets combine

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Table 1
Metal maximum adsorption capacity ($q_m$ (mg g$^{-1}$) calculated from Langmuir model) for some adsorbents

| Heavy metal ion (adsorbate) | Metal(II) | Adsorbent $q_m$ (mg g$^{-1}$) | Conditions | Reference |
|---|---|---|---|---|
| Montmorillonite | $Pb^{2+}$ | 12.89 | pH 6.0, 298 K | [5] |
| Acidified multi-walled CNTs | $Pb^{2+}$ | 49.71 | pH 5.0, 298 K | [6] |
| Original bentonite | $Pb^{2+}$ | 19.19 | 303 K | [7] |
| Pine wood char | $Pb^{2+}$ | 4.13 | pH 5.0, 298 K | [8] |
| Kaolin | $Pb^{2+}$ | 17.5 | pH 5.0, 298 K | [9] |
| | $Hg^{2+}$ | 20.9 | | |
| | $Cd^{2+}$ | 15.9 | | |
| Carbon aerogel | $Cd^{2+}$ | 400.8 | pH 6.0 | [10] |
| | $Hg^{2+}$ | 45.6 | | |
| | $Zn^{2+}$ | 1.84 | | |
| | $Pb^{2+}$ | 0.7 | | |
| Zeolite | $Pb^{2+}$ | 65.7 | pH 4.0 | [11] |
| | $Cd^{2+}$ | 52.1 | | |
| Rice husk | $Cd^{2+}$ | 8.58 | | [12] |
| Polyaniline grafted-Chitosan | $Pb^{2+}$ | 13.2 | pH 6.0, 303 K | [13] |
| | $Cd^{2+}$ | 12.8 | | |
| K-Cyst | $Pb^{2+}$ | 27.8 | pH 5.0, 298 K | This work |
| | $Cd^{2+}$ | 14.8 | | |
| | $Zn^{2+}$ | 7.35 | | |
| K-Meth | $Pb^{2+}$ | 2.3 | pH 5.0, 298 K | This work |
| | $Cd^{2+}$ | 2.5 | | |
| | $Zn^{2+}$ | 1.8 | | |

to form a common layer such that the tips of the silica tetrahedra point toward the octahedral layer [14]. The tetrahedral layer is inverted over the octahedral layer with the apical (O) atoms being shared by the two layers. In the layer common to the octahedral and tetrahedral sheets, two-thirds of the (O) atoms are shared between (Si) and (Al) atoms [15]. Kaolinite has very limited substitution on structure, very small relative surface area to other clay types, low adsorption and cation exchange capacity (CEC). Kaolinite high pH dependency enhances or inhibits the adsorption of metals according to the pH of the environment. The metal adsorption is usually accompanied by the release of hydrogen ions ($H^+$) from the edge sites of the mineral [16]. Adsorption may also take place on the flat exposed planes of the silica and the alumina sheets. The structure of kaolinite can be affected by adsorption of heavy metals, but the effects are likely to be determined by the type of kaolinite used. The substitution of ($H^+$) ions for metal ions could influence the Van der Waal's forces within the kaolinite structure [17]. Any changes in these properties indicate the creation of empty spaces in the clay structure. Similar spaces could also be produced if the adsorption of metal ions produces a reduction in the Van der Waal's forces between the elements in kaolinite, but it is not exactly certain how these forces are affected [18]. Many efforts have been made to increase the adsorption capacity of raw kaolinite through making some modifications in the surface toward various metal ions in aqueous solution. The adsorption of amino acids (Ala, Met, Gln, Cyst, Asp, Lys, His) on clays (bentonite, kaolinite) was studied at different pH (3.00, 6.00, and 8.00). There were two main findings in this study: First, amino acids, Asp, Lys, His and Cyst were adsorbed on clays more than Ala, Met and Gln. Second, Cyst could play an important role in prebiotic chemistry besides participating in the structure of peptides/proteins. The FTIR spectra showed that the adsorption of amino acids on the clays occurs through the amine group. However, the Cyst/clay interaction occurs through the sulfhydryl and amine groups [19]. Previous paper reported the modification of kaolinite by humic acid at different humic acid concentration, pH and temperature [14]. Then the adsorption of unmodified and modified forms toward Pb(II), Zn(II),Cd(II) were studied and found that the adsorption trend was as follows: Pb (II) > Cd (II) > Zn (II) for modified kaolinite clay, which is greater than the unmodified form [20].

Since Jordan is very rich in kaolinite and is available and very cheap [20], so we decieded to study it's properties and behavior as an adsopent for future use in industrial waste water treatment plants. So, the aim of the present work is to modify Jordanian kaolinite by methionine or cysteine amino acids and to investigate the modified forms adsorption properties for the removal of heavy metals from aqueous solution. The heavy metals in this study are Pb(II), Zn(II) and Cd(II), because they are soft metals and could bind to soft sulfur atom in methionine and cysteine easily. The modification of kaolinite with methionine or cysteine amino acids is expected to increase the ability of kaolinite to adsorb these soft heavy metals. XRD and FTIR techniques will be used for the characterization of the modified kaolinite. The sorption properties of the modified kaolinite toward metal ions in aqueous solutions will be studied as a function of certain variables such as contact time, pH, temperature, concentration variation using batch technique, the adsorption and desorption behavior using column technique was also studied. The amount of metal ion uptake will be determined with atomic absorption spectrophotometry. The adsorption isotherm data will be analyzed based on adsorption models such as, Langmuir, Freundlich and Dubinin–Radushkevich (D-R).

## 2. Experimental setup

### *2.1. Materials*

All chemicals were obtained from commercial sources as either analytical reagent grade or chemically pure grade and were used as received. The chemicals were purchased from the corresponding companies: sodium perchlorate ($NaClO_4$) (Acros), lead(II) chloride $PbCl_2$ (PRS Paureac), cadmium(II) nitrate tetrahydrate $Cd(NO_3)_2.4H_2O$ (BDH), zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$ (BDH), sodium hydroxide NaOH (SDS), hydrochloric acid HCl 37% (TEDIA), methionine and cysteine (ALDRICH).The raw Jordanian kaolinite samples have been collected from Batn El-Ghoul area located at 70 km southeast of Ma'an on the way to the Saudi border and 280 km south of Amman. The samples were washed several times with deionized water, dried at 60°C in vacuum oven overnight then crushed using ball mill and sieved at 250 μm particle size.

### *2.2. Instruments*

FT–IR spectra were recorded using Thermo Nicolet NEXUS 670 FT–IR spectrophotometer from 4,000–400 $cm^{-1}$, using KBr disk. The crystallinity measurements were obtained using X-ray diffractometer (Shimadzu XRD-6000) equipped with Cu K$\alpha$ radiation source using Ni as filter and operated at 30 kV/30 mA. All XRD data were collected under the same experimental conditions; in the angular range $3° \leq 2\theta \leq 50°$. The thermal gravimetric analysis (TGA) of the kaolin clay samples was studied using NETZCH STA 409 PG/PC Thermal Analyzer in the temperature range 0°C–1,000°C, at a heating rate of 20°C $min^{-1}$. The scanning electron microscopy technique (SEM) was used to obtain information about the surface of unmodified and modified kaolin clay with methionine and cysteine, and loaded modified kaolin clay with lead ions. The FEI inspect F50 scanning electron microscope was used to record micrographs of the particles after coating with platinum then the energy dispersion spectrum (EDS) was used to determine the elements present. Concentrations of the metal ions were determined using (Varian Spectra AA–250 pulse) atomic absorption spectrometer (AAS). Concentrations of methionine and cysteine were determined using UV–VIS Spectrophotometer (Varian cary100). Shaking of samples was done using Clifton Shaker (BS-11) equipped with a thermostat. The pH was measured using METROHM 605 pH-meter. Mass of samples was measured by using AW120 electronic balance.

### *2.3. Modification of kaolinite*

To obtain the best modification ratio of the kaolinite with methionine (Meth) or cysteine (Cyst), the following was done:

1. Different concentrations of Meth or Cyst are mixed with 1.000 g ± 0.1 mg of kaolinite, The mixture was filtered and the amount of the Meth or Cyst remaining in the filtrate was determined with UV–VIS spectrophotometer at $\lambda = 570$ nm using ninhydrine test [21].
2. To measure the concentration of free Meth or at $\lambda = 500$ nm using p-benzoquinone [22] to measure the concentration of free Cyst.
3. Different concentrations of aqueous Meth or Cyst are mixed with 1.000 g ± 0.1 mg of kaolinite. Optimum modification ratio was obtained using 4,000 mg $L^{-1}$ Meth or 2,000 mg $L^{-1}$ Cyst.

Based on this, a 200 g of the raw kaolinite (particle size 250 μm) was mixed with 8 g ± 0.1 mg of methionine in 2 L distilled water for 24 h. On the other hand, a 150 g of the same raw kaolinite was mixed with 6 g ± 0.1 mg of cysteine in 3 L distilled water for 24 h. Then the mixture in both cases K-Meth or K-Cyst was filtered using filter paper and the solid was dried to a constant weight at 40°C in oven for 24 h [14].

### *2.4. Characterization of raw and modified kaolinite*

The raw and modified kaolinites were characterized by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermo gravimetric analysis (TGA), and scanning electron microscopy (SEM).

### *2.5. Sorption properties of the modified kaolinite (K-Meth or K-Cyst) by batch technique*

The sorption properties for each metal ion were studied using the batch equilibrium technique in the following manner:

Different doses (from 0.1 g ± 0.1 mg to 1.0 g ± 0.1 mg) of K-Meth or K-Cyst were taken in a 100-mL glass bottle to know the optimum dose which has the maximum uptake for each metal ion. At optimum dose, different pH values (from pH 1–5) for each metal ion were tested to know the effect of pH changing on metal ion uptake by the K-Meth or K-Cyst. At optimum dose and pH, different contact times were taken to know the effect of contact time (from 30 min to 48 h) on metal ion uptake by K-Meth or K-Cyst. Optimum dose of K-Meth or K-Cyst was added to 50 mL of 100 mg $L^{-1}$ concentration of metal ion solution at optimum pH in 100 mL glass bottle, and the solution was mechanically shaken to optimum contact time (24 h) at 25°C, the mixture was filtered and the amount of the metal ion remaining in the filtrate solution was determined by atomic absorption spectrometry after constructing up an analytical calibration curve for each element (Pb(II), Cd(II), and Zn(II)) [20].

### *2.6. Rate of metal ion uptake*

For determining the equilibrium time for the metal ion uptake process, optimum dose of K-Meth or K-Cyst was added to 50 mL of 100 mg $L^{-1}$ from each metal ions solution at optimum pH, the resulting mixture was mechanically shaken for various contact time (from 1 to 48 h at 25°C). The mixture was filtered and the amount of the metal ion remaining in the filtrate solution was determined with an atomic absorption spectrophotometer.

The amount of metal ion uptake by the K- Cyst ($q_e$) was calculated by the following Eq. (1):

$$q_e = (C_o - C_e)V/M \tag{1}$$

where $C_o$ is the initial metal concentration (mg $L^{-1}$); $C_e$ is the residual concentration of the metal ion in solution at equilibrium; $V$ is the volume of solution (L); $M$ is the mass of K-Meth or K-Cyst (g).

The loading percentage of metal ion on the K-Meth or K-Cyst expressed as % uptake (Eq. (2)) is:

$$\text{Metal ion uptake (\%)} = (C_o - C_e)/C_o \times 100\% \tag{2}$$

The distribution coefficient $K_d$ was calculated using the following Eq. (3):

$$K_d = \frac{\text{Metal ion on the K-Meth or K-Cyst}\left(\text{mg/L}\right) \times \text{Volume of the solution}\left(\text{L}\right)}{\text{Metal ion in solution}\left(\text{mg/L}\right) \times \text{Mass of K-Meth or K-Cyst}\left(\text{g}\right)} \tag{3}$$

### 2.7. Adsorption isotherms studies

The adsorption of Pb(II), Cd(II), and Zn(II) onto the K-Meth or K- Cyst were carried out by taking the optimum dose of K-Meth or K- Cyst for each metal ion, which was then shaken with 50 mL of solutions having concentrations ranging from 20 to 120 mg $L^{-1}$ for each metal, and shaken for optimum contact time at different temperatures of 25°C, 35°C, and 45°C. The adsorption isotherms were also studied using same conditions but under different pH values 3–5 [14]. The following formulas are used to study the adsorption isotherms:

- Langmuir equation(Form II)

$$1/q_e = (1/(q_m K_L))\,1/C_e + 1/q_m \tag{4}$$

- Freundlich equation

$$\text{Log}q_e = \log K_F + 1/n \log C_e \tag{5}$$

- Dubinin-Radushkevich equations

$$\text{In}q_e = \ln q_{\max} - \beta\varepsilon_2 \tag{6}$$

- The Polanyi potential, which equals to:

$$\varepsilon = RT\ \text{In}\ (1+1/C_e) \tag{7}$$

### 2.8. Column studies

The adsorption using the column experiments for Pb(II), Cd(II) and Zn(II) was done using 30 cm length and 20 mm inner diameter glass column. The column was packed with 2.000 g ± 0.1 mg of dried modified kaolinite (K-Meth or K-Cyst) for each metal ion in 50 mL of 100 mg $L^{-1}$ concentration was passed through the column at the same flow rate (0.5 mL $min^{-1}$).The elute was collected in a 100 mL glass bottle, and the concentration of the metal ion was measured by AAS. The eluting agent 0.1 M nitric acid ($HNO_3$) was used for elution of the sorbent with adsorbed metal ion and keeping the flow rate at 0.5 mL $min^{-1}$, the metal ion in the elute was collected in five portions 10 mL each, and the concentration was measured by AAS [14].

## 3. Results and discussion

### 3.1. Infrared spectroscopy

The FTIR characteristic bands of methionine (Meth), K-Meth, cysteine (Cyst) and K-Cyst are listed in Table 2, Figs. 1 and 2.

The IR spectrum of methionine (Meth), Table 2, shows bands at 707, 749, 1,448, 872, 1,351, 1,390, 1,584, and 2,578 $cm^{-1}$ which refer to the deformation of $COO^-$ group, stretching of C–S, deformation of $CH_2$ group, stretching of C–C, deformation of $NH_3$ group, stretching of $COO^-$ group, deformation of $-NH_3^+$ group, and stretching of C–S, respectively.The IR spectrum of cysteine (Cyst), Table 2, shows bands at 636, 823, 691, 753, 1,423, 866, 1,345, 1,392, 1,586, and 2,549 $cm^{-1}$ refers to deformation of $COO^-$ group, stretching of C–S, deformation of $CH_2$ group, stretching of C–C, deformation of $NH_3$ group, stretching of $COO^-$ group, deformation of $-NH_3^+$ group, and stretching of S–H, respectively. This is in agreement with a previous study by Carneiro et al. [19]. According to Table 2, the IR data for raw kaolinite and, modified kaolinite showed the following characteristic peaks, in the range of the OH stretching vibrations, the band experimentally observed at 3,620cm$^{-1}$ corresponds to the inner OH stretching. The one observed at 3,696 $cm^{-1}$ corresponds to the stretching vibration modes of “‘inner surface hydroxyls” that are located at the surface of octahedral sheets opposite to the tetrahedral oxygen’s of the adjacent kaolinite layer [14]. The band at 3,484 $cm^{-1}$ refers to OH stretching of water, while the bands in the ranges between (1,100 to1,000 $cm^{-1}$) are referred to Si–O stretching vibrations at 1,093, 1,032, and 1,007 $cm^{-1}$ while the bands at 1,032 $cm^{-1}$ are rather caused by Si–O–Si and Si–O–Al lattice vibrations. The OH bending vibration at 913 $cm^{-1}$ is referred to the “inner OH bending”. Further, bands at 796 and 692 $cm^{-1}$ can be largely attributed to different Si–O vibration [24]. On the other hand, the band at 537 $cm^{-1}$ refers to Al–O–Si deformation, but Si–O–Si deformation occurs at 468 $cm^{-1}$, and Si–O deformationat 428 $cm^{-1}$.A weak band at 1,588 $cm^{-1}$ refers to $-NH_3^+$ deformation, while 1,485 $cm^{-1}$ refers to N–H deformation, and 1,407 $cm^{-1}$ refers to $COO^-$ stretching. These are characteristic of amino acid zwitterions, which are a strong indication to the modification of the kaolinite [17].The functional group N–H (deformation) in modified kaolinite by cysteine in a previous study was observed at 1,491 $cm^{-1}$, the band of $COO^-$ stretching at 1,431 $cm^{-1}$, and $-NH_3^+$ deformation at 1,591 $cm^{-1}$, also the following bands were observed, at 776, 838, 869cm$^{-1}$ refer to deformation of $CH_2$ group, deformation of $COO^-$ group, and stretching of C–C, respectively [17].

### 3.2. X-ray diffraction

X-ray diffraction of the raw kaolinite is shown in Fig. 3(a), it showed that kaolinite mineral is the dominant mineral

Table 2
FT-IR bands of raw kaolinite, methionine, modified methionine (K-Meth), cysteine and modified cysteine (K-Cyst)

| Assignment | Raw kaolinite (cm$^{-1}$) | Meth. (cm$^{-1}$) | K-Meth (cm$^{-1}$) | Cyst. (cm$^{-1}$) | K-Cyst (cm$^{-1}$) |
|---|---|---|---|---|---|
| OH stretching of inner surface hydroxyl group | 3,696 | – | 3,695 | – | 3,696 |
| OH stretching of inner hydroxyl group | 3,620 | – | 3,620 | – | 3,620 |
| OH stretching of water | 3,484 | – | 3,484 | – | 3,484 |
| OH deformation of water | 1,624 | – | – | – | – |
| $-NH_3^+$ deformation | – | 1,584 | 1,588 | 1,586 | 1,588 |
| N–H deformation | – | – | 1,485 | – | 1,485 |
| $COO^-$ stretching | – | 1,390 | 1,407 | 1,392 | 1,407 |
| Si–O stretching | 1,112, 1,032, 1,006 | – | 1,093, 1,032, 1,007 | – | 1,093, 1,032, 1,007 |
| OH deformation of inner hydroxyl group | 913 | – | 913 | – | 913 |
| Si–O stretching of quartz | 7,97,693 | – | 7,96,692 | – | 7,96,693 |
| Si–O deformation | 427 | – | 429 | – | 428 |
| Si–O–Si deformation | 468 | – | 468 | – | 468 |
| Al–O–Si deformation | 537 | – | 537 | – | 537 |
| $COO^-$ deformation | – | 6,47,814 | – | 6,36,823 | – |
| C–S stretching | – | 707 | – | 691 | – |
| $CH_2$ deformation | – | 7,49,1448 | – | 7,53,1432 | – |
| C–C stretching | – | 866 | – | 866 | – |
| $NH_3$ deformation | – | 1,351 | – | 1,345 | – |
| S–H stretching | – | 2,578 | – | 2,549 | – |

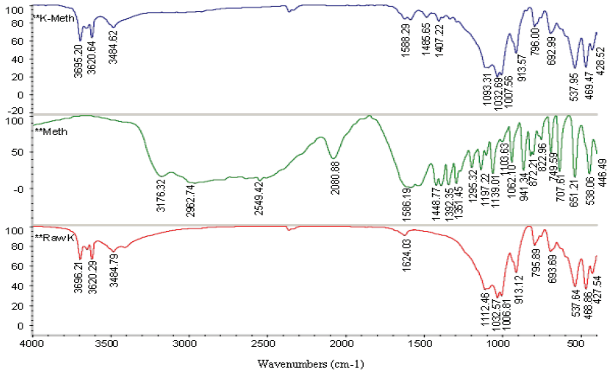

Fig. 1. FT–IR spectra for modified kaolinite (K-Meth), methionine (Meth), and raw kaolinite (K).

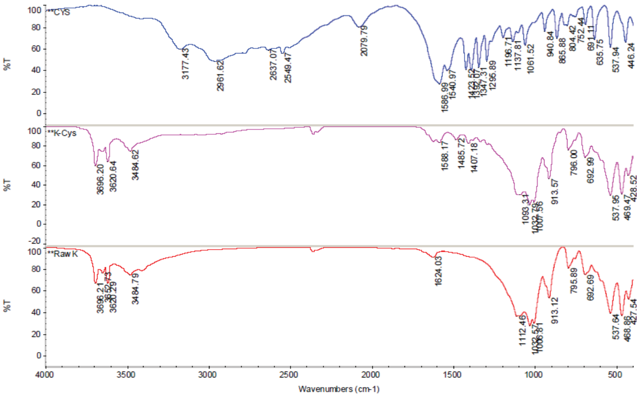

Fig. 2. FT–IR spectra for modified kaolinite (K-Cyst), cysteine (Cyst), and raw kaolinite (K).

phase with some minerals associated like quartz, and illite [23]. Quartz accounted for the highest proportion, which is a common mineral in all soils. The modified kaolinite sample deflocculated by cysteine (Fig. 3(a)) showed the emergence of a small peak at 2θ = 8.9 relative to illite, which is too small to be detected in the raw kaolinite, and the increase in the intensity of the kaolinite peaks at 2θ = 12 and 25, and a decrease in the intensity of the quartz peak, indicates that the modified kaolinite adsorb cysteine. The modified kaolinite sample deflocculated by methionine. (Fig. 3(b)) showed the emergence of a small peak at 2θ = 8.9 relative to illite, which is too small to be detected in the raw kaolinite, and the increase in the intensity of the kaolinite peaks at 2θ = 12 and 25, and a decrease in the intensity of the quartz peak, indicates that the modified kaolinite adsorb methionine.

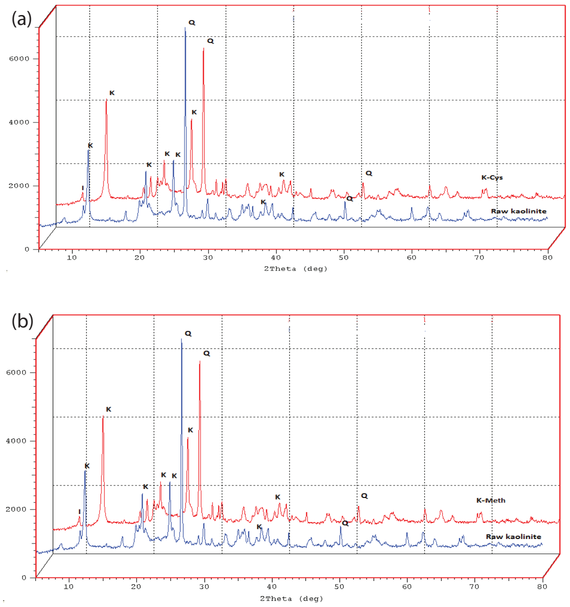

Fig. 3. XRD Spectra of (a) raw kaolinite and K-Cyst and (b) raw kaolinite and K-Meth (*Q* = quartz, *K* = kaolinite, *I* = illite).

Another study showed that the relative intensities of raw kaolinite (from Azraq region) peaks were higher than the modified kaolinite. This decrease in relative intensities indicates that the modified kaolinite adsorb humic acid, also, the decrease in illite peak intensity in going from the raw kaolinite to the modified kaolinite, indicates that the modified kaolinite adsorb humic acid [14].While the relative intensities of raw kaolinite (from the Al-Disi district in Aqaba region south of Jordan) peaks were higher than the modified kaolinite by sodium polyphosphate. This decrease in relative intensities indicates that the modified kaolinite adsorbs sodium polyphosphate, and another decrease in illite peak intensity in going from the raw kaolinite to the modified kaolinite, supported this conclusion [19].

### 3.3. Scanning electron microscope (SEM)

The surface topography of raw kaolinite clay was observed by SEM, and the results are shown in Figs. 4(a) and (b). The clay fractions that are >250 µm of Batn-ElGoul kaolinite clay consists of pseudo hexagonal crystals. The crystals are thin flexible plates. As shown, there are distributed pores and a plate–like structure in the photo–micrographs, with high crystallinity and a high degree of ordering. We can notice the differences between SEM micrographs of raw kaolinite and modified kaolinite by cysteine, (Figs. 4(c) and (d)), the appearance of new cubic crystals (are typically thick), absent in raw kaolinite, indicates that the modified kaolinite adsorbed cysteine. The presence of Cyst on kaolinite leads to increase the surface area by decreasing the degree of ordering on the kaolinite structure as shown in Fig. 4, which will lead to increase in metal ion adsorption. But in the case of K-Meth, there is a decrease in the smoothness of the surface and more flakes type (Figs. 4(e) and (f)), which is a result of surface modification. Since the highest uptake of metal ions by modified kaolinite was for Pb(II), so it was studied by SEM to observe the changes in surface topography that took place (Figs. 4(g)–(j)). The surface topography of modified kaolinite adsorbents gave white particles with irregular structures on the surface of the mineral particles, as shown in Figs. 4(h) and (j), are likely to be lead.

### 3.4. Thermal properties

The thermal stability of the kaolinite clay was investigated by thermogravimetric analysis (TGA) under dry nitrogen atmosphere. TGA has been used vary widely in the study of thermal reactions of clay minerals. These reactions include dehydration of adsorbed water, dehydroxylation (evolution of water from hydroxyls belonging to the clay skeleton) followed by the transformation of the clay to a meta–phase and recrystallization of the meta–phase into a crystalline phase [25]. As shown in the TGA thermogram in Fig. 3 for raw kaolinite and modified kaolinite (K-Cyst) for example, kaolinite was transformed to metakaolinite phase with loss of structural hydroxyl groups at 400°C–650°C.When kaolinite is heated, the adsorbed water is liberated at above 100°C and the weakest part of the chemical bond is broken or perturbed; then dehydroxylation takes place at 400°C–650°C range. The main changes pointed out by TGA, during the heating of the samples are indicated as follows:

1. $T < 100°C$: low temperature release of the absorbed water in pores and on the surfaces of kaolinite structure.
2. 100°C–400°C: mass loss that can be correlated with a pre–dehydration process, which takes place as a result of the reorganization in the octahedral layer, first occurring at the OH of the surface.
3. 400°C–650°C: dehydroxylation of kaolinite and formation of metakaolinite according to the following reaction:

$$2SiO_2 .Al_2O_3 . 2H_2 O(s) \rightarrow 2SiO_2 . Al_2O_3 (s) + 2H_2O (l) \tag{8}$$

The kaolinite structure consists of a single silica tetrahedral sheet and a single alumina octahedral sheet combined to form the kaolinite unit layer. These unit layers are stacked one over the other. During heating, the silicon atoms experience a range of environments of differing distortion due to dehydroxylation. The aluminum atoms mostly transform from octahedral to tetrahedral geometry. As the calcinations temperature increases, the structure becomes more distorted, and finally amorphous silica is liberated. For kaolinite, dehydroxylation might result in the disturbance of the Al(III) octahedral sheets by the outer hydroxyls, but does not affect the $SiO_4$ tetrahedral sheet due to the more stable inner–hydroxyl groups. The outer hydroxyls of octahedral sheets may be more easily removed by heating than the inner ones that will maintain a more ordered $SiO_4$ tetrahedral group in structure during dihydroxylation [25]. The thermogram (Fig. 5) showed a small drop at T < 150°C for raw kaolinite, which represents the release of the absorbed water in pores and on the surfaces. This agrees with the thermal analysis result of other raw kaolinite from Azraq region (Jordan) [14]. While it's absent in modified kaolinite (K-Cyst), this means that adsorption of Cyst is accompanied by water release. The thermogram showed a sharp drop between (200°C–300°C) for modified kaolinite (K-Cyst), which represents the release

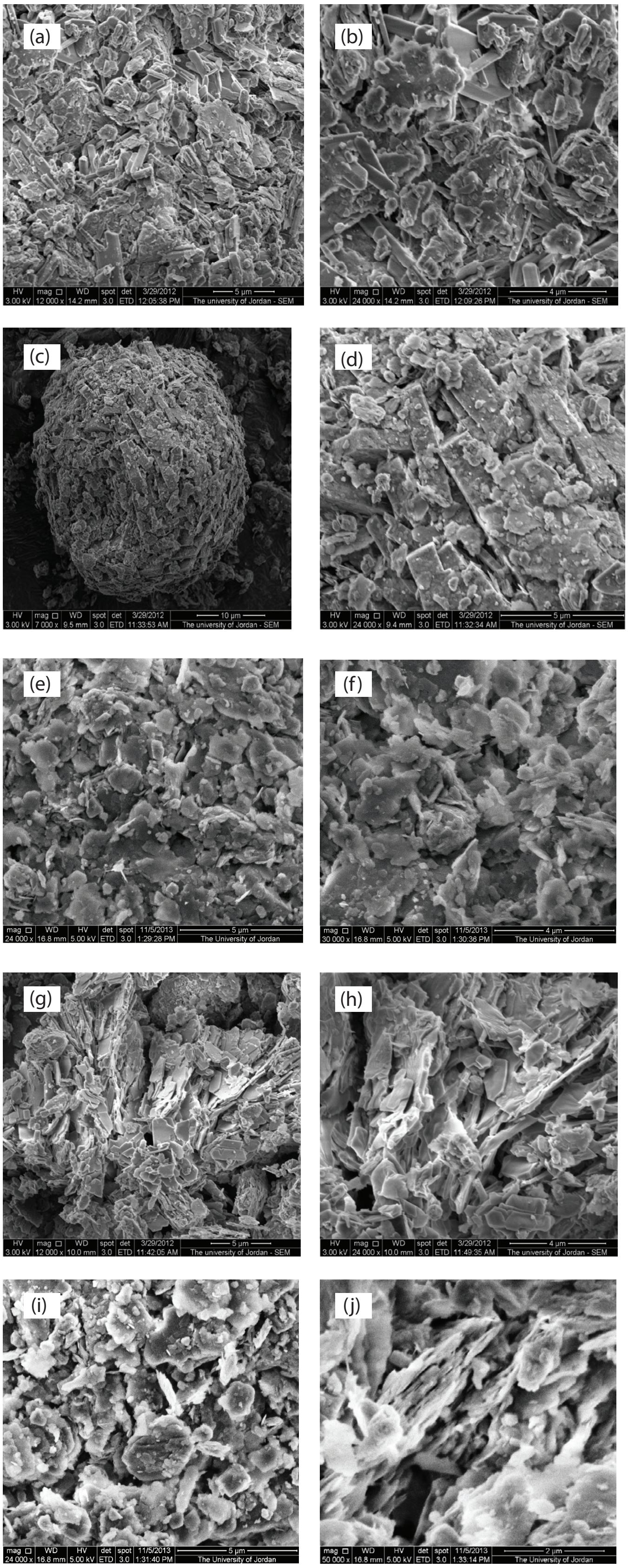

Fig. 4. SEM micrographs for (a) (b) raw kaolinite, (c) (d) modified kaolinite (K-Cyst), (e) (f) modified kaolinite (K-Meth),(g) (h) (K-Cyst) with Pb(II), and (i) (j) (K-Meth) with Pb(II) at different magnifications.

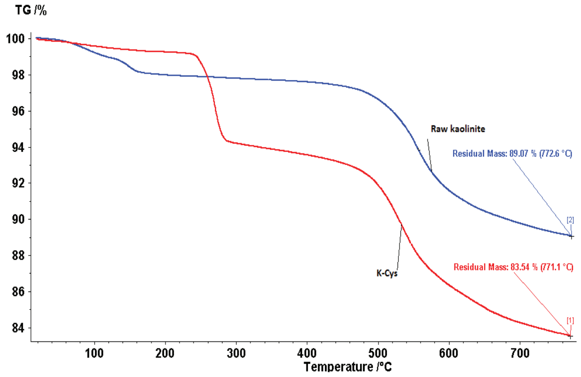

Fig. 5. TGA thermogram for raw and cysteine modified kaolinite (K-Cyst).

of the OH and COOH groups from Cyst that uploaded on kaolinite, while it's absent in raw kaolinite. This is a good indicator of the presence of Cyst in modified kaolinite, which agrees with the thermal analysis results of other modified kaolinite from Minas Gerais (Brazil) (Cd-cysteine complexes by kaolinite) [26].The thermogram showed sharp drop for modified kaolinite (K-Cyst), about 500°C due to dehydroxylation of kaolinite, while a less sharp drop for raw kaolinite, this may indicate there is a slight decrease in thermal stability of modified kaolinite (K-Cyst).The thermogram showed the residual mass percentage at 800°C equal to 89.07%, and 83.54%, for raw kaolinite and modified kaolinite (K-Cyst), respectively. This indicates less thermal stability, less in organic constituents for modified kaolinite (K-Cyst) due to the presence of organic amino acid (Cyst). A similar behavior was observed for modified kaolinite with methionine (K-Meth) with a residual mass of 81.23%.The thermogram in a previous study for raw kaolinite from Batn El-Ghoul area (Jordan) showed small drop at $T < 180$°C (little weight loss) which represent the release of the absorbed water in pores and on the surface of kaolinite, and sharp drop at 400°C–600°C, which is due to the release of interlayer structural water in kaolinite. The temperature at which kaolinite loses its crystal structure is based on the onset temperature is about 430°C while the maximum rate of weight loss was at a temperature of 480°C [27]. The thermogram in a previous study showed the residual mass percentage at 800°C equal to 85.71%, and 76.56%, for raw kaolinite (from brazil) and modified kaolinite (Cd-cysteine complexes by kaolinite), respectively. The thermogram showed a small drop at $T < 100$ for modified kaolinite (Cd-Cyst-K) and a sharp drop between (150°C–250°C) for modified kaolinite (Cd-Cyst-K) due to elimination of OH and COOH group, and a sharp drop refer to dehydroxylation reaction at 500°C for modified kaolinite (Cd-Cyst-K) [26].

### *3.5. Rate of metal ion uptake by the modified kaolinite*

Adsorption of metal ions by the modified kaolinite K-Meth and K-Cyst was determined as mentioned earlier for a contact time of 30 min to 48 h, at pH = 5 and $T = 25$°C, and initial concentration of 100 mg L$^{-1}$. A 1.000 g ± 0.1 mg of the K-Meth or K-Cyst was added to 50 ml of 100 mg L$^{-1}$ concentration of metal ion solution at pH = 5, the solution was mechanically shaken for various contact time of 30 min to 48 h at 25°C, the mixture was filtered and the amount of metal ion remaining in the filtrate solution was determined by AAS. The results of these experiments are shown in Fig. 6.

It can be seen that the uptake of metal ions onto K-Cyst increases with time until complete saturation was reached (plateau) after 24 h of contact with percent uptake: 90.2%, 66.5%, and 45.8% of Pb(II), Cd(II), Zn(II) ions, respectively. While for K-Meth, the percent uptake: 90.2%, 24.2%, and 20.1% were obtained for Pb(II), Cd(II) and Zn(II) ions, respectively.

This could be attributed to:

1. The negatively charged siloxane group in kaolinite structure [2].
2. Variable charged sites on silanol and aluminol edges. The binding of Pb(II), Cd(II), Zn(II) ions on kaolinite could be described by ion exchange at the permanently charged sites on the silanol faces (SiOH), and complexation to aluminol (AlOH) and silanol groups, which occur at the crystal edges, [28].
3. The presence of methionine and cysteine in the kaolinite structure [26] supported the adsorption process by decreasing the order of kaolinite structure (increase surface area) as shown from SEM, and increasing the negative charge, since FTIR showed that the kaolinite/Meth or kaolinite/Cyst interaction occurs through the ammonium group(–NH$^{3+}$). It was found that the Cyst is mainly present as (–N H$_2$CH (CH$_2$SH) COO$^-$) in acidic and neutral aqueous solutions [29], whereas the deprotonated form (NH$_2$CH (CH$_2$S$^-$) COO$^-$) links metal ions in alkaline solution, but the amount of dissociated –SH group is very low at pH = 5 [26]. Thus we can suppose that the metal ion bind to COO$^-$ on Cyst structure. The order of metal ion uptake was found as follows; Pb(II) > Cd(II) > Zn(II). In general, the most important factors that influence the relative selectivity of metal ions in solution are their valence and ionic radii [30]. The ionic radius for Pb(II), Cd(II)and Zn(II) are 1.33A°, 1.09 A°, and 0.88 A° respectively [31]. From comparison of the three elements studied, Pb(II) ion has the largest ionic radius, if metal adsorption on the kaolinite clay were entirely electrostatic, ions of higher ionic radius should be adsorbed more strongly. The selectivity sequence observed that Pb(II) adsorbed more than Cd(II) more than Zn(II). Another factor that has an effect is the hydration energy, the hydration energy values decreases as the ionic radius increases [32]. Increasing the hydration energy values are due to the increase in the hydration shell, this makes it more difficult for metal ions to discharge the water of hydration. The formation of aqua complex $[M(OH_2)_m]^{n+}$ takes place (where $m$ is six), the aqua complex, having m H$_2$O molecules surrounding the central metal ion, has a definite structure and the cloud of water molecules (hydration shell) has another geometry than the rest of the water. A stronger hydration shell will surround small metal ion, which has smaller ionic radius, than the metal ion with larger radius, so the adsorptivity of an ion of larger radius is higher than small radius ion. Also K-Meth is highly selective to soft Pb(II) since there is large difference in uptake in comparison with Cd(II) and Zn(II) due to the presence of soft S atom in CH$_3$–S–C in methionine.

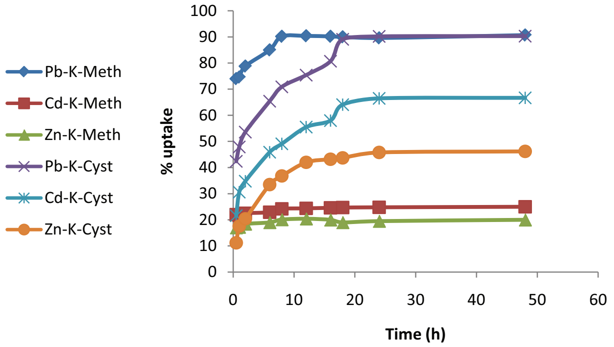

Fig. 6. Metals uptake as a function of contact time for K-Meth and K-Cyst, at pH = 5, $T$ = 25°C, and initial concentration of 100 mg $L^{-1}$.

### 3.6. pH-dependence of metal ion sorption by the modified kaolinite K-Meth and K-Cyst

The effect of varying pH values on metals uptake was studied using batch procedure in the range of pH from 1–5 for a fixed contact time of 24 h (Fig. 7). The sorption quantity of metal ions increases slightly until pH = 5 because the surface becomes negatively charged favoring higher metal uptake, where the sorption capacity reaches its optimal value and a plateau is obtained. Fig. 7 shows that the K-Meth and K-Cyst interaction toward Pb(II), Cd(II) and Zn(II) ions reach maximum at pH = 5.It is obvious that the higher the initial pH value the larger the adsorption capacity. At very low pH, the concentrations of protons exceed that of the metal ions several times and the surface is most likely covered with $H_3O^+$ ions, then the metal ions can hardly compete with protons for the binding sites on the adsorbents. As pH increases, the uptake increases which can be explained on the basis of a decrease in competition between protons and metal species for the surface sites, and by the decrease in positive surface charge, which results in a lower columbic repulsion of the adsorbing metal ion, then more and more protons leave the clay mineral surface. So the adsorbed methionine and cysteine makes the sites available to the metal ions which now increasingly bind to clay surface through a mechanism similar to that of exchange interactions ($H_3O^+$/metal ion(II)) [33].

### 3.7. Dose dependence of metal ion sorption by the modified kaolinite

The effect of varying dose of K-Cyst or K-Meth on metals uptake was studied using batch technique in the range of doses (0.1–1.0 g) for a fixed contact time of 24 h, pH = 5 and $T$ = 25°C (Fig. 8). The sorption quantity of metal ions increases slightly until they reach the maximum sorption capacity saturation, the optimal value and a plateau was obtained. The dose of K-Cyst in uptake experiments was selected to be 0.3 g ± 0.1 mg for Pb(II), 0.4 g ± 0.1 mg for Zn(II), and 0.6 g ± 0.1 mg for Cd(II) was selected as. However, the mass of K-Meth uptake experiments was selected to be 1.0 g ± 0.1 mg for Pb(II) and 0.8 g ± 0.1 mg for Zn(II) and Cd(II). The optimum mass of polyphosphate modified kaolinite for Pb(II) and Zn(II) was found to be 0.3 g, and for Cd(II) is 0.6 g [19].

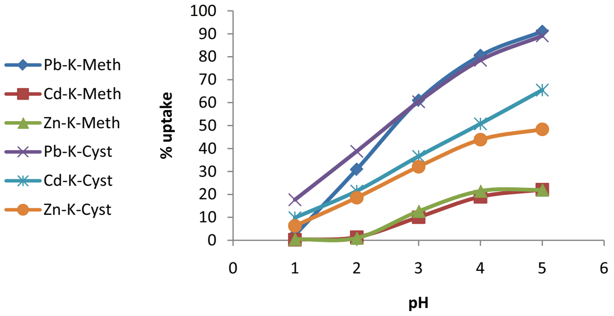

Fig. 7. Metal uptake as a function of pH at 25°C and 24 h and initial concentration of 100 mg $L^{-1}$.

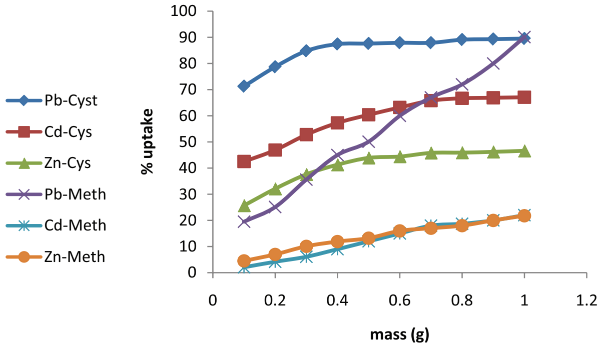

Fig. 8. Metal uptake as a function of dose of K-Cyst or K-Meth at 25°C, pH = 5, 24 h, and initial concentration of 100 mg $L^{-1}$.

### 3.8. Adsorption isotherms of the K-Meth and K-Cyst

The adsorption isotherms were determined for Pb(II), Zn(II), and Cd(II) at different pH values (3.0, 4.0, and 5.0) and different temperatures (25°C, 35°C, 45°C) in the range of concentrations from 10–120 mg $L^{-1}$. Adsorption isotherms for Pb(II) as an example (Fig. 9), linearized forms of Langmuir (Fig. 10), Freundlich (Fig. 11), and Dubinin-Radushkevich (Fig. 12) are shown. Their analyzed data are presented in Tables 3–5, respectively.

The adsorption of metal ions on modified kaolinite fitted Langmuir model shown in Table 3 and Fig. 10, and it had an excellent linearity ($R^2 > 0.90$). From Table 1, the values of $q_m$ which related to adsorption capacity indicated that increasing of temperatures and pH lead to increase in the adsorption capacities of modified kaolinite for all metal ions. These results showed the following trend Pb(II) > Cd(II) > Zn(II). Modified kaolinite with orthophosphate enhanced adsorption of Pb and Cd ions from aqueous solutions of these metal ions [2]. Adsorption data were fitted against Langmuir, they found that the values of $q_m$ at 0.01 M of $NaNO_3$ for Pb(II) were 17.89 mg $g^{-1}$, and for Cd(II) was 8.39 mg $g^{-1}$ which are very close to our values for K-Cyst and less than for K-Meth. Besides that, they calculated $K_L$ values for both metal ions and were equal to 0.0437 L $g^{-1}$ for Pb(II) and 0.0290 L $^{-1}$g for Cd(II), which are very close to the values in this study (Table 3). This indicates that the modified kaolinite K-Cyst adsorbed heavy metals from aqueous solution similar to the modified kaolinite with orthophosphate but better than K-Meth.

The potential application of modified kaolinite with humic acid (KTD-K) was determined as an adsorbent for the

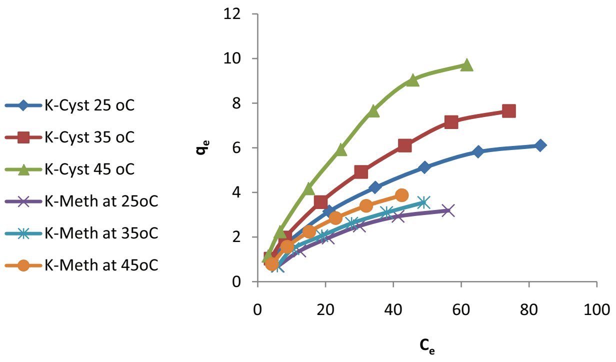

Fig. 9. Plots of adsorption isotherms of Pb(II) with K-Meth or K-Cyst, at pH = 3 and at 25°C, 35°C and 45°C.

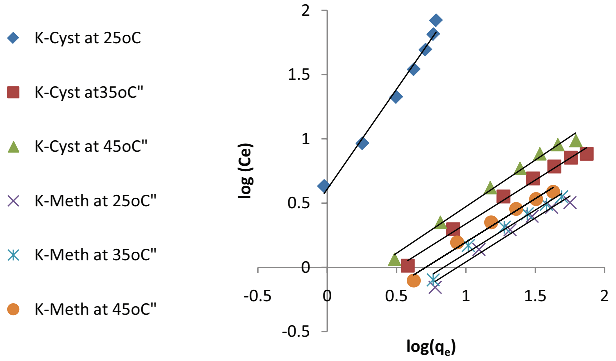

Fig. 11. Plots of linearized Freundlich of Pb(II) with K-Cyst or K-Meth, at pH = 3 and at 25°C, 35°C and 45°C.

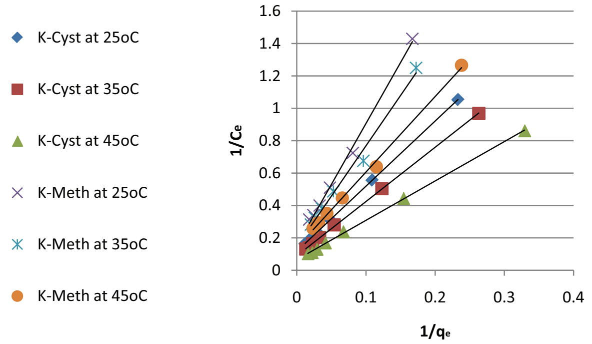

Fig. 10. Plots of linearized Langmuir of Pb(II) with K-Cyst or K-Meth, at pH = 3 and at 25°C, 35°C and 45°C.

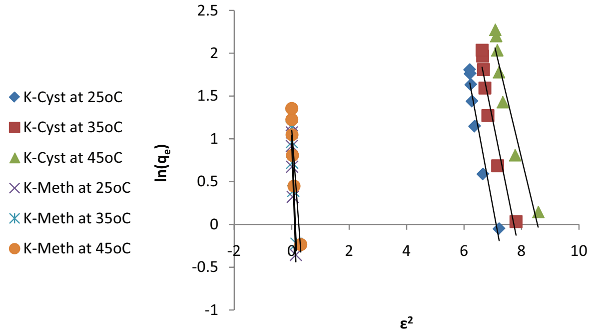

Fig. 12. Plots of Dubinin-Radushkevich of Pb(II) with K-Cyst or K-Meth, at pH = 3 and at 25°C, 35°C and 45°C.

Table 3
$R^2$, $q_m$ and $K_L$ values obtained from the Langmuir plots of Pb(II), Zn(II) and Cd(II) at pH = 3.0, 4.0 and 5.0 with K-Cyst/ K-Meth

| $T$(°C) | $R^2$ | $q_m$ (mg g$^{-1}$) | $K_L$ (L mg$^{-1}$) | $R^2$ | $q_m$ (mg g$^{-1}$) | $K_L$ (L mg$^{-1}$) | $R^2$ | $q_m$ (mg g$^{-1}$) | $K_L$ (L mg$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| Pb(II) | pH = 3.0 | | | pH = 4.0 | | | pH = 5.0 | | |
| 25 | 0.9997 | 8.54 | 0.0291 | 0.9994 | 16.81 | 0.0287 | 0.9996 | 27.86 | 0.0441 |
| | 0.9985 | 6.24 | 0.0368 | 0.9997 | 11.25 | 0.1191 | 0.9987 | 2.36 | 0.0118 |
| 35 | 0.9996 | 11.20 | 0.0267 | 0.9994 | 21.79 | 0.0346 | 0.9989 | 29.50 | 0.0542 |
| | 1.000 | 7.68 | 0.0481 | 0.9985 | 12.95 | 0.2667 | 0.9978 | 2.64 | 0.0131 |
| 45 | 0.9994 | 15.38 | 0.0267 | 0.9997 | 23.98 | 0.0405 | 0.9992 | 35.84 | 0.0622 |
| | 0.9905 | 8.97 | 0.0515 | 0.9933 | 14.06 | 0.4175 | 0.9985 | 2.66 | 0.0163 |
| Zn(II) | pH = 3.0 | | | pH = 4.0 | | | pH = 5.0 | | |
| 25 | 0.9981 | 7.62 | 0.0084 | 0.9988 | 9.51 | 0.0102 | 0.9985 | 7.35 | 0.0274 |
| | 0.9987 | 1.25 | 0.0139 | 0.9985 | 0.79 | 0.0634 | 0.9978 | 1.80 | 0.0250 |
| 35 | 0.9947 | 6.17 | 0.0178 | 0.9971 | 6.29 | 0.0281 | 0.9869 | 5.71 | 0.0761 |
| | 0.9958 | 1.76 | 0.0399 | 0.9947 | 1.74 | 0.0306 | 0.9917 | 1.59 | 0.0465 |
| 45 | 0.9984 | 6.30 | 0.0242 | 0.9998 | 7.35 | 0.0389 | 0.9972 | 6.36 | 0.1379 |
| | 0.9993 | 2.26 | 0.0200 | 0.9987 | 1.75 | 0.0532 | 0.9930 | 3.02 | 0.0254 |
| Cd(II) | pH = 3.0 | | | pH = 4.0 | | | pH = 5.0 | | |
| 25 | 0.9999 | 3.29 | 0.0143 | 0.9994 | 5.45 | 0.0243 | 0.9984 | 14.81 | 0.0132 |
| | 0.9987 | 2.36 | 0.0118 | 0.9964 | 2.16 | 0.0196 | 0.9983 | 2.56 | 0.0205 |
| 35 | 0.9989 | 3.42 | 0.0236 | 0.9996 | 7.33 | 0.0261 | 0.9985 | 18.52 | 0.0127 |
| | 0.9978 | 2.64 | 0.0131 | 0.9970 | 2.70 | 0.0195 | 0.9968 | 2.56 | 0.0246 |
| 45 | 0.9997 | 6.74 | 0.0137 | 0.9997 | 8.43 | 0.0260 | 0.9974 | 23.36 | 0.0125 |
| | 0.9985 | 2.66 | 0.0163 | 0.9962 | 3.75 | 0.0153 | 0.9954 | 2.51 | 0.0596 |

Table 4
$R^2$, $K_F$ and $n$ values obtained from the Freundlich plots of Pb(II), Zn(II) and Cd(II) at pH = 3.0, 4.0 and 5.0with K-Cyst/ K-Meth

| $T$(°C) | $R^2$ | $K_F$ | $n$ | $R^2$ | $K_F$ | $n$ | $R^2$ | $K_F$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|
| Pb(II) | pH = 3.0 | | | pH = 4.0 | | | pH = 5.0 | | |
| 25 | 0.9855 | 0.4185 | 1.579 | 0.9909 | 0.6366 | 1.370 | 0.9887 | 1.3301 | 1.287 |
| | 0.9748 | 0.2280 | 1.461 | 0.9825 | 0.3187 | 1.455 | 0.9847 | 1.0380 | 1.866 |
| 35 | 0.9908 | 0.4549 | 1.468 | 0.9890 | 0.9005 | 1.327 | 0.9918 | 1.6233 | 1.260 |
| | 0.9801 | 0.2718 | 1.483 | 0.9293 | 0.5142 | 1.377 | 0.9686 | 1.5970 | 1.694 |
| 45 | 0.9912 | 0.5607 | 1.381 | 0.9814 | 1.1437 | 1.353 | 0.9903 | 2.1667 | 1.237 |
| | 0.9825 | 0.3303 | 1.476 | 0.9815 | 0.5357 | 1.365 | 0.9384 | 2.4030 | 2.293 |
| Zn(II) | pH = 3.0 | | | pH = 4.0 | | | pH = 5.0 | | |
| 25 | 0.9971 | 0.0864 | 1.203 | 0.9946 | 0.1424 | 1.270 | 0.9835 | 0.3298 | 1.536 |
| | 0.9851 | 0.0442 | 1.624 | 0.9426 | 0.1770 | 3.410 | 0.9632 | 0.1291 | 1.963 |
| 35 | 0.9884 | 0.1885 | 1.455 | 0.9922 | 0.2783 | 1.508 | 0.9830 | 0.6163 | 1.880 |
| | 0.9446 | 0.1187 | 2.851 | 0.9552 | 0.2001 | 2.128 | 0.9586 | 0.2280 | 2.564 |
| 45 | 0.9804 | 0.2697 | 1.560 | 0.9781 | 0.4610 | 1.653 | 0.9643 | 1.0814 | 2.287 |
| | 0.9762 | 0.1427 | 1.739 | 0.9481 | 0.2782 | 2.658 | 0.9613 | 0.2438 | 1.846 |
| Cd(II) | pH = 3.0 | | | pH = 4.0 | | | pH = 5.0 | | |
| 25 | 0.9895 | 0.0803 | 1.404 | 0.9863 | 0.2120 | 1.483 | 0.9848 | 0.2630 | 1.256 |
| | 0.9826 | 0.0608 | 1.484 | 0.9753 | 0.1095 | 1.757 | 0.9793 | 0.1541 | 1.696 |
| 35 | 0.9643 | 0.1580 | 1.636 | 0.9894 | 0.2963 | 1.400 | 0.9875 | 0.3042 | 1.229 |
| | 0.9745 | 0.0733 | 1.523 | 0.9738 | 0.1299 | 1.732 | 0.9664 | 0.1621 | 1.836 |
| 45 | 0.9944 | 0.1318 | 1.290 | 0.9887 | 0.2993 | 1.375 | 0.9875 | 0.3628 | 1.208 |
| | 0.9780 | 0.0972 | 1.605 | 0.9712 | 0.1561 | 1.522 | 0.9447 | 0.3882 | 2.540 |

removal of Pb(II), Zn(II)and Cd(II)ions from aqueous solutions [34]. The adsorption isotherms of all three metal ions followed well Langmuir equation. The Langmuir constants were calculated at different temperatures. For Pb(II), the $K_L$ values were equal to 0.33, 0.36 and 1.30 L mg$^{-1}$ at 25°C, 35°C and 45°C, respectively. While for Cd(II), $K_L$ values were equal to 0.039, 0.043 and 0.049 L mg$^{-1}$, and for Zn(II) were 0.029, 0.035 and 0.038 L mg$^{-1}$, at 25°C, 35°C and 45°C, respectively. KTD-K was found to remove heavy metal ions efficiently from aqueous solutions than K-Cyst and K-Meth with selectivity in the order of Pb(II) > Cd(II) > Zn(II). The $q_m$ values were found to be 9.89, 9.62 and 9.23 mg g$^{-1}$, for Pb(II), Cd(II) and Zn(II), respectively [34] which are smaller than the values of $q_m$ for K-Cyst and larger than the values of $q_m$ for K-Meth, indicates that the modified kaolinite with K-Cyst adsorbed Pb(II), and Cd(II) from aqueous solution better than the humic acid modified kaolinite. The potential of sodium polyphosphate modified kaolinite was determined as an adsorbent for the removal of Pb(II), Zn(II)and Cd(II) ions from aqueous solutions [19]. The Langmuir constants were calculated at different temperatures. For Pb(II) the $K_L$ values were equal to 0.062, 0.106 and 0.111 L mg$^{-1}$, for Zn(II), $K_L$ values were equal to 0.032, 0.044 and 0.044 L mg$^{-1}$, and for Cd(II) were 0.014, 0.015 and 0.016 L mg$^{-1}$, at 25°C, 35°C and 45°C, respectively. The $q_m$ values were found to be 25.13, 22.83 and 10.37mg g$^{-1}$ for Pb(II), Zn(II) and Cd(II), respectively, which are close to the values of $q_m$ in this study for Pb(II), indicating that the K-Cyst adsorbed Pb(II) from aqueous solution better than the polyphosphate–kaolinite and K-Meth. The potential of kaolinite clay was determined as an adsorbent for the removal of lead ions from aqueous solutions [35]. The Langmuir constants were calculated at different temperatures. For Pb(II) the $K_L$ values were equal to 0.0132, 0.08482 and 0.40625 L mg$^{-1}$, at 25°C, 35°C and 45°C, respectively, which are lower to the $K_L$ values in this study, indicating that the K-Cyst and K-Meth adsorbed Pb(II) from aqueous solution better than the kaolinite clay. The high values of $K_L$ which are listed in Table 3 indicate a higher ability of modified kaolinite to adsorb lead ions and to form stable complexes. The increased values of $K_L$ with increasing temperature, represents evidence that a chemical interaction between lead ions and modified kaolinite occurs.

The adsorption of metal ions on the two modified kaolinite fitted Freundlich model as shown in Table 4 and Fig. 10, it has an excellent linearity ($R^2 > 0.90$). When the experimental values for the metal ions were fitted to the Freundlich model, the following observations were obtained. There is an indication that some other adsorption sites were non–uniform and nonspecific in nature. It was in conformity with the existence of different types of possible adsorption sites on kaolinite modified surface with cysteine and methionine with considerable difference in energy if the site was on an edge and surface or was located in a defect position. This agrees with the hypothesis of Freundlich model [33]. The $K_F$ parameter is related to adsorption capacity, and the Freundlich constant $n$ indicates degree of favorability of adsorption, the adsorption coefficients ($K_F$, $n$) agreed well with the condition supporting favorable adsorption. From the Freundlich model, the better adsorptions have the higher $K_F$ value, so K-Cyst has better adsorption capacity than K-Meth.

Table 5
Dubinin–Radushkevich (D–R) isotherm parameters of Pb(II), Zn(II) and Cd(II) at pH = 3.0, 4.0 and 5.0 with K-Cyst/ K-Meth

| $T$(°C) | $R^2$ | β (mol² (kJ²)⁻¹) | $q_m$/ (mg g⁻¹) | $E$ (kJ mol⁻¹) | $R^2$ | β (mol² (kJ²)⁻¹) | $q_m$/ (mg g⁻¹) | $E$ (kJ mol⁻¹) | $R^2$ | β (mol² (kJ²)⁻¹) | $q_m$/ (mg g⁻¹) | $E$ (kJ mol⁻¹) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pb(II) | pH = 3.0 | | | | pH = 4.0 | | | | pH = 5.0 | | | |
| 25 | 0.9754 | 1.1773 | 8482 | 0.6517 | 0.9618 | 0.9336 | 3220 | 0.7318 | 0.9606 | 0.5273 | 382 | 0.9738 |
| | 0.8884 | 9.6230 | 2.627 | 0.2280 | 0.8654 | 5.1312 | 3.026 | 0.3121 | 0.8748 | 0.536 | 4.133 | 0.9658 |
| 35 | 0.9666 | 1.1143 | 11295 | 0.6699 | 0.9609 | 0.7001 | 1256 | 0.8451 | 0.9594 | 0.4305 | 269 | 1.0777 |
| | 0.8979 | 8.2230 | 2.875 | 0.2466 | 0.9072 | 2.1066 | 3.775 | 0.4871 | 0.9020 | 0.2259 | 4.287 | 1.4880 |
| 45 | 0.9629 | 0.9591 | 7876 | 0.7220 | 0.9685 | 0.5727 | 752 | 0.9344 | 0.9664 | 0.3382 | 186 | 1.2160 |
| | 0.8784 | 4.5060 | 3.133 | 0.3331 | 0.8639 | 1.6291 | 3.728 | 0.5540 | 0.8962 | 0.0704 | 4.293 | 2.6650 |
| Zn(II) | pH = 3.0 | | | | pH = 4.0 | | | | pH = 5.0 | | | |
| 25 | 0.9633 | 2.2646 | 3840450 | 0.4699 | 0.9599 | 1.8305 | 330943 | 0.5226 | 0.9672 | 1.1577 | 6186 | 0.6572 |
| | 0.9063 | 50.1500 | 0.654 | 0.0998 | 0.9553 | 20.4600 | 0.637 | 0.1563 | 0.9294 | 29.3600 | 1.131 | 0.1305 |
| 35 | 0.9480 | 1.4724 | 58906 | 0.5828 | 0.9569 | 1.2303 | 14877 | 0.6375 | 0.9684 | 0.6562 | 394 | 0.8729 |
| | 0.9453 | 19.9000 | 0.855 | 0.1585 | 0.9308 | 23.7000 | 1.169 | 0.1452 | 0.9145 | 17.2400 | 1.610 | 0.1703 |
| 45 | 0.9688 | 1.1980 | 18372 | 0.6460 | 0.9831 | 0.8692 | 2413 | 0.7585 | 0.9688 | 0.3507 | 69 | 1.1940 |
| | 0.9011 | 27.0300 | 1.280 | 0.1360 | 0.9381 | 13.2100 | 1.3380 | 0.1945 | 0.9246 | 18.1400 | 1.776 | 0.1660 |
| Cd(II) | pH = 3.0 | | | | pH = 4.0 | | | | pH = 5.0 | | | |
| 25 | 0.9791 | 1.8613 | 178706 | 0.5183 | 0.9731 | 1.2014 | 5669 | 0.6451 | 0.9761 | 1.1125 | 5175 | 0.6704 |
| | 0.9035 | 44.5300 | 1.090 | 0.1060 | 0.9162 | 32.2500 | 1.224 | 0.1245 | 0.8828 | 28.2100 | 1.431 | 0.1331 |
| 35 | 0.9968 | 1.2939 | 11223 | 0.6216 | 0.9664 | 1.01800 | 3656 | 0.7008 | 0.9754 | 0.9772 | 3758 | 0.7153 |
| | 0.9088 | 38.1100 | 1.199 | 0.1145 | 0.9069 | 26.2200 | 1.449 | 0.1381 | 0.9214 | 22.6200 | 1.553 | 0.1487 |
| 45 | 0.9654 | 1.5011 | 127159 | 0.5771 | 0.9664 | 0.9257 | 3263 | 0.7349 | 0.9737 | 0.8379 | 2383 | 0.7725 |
| | 0.9041 | 29.8700 | 1.342 | 0.1293 | 0.9118 | 24.6900 | 1.826 | 0.1423 | 0.9351 | 8.5730 | 1.881 | 0.2415 |

As shown in Table 4, $K_F$ values increase with increasing both temperature and pH for all metal ions. These results agree with that obtained in Table 3 of metal ions uptake with the same trend (Pb(II) > Cd(II) > Zn(II)). The values of $n$ represent the degree of favorability of adsorption. The value of $n$ was greater than one, indicating that the adsorption was favorable [36]. Modified kaolinite with aluminum sulphate was used to remove Pb(II) from aqueous solution [33]. The results showed that the amount of Pb(II) adsorbed onto modified kaolinite is 20 mg g$^{-1}$ under the optimized condition. In addition, the Freundlich model was used to describe equilibrium isotherm. The $n$ value from Freundlich model was 3.56.

The $R^2$ values shown in Table 5 and Fig. 12 are greater than 0.90, indicating that D–R model can describe the adsorption data very well, which means that the adsorption on both homogeneous and heterogeneous surfaces. The magnitude of E from D–R isotherm can give a good idea about the overall mechanism of the adsorption. As illustrated in Table 5, the highest value of $E$ is for Pb(II) which is greater than Cd(II) > Zn(II) and for K-Cyst than K-Meth. All $E$ values are <8.00 kJ mol$^{-1}$, this indicate that physical forces dominate the adsorption process [37].

### *3.9. Thermodynamics of adsorption of K-Cyst and K-Meth*

Thermodynamic functions can be determined using the distribution coefficient, $K_d = q_e/C_e$ which depends on temperature. The change in free energy (Δ$G$°), enthalpy (Δ$H$°) and entropy (Δ$S$°) associated with the adsorption process were calculated by using the following equations:

$$\Delta G° = \Delta H° - T\Delta S° \tag{9}$$

where $R$ is the universal gas constant (8.314 J mol$^{-1}$ K) and $T$ is temperature (K).

$$\ln K_d = \Delta S°/\mathrm{R} - \Delta H°/RT \tag{10}$$

According to the above equation, Δ$H$° and Δ$S$° functions (Table 6) can be obtained from the slope and intercept of the plot of ln$K_d$ vs. 1/$T$ yields, respectively. The adsorption process was found to be endothermic for Pb(II), Cd(II) and Zn(II) by K-Cyst and K-Meth, because Δ$H$° has positive values for the adsorption of metals ions, which means that the dehydration energy is greater than the adsorption energy. The positive entropy values for metals ions may be due to some structural changes in the adsorbate and adsorbent during the adsorption process from aqueous solution onto the adsorbent, such as the dehydration of the metal ions upon adsorption. In addition, positive value of Δ$S$° indicates the increasing randomness at the solid–liquid interface during the adsorption of metals ions on the adsorbent. The free energy change Δ$G$° calculated for adsorption of metals ion decreases as the temperature and pH increase, indicates that the interactions are thermodynamically favorable. From free energy change Δ$G$° calculated for adsorption, the spontaneity of metals ions have the following order: Pb(II) > Cd(II) > Zn(II), and the spontaneity for K-Cyst is higher than for K-Meth [36]. The thermodynamic functions of sodium polyphosphate modified kaolinite was determined as an adsorbent for the removal of Pb(II), Zn(II) and Cd(II) ions from aqueous solutions [19]. The adsorption reaction was found to have positive values of both Δ$H$° and Δ$S$° in a similar way to this work. The interactions are thermodynamically favorable and are accompanied by decrease in Gibbs energy as temperature and pH increased. The spontaneity of metals ions have the following order: Pb(II) > Zn(II) > Cd(II).The thermodynamic functions for the removal of Pb(II)ions from aqueous solutions by kaolinite clay as adsorbent was determined [35]. The adsorption has positive values for both Δ$H$° (135.2 kJ mole$^{-1}$) and Δ$S$° (417 J mol$^{-1}$.K) at 25°C, which are higher than our values, Table 6. The interactions are thermodynamically favorable and are accompanied by decrease in Gibbs energy in modified kaolinite compared with kaolinite clay. Indicating that the K-Cyst and K-Meth adsorbed Pb(II) from aqueous solution better than the kaolinite clay.

Table 6
Thermodynamic functions for the adsorption of 100 mg L$^{-1}$ Pb(II), Cd(II) and Zn(II) onto K-Cyst/ K-Meth at 298 K

| Metals | pH | Δ$H$° (kJ mol$^{-1}$) | Δ$S$° (J mol.K$^{-1}$) | Δ$G$° (kJ mol$^{-1}$) |
|---|---|---|---|---|
| Pb(II) | 3 | 31.29 | 84.71 | 6.04 |
| | | 15.95 | 31.32 | 6.62 |
| | 4 | 29.87 | 88.74 | 3.42 |
| | | 35.21 | 99.39 | 5.59 |
| | 5 | 25.32 | 82.45 | 0.75 |
| | | 24.08 | 75.49 | 1.58 |
| Zn(II) | 3 | 12.17 | 14.42 | 7.87 |
| | | 32.38 | 67.85 | 12.16 |
| | 4 | 15.54 | 28.41 | 7.08 |
| | | 36.33 | 81.66 | 12.00 |
| | 5 | 11.65 | 17.82 | 6.34 |
| | | 25.06 | 48.43 | 10.63 |
| Cd(II) | 3 | 33.95 | 81.63 | 9.63 |
| | | 10.08 | –1.41 | 10.50 |
| | 4 | 26.54 | 65.41 | 7.05 |
| | | 20.40 | 34.22 | 10.20 |
| | 5 | 17.83 | 42.50 | 5.16 |
| | | 50.21 | 133.30 | 10.49 |

### *3.10. Column experiments*

#### *3.10.1. Metal ion uptake by K-Cyst and K-Meth*

The investigation of metal ion uptake by K-Cyst and K-Meth using column experiments for Pb(II), Zn(II), and Cd(II) were determined at pH = 5, for solutions with initial concentration of 100 mg L$^{-1}$, at 25°C, and a flow rate of 0.5 mL min$^{-1}$. The results are expressed as percent metal uptake by the column and are represented in Table 7 and Fig. 13.

It can be seen that the uptake capacities of the raw kaolinite, K-Cyst and K-Meth with the metal ions fall in the order: Pb(II) > Cd(II) > Zn(II).This result is in compliance with the order found in batch experiments. The values of percentage metal ion uptake in this experiment are however; smaller than those obtained in batch experiments, this result was

Table 7
Percent of metal ion uptake by the K-Cyst/K-Meth using column experiment

| Metal ion (II) | Initial concentration (mg L$^{-1}$) | Final concentration (mg L$^{-1}$) | Loaded concentration (mg L$^{-1}$) | % Uptake |
|---|---|---|---|---|
| Pb | 100 | 22.5 | 77.5 | 77.5 |
| | | 11.1 | 89.9 | 89.9 |
| Cd | 100 | 47.6 | 52.4 | 52.4 |
| | | 80.8 | 19.2 | 19.2 |
| Zn | 100 | 66.8 | 33.2 | 33.2 |
| | | 81.9 | 18.1 | 18.1 |

Table 8
Desorption of metal ions from the K-Cyst/K-Meth using 0.1M $HNO_3$ as eluting agent

| Eluting agent 0.1 M $HNO_3$ | % Recovery (first portion) | % Recovery (second portion) | % Recovery (third portion) | % Recovery (fourth portion) | % Recovery (fifth portion) | % Cumulative recovery |
|---|---|---|---|---|---|---|
| Pb (II) | 85.45 | 3.25 | 1.03 | 0.46 | 0.13 | 90.32 |
| | 85.30 | 3.25 | 1.03 | 0.48 | 0.11 | 90.17 |
| Cd (II) | 81.92 | 2.43 | 0.96 | 0.28 | 0.18 | 85.77 |
| | 81.92 | 2.43 | 0.96 | 0.28 | 0.18 | 85.77 |
| Zn (II) | 80.33 | 2.08 | 0.77 | 0.17 | 0.10 | 83.45 |
| | 80.33 | 2.08 | 0.77 | 0.17 | 0.10 | 83.45 |

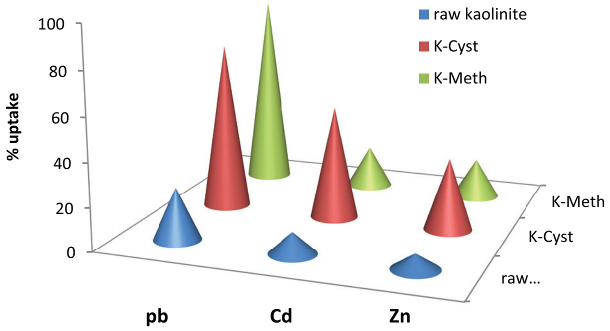

Fig. 13. Comparing the percentage uptake by raw kaolinite, K-Cyst and K-Meth.

expected since there is no mechanical shaking of the solution and a lower contact time as in the batch experiments.

### *3.10.2. Desorption studies*

The eluting agent 0.1M HNO3 was used for removal of metal ions and regeneration of the K-Cyst and K-Meth, keeping the flow rate of the elution at 0.5 mL min–1. The eluate was collected in five portions; 10 mL for each portion; and the concentration of desorbed metal ions were then determined by AAS. The results are expressed as percent recovery and presented in Table 8.

It can be noticed that a high desorption ability for the three metal ions was observed using 0.1 M HNO3 as eluting agent, where good percent recoveries were achieved for all three metals.

The sorption experiment was repeated for the regenerated K-Cyst and K-Meth under the same condition for column experiment, this result is in compliance with the order found in sorption by column experiments. The values of percentage metal ion uptake in this experiment are however; smaller than those obtained in the first sorption by column experiments, this result was expected since the regeneration of K-Cyst and K-Meth in desorption experiment was not fully completed. So these two modified kaolinite can be used for preconcentration and solid disposal of heavy metal ions.

## 4. Conclusions

Modification of Jordanian kaolinite clay by cysteine (K-Cyst) or methionine (K-Meth) was achieved and characterized using different techniques. The investigations demonstrated that the K-Cyst has high metal-ion uptake capacity for Pb(II) than K-Meth, and the extent of metal-ion uptake for both followed the order: Pb(II) > Cd(II) > Zn(II) at all pH values and temperatures, in batch and column experiments. Desorption by 0.1 M $HNO_3$ as eluting agent was very effective, so the modified forms can be reused several times.

## Symbols

$C_o$ – Initial metal concentration, mg L$^{-1}$
$C_e$ – Residual concentration of the metal ion in solution at equilibrium, mg L$^{-1}$
$V$ – Volume of solution, L
$M$ – Mass of K-Meth or K-Cyst, g
$K_L$ – Langmuir affinity constant, L mg$^{-1}$
$q_m$ – Langmuir monolayer adsorption capacity, mg g$^{-1}$
$q_e$ – Equilibrium amount of metal ion adsorbed per unit mass of adsorbent, mg g$^{-1}$
$q_t$ – Amount of metal ions adsorbed, mg g$^{-1}$ at contact time *t*
$k_2$ – Second order reaction constant, g mg·min$^{-1}$

## References

[1] X. Quintelas, Z. Rocha, B. Silva, B. Fonseca, H. Figueiredo, T. Tavares, Removal of Cd(II), Cr(VI), Fe(III) and Ni(II) from aqueous solutions by an E. coli biofilm supported on kaolin, Chem. Eng. J., 149 (2009) 319–324.

[2] K.O. Adebowale, I.E. Unuabonah, B.I. Olu-Owolabi, The effect of some operating variables on the adsorption of lead and cadmium ions on kaolinite clay, J. Hazard. Mater., 134 (2006) 130–139.

[3] S. Chang, The biosorption of heavy metals from aqueous solution by *Spirogyra* and *Cladophora* Filamentous macro algae, Bioresour. technol., 102 (2011) 5297–5304.

[4] B. Volesky, Detoxification of metal-bearing effluents: biosorption for the next century, Hydrometallurgy, 95 (2001) 203–216.

[5] C.O. Ijagbemi, M.H. Baek, D.S. Kim, Montmorillonite surface properties and sorption characteristics for heavy metal removal from aqueous solutions, J. Hazard. Mater., 166 (2009) 538–546.

[6] H.J. Wang, A.L. Zhou, F. Peng, H. Yu, L.F. Chen, Adsorption characteristic of acidified carbon nanotubes for heavy metal Pb(II) in aqueous solution, Mater. Sci. Eng., A, 466 (2007) 201–206.

[7] A.R. Kul, H. Koyuncu, Adsorption of Pb(II) ions from aqueous solution by native and activated bentonite: kinetic, equilibrium and thermodynamic study, J. Hazard. Mater., 179 (2010) 332–339.

[8] D. Mohan, Jr. Pittman, M. Bricka, F. Smith, B. Yancey, J. Mohammad, P.H. Steele, M.F. Alexandre-Franco, V. Gómez-Serrano, H. Gong, Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production, J. Colloid. Interface. Sci., 310 (2007) 57–73.

[9] A.A. Emama, L.F.M. Ismaila, M.A. AbdelKhalek, Adsorption Study of Some Heavy Metal Ions on Modified Kaolinite Clay, Int. j. adv. eng. technol. manage. appl. sci., 03 (2016) 152–163.

[10] A.K. Meenaa, G.K. Mishra, P.K. Rai, C. Rajagopal, P.N. Nagar, Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent, J. Hazard. Mater., 122 (2005) 161–170.

[11] K. He, Y. Chen, Z. Tang, Y. Hu, Removal of heavy metal ions from aqueous solution by zeolite synthesized from fly ash, Environ. Sci. Pollut. Res., 23 (2016) 2778–2788.

[12] U. Kumar, M. Bandyopadhyay, Sorption of cadmium from aqueous solution using pretreated rice husk. Bioresource. Technol., 97 (2006) 104–109.

[13] R. Karthik, S. Meenakshi, Removal of Pb(II) and Cd(II) ions from aqueous solution using polyaniline grafted chitosan, Chem. Eng. J., 263 (2015) 168–177.

[14] K. Al-Essa, F. Khalili, Adsorption of Humic acid onto Jordanian Kaolinite Clay: effects of Humic acid Concentration, pH, and Temperature, Sci. J. Chem., 6 (2018) 1–10.

[15] V. Vipasiri, L. Shaomin, J. Bo, C.W. Chris, S. Chris, Adsorption of Congo red by three Australian kaolin's, Appl. Clay Sci., 43 (2009) 465–472.

[16] V.K. Guptaabc, I. Tyagia, S. Agarwala, O. Moradid, H. Sadeghi, R. Shahryari-ghoshekandid, A.S.H. Makhlouf, M. Goodarzi, A. Garshasbig, Study on the removal of heavy metal ions from industry waste by carbon nanotubes: effect of the surface modification-A review, Crit. Rev. Environ. Sci. Technol., 46 (2016) 93–118.

[17] M. Matłok, R. Petrus, J.K. Warchoł, Equilibrium study of heavy metals adsorption on Kaolin, Ind. Eng. Chem. Res., 54 (2015) 6975–6984.

[18] B.K. Nandi, A. Goswami, M.K. Purkait, Adsorption characteristics of brilliant green dye on kaolin, J. Hazard. Mater., 161 (2009) 387–395.

[19] C.E.A. Carneiro, G. Berndt, I.G. de Souza Junior, C.M.D. de Souza, A. Paesano Jr, A.C.S. da Costa, E. di Mauro, H. de Santana, C.T.B.V. Zaia, D.A.M. Zaia, Adsorption of adenine, cytosine, thymine, and uracil on sulfide-modified montmorillonite: FT-IR, Mössbauer and EPR spectroscopy and X-ray diffractometry studies, Orig. Life. Evol. Biosph., 41 (2011) 453–468.

[20] M. Amer, F. Khalili, A. Awwad, Adsorption of lead, zinc and cadmium ions on polyphosphate modified kaolinite clay, J. Environ. Chem. Ecotoxicol., 2 (2010) 001–008.

[21] W. Trolland, K. Cannan, A modified photometric ninhydrine method for the analysis of amino and imino acids, J. Biol. Chem., 200 (1953) 803–811.

[22] D. Zaia, Spectrophotometric determination of cysteine and/or carbocysteine in a mixture of amino acids, shampoo, and pharmaceutical products using p-benzoquinone, Talanta, 50 (1999) 1003–1010.

[23] D.L. Bish, Rietveld refinement of the kaolinite structure at 1.5 K, Clays Clay Miner., 41 (1993) 738–744.

[24] C.A. Reyes, C. Williams, O.M. Alarcón, Synthesis of zeolite LTA from thermally treated Kaolinite, Antioquia, 53 (2010) 30–41.

[25] G. Kakali, T. Perraki, S. Tsivilis, E. Badogiannis, Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity, Appl. Clay Sci., 20 (2001) 73–80.

[26] E. Benincasa, M.F. Brigatti, D. Malferrari, L. Medici, L.Poppi, Sorption of Cd-cycteine complexes by kaolinite, Appl. Clay Sci., 21 (2002) 191–201.

[27] M. AL-Harahsheh, R. Shwabkeh, A. AL-Harahsheh, K.Tarawneh, M. Batiha, Surface Modification and Characterization of Jordanian Kaolinite: application for Lead Removal from Aqueous Solution, Appl. Surf. Sci., 255 (2009) 8098–8103.

[28] P.W. Schindler, P. Leichti, J.C. Westall, Adsorption of copper, cadmium and lead from aqueous solution to the kaolinite/water interface, Neth. J. Agri. Sci., 35 (1987) 219–230.

[29] E. Bottari, M. Festa, On the behavior of cysteine as ligand of cadmium(II), Talanta, 44 (1997) 1705–1718.

[30] W.R. Puls, H.L. Bohn, Sorption of cadmium, nickel, and zinc by kaolinite and montmorillonite suspensions, Soil. Sci. Soc. Am. J., 52 (1988) 1289–1292.

[31] F. Cotton, G. Wilkinson, C. Murillo, M. Bochmann, Advanced Inorganic Chemistry, Wiley Sixth Edition, New York, 1999.

[32] J.P. Hunt, Metal Ions in Aqueous Solutions, 2nd edition, Benjamin Inc., New York, 1965.

[33] M.Q. Jiang, Q.P. Wang, X.Y. Jin, Z.L, Chen, Removal of Pb(II) from aqueous solution using modified and unmodified kaolinite clay, J. Hazard. Mater., 170 (2009) 332–339.

[34] K. Al-Essa, F. Khalili, Heavy Metals Adsorption from Aqueous Solutions onto Unmodified and Modified Jordanian Kaolinite Clay: Batch and Column Techniques, AJAC., 6 (2018) 25–34.

[35] H. Al-Itawi, W. Omar, Removal of $Pb^{2+}$ Ions from Aqueous Solutions by Adsorption on Kaolinite Clay, Am. J. Applied. Sc., 4 (2007) 502–507.

[36] E.I. Unuabonaha, B.I. Olu-Owolabi, K.O. Adebowale, A.E. Ofomaja, Adsorption of lead and cadmium ions from aqueous solutions by tripolyphosphate-impregnated Kaolinite clay, Colloids. Surf., A., 292 (2007) 202–211.

[37] D. Xu, X.L. Tan, C.L. Chen, X.K. Wang, Adsorption of Pb(II) from aqueous solution toMX-80 bentonite: effect of pH, ionic strength, foreign ions and temperature, Appl. Clay Sci., 41 (2008) 37–46.