ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Characterization and application of kaolinite clay as solid phase extractor for removal of copper ions from environmental water samples

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Manuscript Info

Manuscript History:

Received: 15 January 2015
Final Accepted: 22 February 2015
Published Online: March 2015

Key words:
kaolin sorbents, batch technique, removal, copper ions, environmental water samples

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Abstract

Reactions of copper with kaolinite clays are important in determining copper fate in the environment. Fourier Transform Infrared (FTIR), X-ray diffraction (XRD), X-ray fluorescence (XRF), thermal gravimetric analysis (TGA), energy dispersive x-ray (EDX) and particle size distribution (PSD) techniques investigated for characterization of kaolin sorbents (kaolin, metakaolin and dealuminated kaolin). Furthermore, the scan electron microscope (SEM) used for their surface morphology. Thus, the present study includes the removal of Cu(II) from aqueous solutions on kaolin sorbents through the process of adsorption under various conditions (pH, equilibrium time, amount of sorbent and concentration of copper ion) using batch technique. Increasing pH favors the removal of copper ions till they are precipitated as the insoluble hydroxides. The interaction of Cu(II) with natural kaolin sorbent is rapid within 60 min equilibrium time with maximum extraction percentage (100%) and high distribution coefficient (8.406×10^4) at pH 6.5 compared with the other two sorbents. In addition, the adsorption kinetics data were best fitted with the pseudo-second-order ($r^2 = 0.994$). Also, the results of adsorption isotherm indicated that these data can be better fitted with the Langmuir model with $r^2 = 0.986$. Finally, kaolin sorbent was be applicable for removing copper ions from environmental water samples and it was found that these ions were highly recovered (90.0-100.0% with RSD%=0.001-0.017%) using batch experiments.

INTRODUCTION

Heavy metal ions occur in many industrial activities such as those produced by metal-plating facilities, mining operations, battery manufacturing processes, production of paints and pigments, fertilizer manufacturing as well as ceramic and glass industries (Erses et al., 2005). The contamination with heavy metal ions causes a serious threat to the environment and human health, as these metals are non-biodegradable, toxic, even at low concentration, and enter the food chain (Xuea et al., 2009). Copper ions are one of these widespread heavy metal ions. Although it is an essential metal in a number of enzymes for all forms of life, its accumulation in the human body causes brain, skin, pancreas, and heart diseases and central nervous system disorder (Dalida et al., 2011). Also, the co-carcinogenic character of copper is implicated in stomach and lung cancers. On the other hand, the permissible limit for copper ions in the drinking water approved by World Health Organization (WHO) is 2 ppm. So, the removal of Cu(II) and other heavy metals from natural water and wastewater is important in terms of protecting public health and environment and it has been a focus area of research in recent years. These pollutants can be treated by various methods including chemical precipitation, (Hui et al., 2005) ion exchange, (Ijagbemi et al., 2009) adsorption, (Zaini et al., 2010) membrane separation, (Qdaisa and Moussab, 2004) and solid phase extraction (SPE) (Xuea et al., 2009; Dalida et al., 2011). Among these methods, chemical precipitation is the most common technique. However, under such circumstances, it does not seem to be a promising method to meet the requirements of stringent effluent standard. Of all the various water-treatment processes, SPE is generally preferred for the removal of heavy metal ions. It has several advantages over other separation techniques including high stability and reusability of the solid phase, easiness of separation, minimal costs due to low consumption of reagents and no need for organic solvents which may be toxic (Ijagbemi et al., 2009; Bhattacharya et al., 2006) Several different solid phases have been found useful in taking up of Cu(II) from solution, viz. activated carbon, (Zaini et al., 2010) cellulosic derivatives (Soliman et al., 2011a) and chelating ion exchange resins (Pohl and Prusisz, 2004) In the past two decades, research has been focused on using low-cost, effective solid phase extractors for adsorption and removal of pollutants. These adsorbents include clay minerals (Ijagbemi et al., 2009; Ma'rquez et al., 2004) agricultural by-products (Šćiban et al., 2008) some aquatic plants (Keskinkan et al., 2004) and microorganisms (Li et al., 2004) Clays are readily available, cheap and environment friendly with high specific surface area, chemical and mechanical stability. Clay minerals have different adsorption capacities for metal ions which depend on the adsorption conditions. Whatever, they have been found to be very effective, economical, versatile and simple (Ijagbemi et al., 2009; Zaini et al., 2010). In this context, a number of studies concerning kaolinite clay used to remove heavy metals from aqueous solutions have been reported (Bhattacharyya and Gupta 2011; Arias et al., 2002; Jiang et al., 2011; Adebowale et al., 2005).

Our goal in this paper is to reach the best conditions to remove the copper ions from aqueous solutions using unmodified kaolin sorbent, which may be better than or similar to the use of the modified one in the previous literature. So, in this study a simple and direct extraction method (SPE) with the aid of low cost kaolin sorbent for the removal of Cu(II) ions from aqueous solutions using batch technique was employed. Moreover, it is aimed in this manuscript to throw light on the efficiency of kaolin to act as a waste benign sorbent for selective removal of trace amounts of Cu(II) spiked to natural water samples prior to determination by atomic absorption spectrometry (AAS).

2. Experimental

2.1. Materials and methods

All chemicals, reagents and indicators that were used are of analytical grade and were purchased from E. Merck, India/German. Kaolin used in this study is from Russian kaolin commonly used in ceramic and porcelain manufacture. Metal salts of $CuCl_2.2H_2O$, $NiCl_2.6H_2O$, $CdCl_2.H_2O$, $ZnCl_2$ and ethylene di-amine tetra acetic acid sodium salt dehydrates (EDTA) were obtained from BDH (England) and Aldrich Company (Milwaukee, WI, USA). Water samples including: Nile river water (NRW), ground water (GW), drinking tap water (DTW) and mineral water (MW) were collected from Minia governorate. Doubly distilled water (DDW) was obtained from our lab.

Kaolin (K) ($Al_2Si_2O_5(OH)_4$) was grinded to passes 90 µm sieve. To prepare metakaolin (MK) from kaolin, the later was calcined in an electrical muffle furnace with a heating rate 10^oC/min at the 750^oC for 5 h, recharged from the muffle furnace, cooled to room temperature in desiccator and was ground to pass 90 µm sieve. Dealuminated kaolin waste (DAK) was provided from the Egyptian Shaba Company after the recovery of alumina from kaolin with concentrated sulfuric acid under hydrothermal conditions. The pH of DAK in water (1 g in 100 ml DDW) was found to be acidic as a result of residual concentrated sulfuric acid. Hence, DAK was washed several times with 0.1N NaOH solution and distilled water to remove the residual acidity till reaching pH=7. Washed DAK was filtered, dried in an electric oven for three days at $75\text{-}100^oC$ and grinded to passes 90µm sieve (Liew et al., 2012).

2.2. Instrumentation

The infrared spectra were obtained using FTIR model 410 JASCO (Japan). SEM/EDX analysis was obtained using JSM-5400 LV JEOL. EDX (ISIS link) as option in SEM (Japan). XRD and XRF analysis were carried out by Philips X-ray diffractometer PW 1370, Co. With Ni filtered Cu Kα radiation (1.5406Å). PSD was carried out by Mastersizer 2000 (Malvern). A Fisher Scientific Accumet pH-meter (Model 825) (Germany) calibrated against two standard buffer solutions at pH 4.0 and 9.2 was used for all pH measurements. Atomic absorption measurements were performed with Aquanova-Genway spectrometry.

2.3. Factors controlling Cu(II) extraction using different kaolin sorbents

The percentage of extraction of Cu(II) using different kaolin sorbents (K, MK and DAK) were determined in triplicate under static conditions by the batch equilibrium technique. 3.0 g of each of the sorbents was added to a 0.5 mL of 0.1M of the Cu(II) salt solution; the total volume was completed to 50 ml by DDW at pH range 1.0 - 10.0 in a 100.0 ml measuring flask. For the pH adjustment, solutions of 0.1M HCl and 0.1M NaOH were used. The mixture was mechanically shaken for 60 min at room temperature to attain equilibrium. The sorbents were separated by filtration and washed with DDW; the un-retained metal ion in the filtrate was determined by complexometric EDTA titration (Ma'rquez et al., 2004).

The effect of the contact time on the Cu(II) extraction was determined under the same batch conditions for different shaking periods (5-120 min) (Ahmed 2008) at the pH of the highest Cu(II) extraction. The effect of Cu(II) concentration ($2x10^{-4}$ – $2x10^{-3}$ M) and weight of the sorbent (0.05-4.0g) on extraction efficiency were also systematically investigated.

3. Results and Discussion

3.1. Characterization of kaolin and its treated forms

3.1.1. XRF analysis

Table (1) illustrates the chemical composition in weight % of kaolin heated at 750°C for 5 h. It was indicated that the kaolin sample is mainly composed of the kaolinite mineral ($Al_2O_3.2SiO_2.2H_2O$) in addition to some of impurities such as TiO_2. Small proportions of Fe_2O_3, Na_2O, MgO, K_2O, CaO and sulphites (i.e.SO_3) also exist. This may be due to substitution of some Al^{3+} and Si^{4+} ions with Fe^{3+}, Na^+, Mg^{2+}, K^+, Ca^{2+}, and SO_4^{2-} ions in the kaolinite structure (Grim, 1968) Calcination of kaolin at 750°C for 5 h leads to decomposition of kaolinite mineral into metakaolinite containing about 42 and 52 weight % of Al_2O_3 and SiO_2 respectively. Whereas the percentages of pure metakaolinite mineral derived from its molecular formula ($Al_2O_3.2SiO_2$) are about 45 and 54 weight % of Al_2O_3 and SiO_2 respectively. This indicates that this sample is of high grade (i.e. about 42/45x100=93% purity).

3.1.2. XRD analysis

Figure (1) illustrates the XRD patterns of kaolin and metakaolin. It was clear that the kaolin sample is mainly composed of kaolinite mineral (K) as indicated from peaks existing at 2θ values 12.46, 25, 38.56, 45.94, 51.28, and 55.42° respectively. The XRD spectrum is matched with the JCPDS database file (PDF-01-089-6538). This indicates that the kaolin used in our work is ideal kaolinite with anorthic (triclinic) lattice structure. Small proportion of quartz mineral (Q) was detected from peaks existing at 2θ values 26.7, 39.76 and 50.38° respectively (Liew et al., 2012). The thermal treatment at 750°C for 5 h decomposes the kaolinite structure into amorphous metakaolin that has no diffraction patterns. This can be detected from the hump in the 2θ range 15-35°. The XRD results are in a good agreement with XRF results. The mineralogical composition of dealuminated kaolin reveals it to contain quartz, a small proportion of titanium oxide (anatase) and a considerable amount of amorphous material as indicated from the hump. This confirms that the process of dealumination of kaolin with concentrated sulfuric acid leads to the formation of residual quartz and anatase as well as highly amorphous silica and alumina (Mostafa et al., 2001).

3.1.3. FTIR spectra

Figure (2) illustrates the FTIR spectra of kaolin, metakaolin and dealuminated kaolin. In the 3000-4000 cm^{-1} frequency range, kaolin shows bands at 3700, 3680, 3654, and 3621 cm^{-1} due to stretching vibrations of hydroxyl groups. The band at 3700 cm^{-1} is a contribution of the hydroxyl groups sitting at the edges of the kaolin platelets. The bands at 3680 and 3654 cm^{-1} correspond to hydroxyl groups at the surface of the alumina octahedral layers that interact with the oxygen atoms of the adjacent silica tetrahedral layers. The band at 3621 cm^{-1} is connected with the internal hydroxyl groups. The bending vibrations of free water molecules adsorbed to kaolin surface (hygroscopic moisture) are responsible for the bands at 1660 and 3470 cm^{-1}. None of these bands are present on the FTIR spectrum of metakaolin. It suggests that after a thermal treatment, most of the hydroxyl groups have been removed (Liew et al., 2012; Heah et al., 2012; Lin et al., 2008). In the 400-1800 cm^{-1} domain, kaolin presents bands at 1110, 1024, 918, 800, 754, 698, 542 and 480 cm^{-1}. Asymmetric Si-O-Si stretching vibrations are responsible for the band at 1110 cm^{-1}. Alternating Si-O-Si and Al-O-Al stretching vibrations are responsible for the band at 1024 cm^{-1} (Galan et al., 1996). The band at 918 cm^{-1} is attributed to the bending Al-O-

H vibrations (hydroxyl groups sitting on the alumina faces). The bands at 800, 754, and 698 cm^{-1} correspond to Si-O-Al vibrations and to hydroxyl group perpendicular to the surface as well as symmetric Si-O-Si stretching vibration (Galan et al., 1996). Band at 542 cm^{-1} is due to Al^{4+}-O-Si vibrations, where Al^{4+} is in octahedral coordination (Liew et al., 2012). Lastly, bending O-Si-O vibrations are responsible for the band at 480 cm^{-1} (Liew et al., 2012; Galan et al., 1996). In the case of metakaolin FTIR spectrum, major changes are observed on the intensity, the shape, and the position of adsorption bands mentioned above. Indeed, the thermal treatment induces a deformation of the silica tetrahedral. Therefore, thermal treatment leads not only to a de-hydroxylation of kaolinite but also to a structural modification. The peak at 800 cm^{-1}, which is fairly intense and narrow for kaolin, becomes in the case of metakaolin a broad band, with a small intensity and shifted at 823 cm^{-1}. This broad band is characteristic of the degree of disorder in metakaolinite structure (Liew et al., 2012). In the case of dealuminated kaolin FTIR spectrum, the intensity of the absorption bands mentioned above decreases. This indicates that the hydrothermal treatment of kaolin with concentrated H_2SO_4 dissolutes much of aluminate leaving behind silicate rich residue. Dealuminated kaolin spectrum also shows a band at 1170 cm^{-1} attributed to presence of sulfate ion and at 972 cm^{-1} attributed to Si-O stretching mode of non-bridging oxygen (Mitchell et al., 1998).

3.1.4. TGA

Figure (3) illustrates the TGA, and DTA thermograms of kaolin. It was observed that the endothermic peak centered at 53^{o}C (accompanied with about 1.8% weight loss) is due to the loss of moisture. The large endothermic peak centered at 522^{o}C (accompanied with about 12.8% weight loss) is due to the loss of water of crystallization and decomposition of kaolin into metakaolin. Taking in consideration that the dehydroxylation of pure kaolinite is accompanied with a weight loss equals to 13.76% (Konan et al., 2009).

The dehydroxylation reaction of pure kaolinite is:

$$\underset{\text{Kaolinite}}{Al_2O_3.2SiO_2.2H_2O} \xrightarrow{522^{o}C} \underset{\text{metakaolinite}}{Al_2O_3.2SiO_2 + 2H_2O}$$

Which is corresponding to the transformation of four hydroxyl groups into two water molecules, and two oxygen anions are left in the material (Liew et al., 2012).

The exothermic peak centered at 982^{o}C (without weight loss) may be attributed to various phenomena such as formation of a spinel type phase and/or germination of mullite, evolution of aluminum co-ordinance toward VI, extraction of amorphous silica from metakaolinite and germination of mullite, or separation into a silica-rich and an alumina-rich domains (Konan et al., 2009).

3.1.5. SEM

Figure (4) illustrates the SEM micrographs of kaolin and metakaolin. The SEM micrograph of the kaolin shows hexagonal platelets of kaolinite mineral in addition to small proportion of halloysite tubular crystals (Aparicio et al., 2009). Although the chemical composition of dehydrated halloysite, dickite, and nacrite are similar to that of kaolinite, their structural characteristics are quite different. After being thermally treated, metakaolin attains its original shape. Therefore, the thermal treatment does not drastically modify the morphology (Konan et al., 2009).The spectrum of kaolin samples by using elemental microprobe analysis of SEM/EDX is illustrated in Fig.(5), Table (2). Only Al and Si signals can be observed in this figure which has been known as the principal elements of natural kaolin sample. So, EDX analysis proves the qualitative and quantitative structure of kaolin sorbent (Mane et al., 2005).Moreover, the particle size distribution of kaolin, metakaolin and dealuminated kaolinwere carried out and the specific areas were: 1.77, 1.2 and 2.1 m^2/g, respectively (Arias and Sen, 2009).

3.2. Characterization of kaolin after adsorption of Cu(II)

3.2.1. XRD analysis

Figure (6) illustrates the XRD patterns of kaolin and kaolin-Cu^{+2}. The intensity of kaolinite mineral is greatly reduced in case of waste kaolin. This may be due to modification of the crystal structure of kaolinite mineral as a result of the adsorption of Cu^{+2} ions on the surface of kaolinite crystals. The shift of the peak of kaolinite mineral from 24.94 to 24.58 proves the crystal modification by adsorbed Cu^{2+} ions. There is no indication for the existence of new crystalline phases in the case of waste kaolin. This may indicate that the bonding between kaolin surface and Cu^{+2} ions is by adsorption forces not via precipitation of Cu^{+2} compounds such as $Cu(OH)_2$ (Liew et al., 2012; Arias and Sen, 2009; Roach et al., 2009).

3.2.2. FTIR spectra

Figure (7) illustrates the FTIR spectra of kaolin and kaolin-Cu^{+2}. It was observed that the intensity of absorption bands of free water (moisture) centered around 1660 and 3470 Cm^{-1} are strongly reduced in case of kaolin-Cu^{+2}sorbent. This indicates that the adsorption sites on the kaolin surface which is occupied by free water molecules in case of kaolin were occupied with Cu^{+2} ions that have been adsorbed from aqueous solutions. This suggests that the adsorption may have been done on the OH bending of water, the inner surface -OH stretching vibration (Jiang et al., 2009) and the Si–O bond linkage in kaolin (Adebowale et al., 2006).

3.2.3. SEM

Figure (8) illustrates the SEM of kaolin and kaolin-Cu^{+2}. Results showed that the microstructure and morphology of kaolin are greatly affected by the adsorption of Cu^{+2} ions from aqueous solutions. This is due to that the interactions of the heavy metal cations with the kaolinite could affect the structure of the kaolinite (Miranda-Trevino and Coles, 2003). Whatever, the Cu^{+2} ions distribution in kaolin sample was not observable using SEM technique. This suggest that ions are adsorbed to kaolinite particle surfaces as a thin coating (Roach et al., 2009).An important consideration is that the small proportion of halloysite tubular crystals was detected in SEM not in XRD analysis. This is may be due to the following facts: (1) One of the main difficulties of X-ray identification of clay minerals is to obtain poorly defined diagrams arising from poor crystallinity of clay minerals such as hydrated halloysite that could be recognized either by low-temperature dehydration giving characteristically diminished spacings or by the formation of organic complexes giving characteristically increased spacings (Gibbs, 1967).The problems arising from the poor crystallinity of clay minerals was also overcome to a great extent by the use of standards extracted from the samples (Brindley, 1952). (2) The amount of hallosyite in the sample is under the detection limit of the XRD apparatus. The smallest amount of a given phase that can be identified in a given XRD technique (i.e. the limit of detection) is clearly depend on the square root of the count time (Connolly, 2003).

3.3. Equilibrium studies on Cu(II) ions extraction by kaolin sorbents using batch technique

3.3.1. Influence of pH

pH of the aqueous solutions is one of the important factors in metal adsorption. The predominant metal species at pH between 2.0 and 7.0 are positively charged M^{n+} and $M(OH)^{(n-1)+}$, therefore, uptake of metals may proceed through M^{n+} exchange process with acidic sites H^+, complexing with functional groups and/or chelation (Pohl and Prusisz, 2004; Soliman et al., 2011b).According to the composition of kaolin as characterized in the previous sections and shown in Table (1), the interaction of copper ions onto this sorbent mainly based on a direct complex formation according to the presence of oxygen donor atoms of hydroxyl groups of silica and alumina surfaces. Fig.9 showed a gradual increase in the Cu(II) percentage of extraction (%E) with increasing pH. However, the experiments could not be done at pH >7.0 due to low solubility of copper ions (Bhattacharyya and Gupta, 2011; Rao et al., 2005). At low pH, the number of available H^+ ions is high in the adsorption medium and Cu(II) ions have to compete with them for the adsorption sites on the surface of the three sorbents; kaolin, metakaolin and dealuminated kaolin resulting in a lower percentage of extraction of Cu(II) ions (Nuhoglu and Oguz, 2003). With gradual increase of pH, the concentration of H^+ ions decreases and some of sites become available to the metal ions resulting in a higher percentage extraction of Cu(II). As shown in Fig.9, although all the kaolin sorbents showed an identical behavior of increased percentage extraction of Cu(II) ions with gradually increasing pH, the differences in the % extraction still existed. At pH > 5.0, the order of adsorption of Cu(II) ions was:kaolin > de-aluminated kaolin > meta-kaolin.

3.3.2. Influence of sorbent weight

The weight of kaolin sorbents were varied from 0.05 – 4.0 g keeping all the other experimental variables constant (pH 6.5, initial concentration of Cu(II) 0.05 mmol and contact time 60 min). It may be observed that on increasing the sorbent weight, the percentage of extraction of Cu(II) increased up to a weight of 3.0 g and remained constant for the three sorbents. This can be explained as follows: for a fixed Cu(II) ion concentration, higher amounts of kaolin sorbent means the availability of a larger surface area or a larger number of adsorption sites (Bhattacharyya and Gupta, 2011; Arias and Sen, 2009) and therefore higher percentage of extraction of metal. It was found that by increasing the kaolin amount from 0.4 to 3.0 g, the percentage of extraction increased from 64.02 to 100.0%. On the other hand, the percentage of extraction for the other sorbents not exceeds 89.2% with the same amount of sorbent (3.0g), Fig.10.

3.3.3. Influence of equilibrium time

Equilibrium time is another important factor in the process of evaluation of the adsorption of Cu(II) by different kaolin sorbents. The batch experiments were carried out at different contact times 10, 15, 20, 30, 45, 60, 90 and 120 min using mechanical shaker. The obtained results clarified that the equilibrium is reached after 60 min of contact with all kaolin sorbents. Firstly, the ions adsorbed, occupied the active sites on the three sorbents. As the contact time increased the active sites on the sorbent were filled. It is important to mention that values of the percentage of extraction and time needed to attain equilibrium using the kaolin sorbents are higher and shorter respectively than values reported by other researchers (Bhattacharyya and Gupta, 2011; Soliman et al., 2011b**.** From the previous results, kaolin clarified a maximum percentage of extraction (100%) compared with the other two kaolin sorbents (MK and DAK).So, it was decided to choose the kaolin sorbent (K) as the major one for the remaining batch studies.

3.3.4. Adsorption Kinetics

The sorption kinetic data of Cu(II) measured on kaolin sorbent, was analyzed in terms of pseudo-first-order and pseudo-second-order sorption equations (Kamaria and Ngah, 2009). The pseudo-first-order equation is shown below:

$$dq_t/d_t = k_1 (q_e - q_t), \qquad (1)$$

where k_1 (min^{-1}) is the rate constant of the pseudo-first-order sorption, q_t (mmol g^{-1}) denotes the amount of sorption at time t (min), and q_e (mmol g^{-1}) is the amount of sorption at equilibrium. After definite integration by application of the condition q_t =0 at t = 0 and $q_t = q_t$ at t = t, Eq. (1) becomes:

$$\log (q_e - q_t) = \log q_e - (k_1/2.303)\, t \qquad (2)$$

The kinetic plots were drawn for kaolin sorbent and the adsorption rate constant (k_1 = 0.142) and adsorption capacity (q_e= 4.462 mmol g^{-1}) were calculated from the slope and intercepts of plots of $\log(q_e - q_t)$ against ‘t’. The regression coefficient equal 0.89 which shows that the pseudo first order equation is not appropriate to describe the entire process, see Table (3).

The sorption kinetic data of Cu(II) measured on kaolin sorbent was analyzed in terms of pseudo-second-order sorption equation (Soliman et al., 2011a; Soliman et al., 2011b). This equation can be written as:

$$dq_e/d_t = k_2(q_e - q_t)^2. \qquad (3)$$

Where, k^2 (g/mmol/min) is the rate constant. Integration of Eq. (3) and application of the conditions q_t = 0 at t = 0 and $q_t = q_t$ at t = t, give:

$$1/q_e - q_t = 1/q_e + k_2 t \qquad (4)$$

The following equation can be obtained on rearranging Eq. (4) into a linear form as follows:

$$t/q_t = 1/\upsilon_o + (1/q_e)\, t \qquad (5)$$

$\upsilon_o = kq_e^2$ is the initial sorption rate (mmol g^{-1} min^{-1}), υ_o and q_e can be obtained from the intercept and slope of plotting t/q_t vs. t Fig.11, respectively. They were calculated to be $\upsilon_o = 0.055$, $q_e = 0.241$ mmol g^{-1} and $k_2 = 0.948$ min^{-1}. Since, the kinetic of the uptake has to be determined in order to establish the time course of the uptake process; the previous results showed that the adsorption kinetics data were best fitted with the pseudo-second-order equation, which give a correlation factor (r^2) of 0.994, Table (3).

3.3.5. Influence of initial Cu(II) concentration

With increasing Cu(II) ion loading, the percentage of extraction decreases gradually. At lower concentrations, a large number of adsorption sites of kaolin sorbent are available to the Cu(II) ions and the adsorption is independent of its initial concentration. The situation changes with increasing Cu(II) concentration and the competition for adsorption sites become strong (Bhattacharyya and Gupta, 2011; Jiang et al., 2011). Under these circumstances, the unit mass of the kaolin sorbent could take up many more Cu(II) ions compared to that at lower concentrations. This showed a decreasing trend in the overall percentage of extraction. So, by increasing Cu(II) ions concentration from $2x10^{-4}$ - $2x10^{-3}$M, % extraction decreases from 100.0 to 81.48 % for kaolin sorbent. Similar observation for Cu(II) ions uptake on different sorbents have been reported (Bayat, 2002).

3.3.6. Binding performance (sorption isotherms) of kaolin sorbent

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface (Soliman and Ahmed, 2009). The simplest adsorption isotherm is based on the assumptions that every adsorption site is equivalent and the ability of a particle to bind is independent of whether or not adjacent sites are occupied (Soliman et al., 2011a; Soliman et al., 2011b; Nuhoglu and Oguz, 2003). To find out the mechanistic parameters associated with Cu(II) sorption, the results obtained by the adsorption experiments were analyzed by the well-known models given by Freundlich and Langmuir models. The sorption isotherms for binding of Cu(II) with kaolin were determined by the batch technique at pH 6.5. Thus, solutions of Cu(II) in the concentration range: ($2.0x10^{-4}$–$2.0x10^{-3}$ M) were shaken for 60 min with a constant weight 3.0 g of kaolin sorbent.

The basic assumption of Freundlich isotherm is that if the concentration of the solute in the solution at equilibrium, C_e was raised to the power 1/n, the amount of solute sorbet being q_e, then $C_e^{1/n}q_e$ was a constant at a given temperature. This model is more widely used but provides no information on the monolayer biosorption capacity (Soliman et al., 2011b) and it assumes neither homogeneous site energies nor limited levels of sorption. The non-linear form of Freundlich equation expressed as follows:

$$q_e = K_f \,.\, C_e^{1/n} \qquad \text{(non-linear form)} \qquad (6)$$

Where, K_f and 1/n are Freundlich constants (indicators of sorption capacity and intensity, respectively). Taking logs and rearranging of Eq. (6), it can give the linear form of Freundlich model which expressed as:

$$\log q_e = \log K_f + 1/n \log C_e \qquad \text{(linear form)} \qquad (7)$$

The constants (K_f) and (1/n) can be calculated from the intercept and slope of this linear equation, respectively. It is clearly showed that the data is not fitting very well to the Freundlich model, Table (4) (Delle Site, 2001).

The Langmuir equation, which is valid for monolayer sorption onto a completely homogeneous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules is given by the following equation:

$$C_e/q_e = (1/Q_o)\,C_e + (1/Q_o b) \qquad \text{(linear form)} \qquad (8)$$

Where, C_e and q_e are the equilibrium concentrations of adsorbate in the liquid and adsorbed phases in mmol ml^{-1} and mmol g^{-1}, respectively (Soliman et al., 2011b; Soliman and Ahmed, 2010). Q_o and b are Langmuir constants, which are related to maximum Cu(II) sorption capacity (mmol g^{-1}) and affinity parameter (ml $mmol^{-1}$), respectively, and can be calculated from the intercept ($1/Q_o b$) and slope ($1/Q_o$) of the linear plot, C_e / q_e vs. C_e given in Fig.12. The correlation coefficient (r^2= 0.986) showed that the Langmuir model fitted the results better than Freundlich model, Table (4). Moreover, the essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined as: $R_L = 1 / (1 + bC_o)$ where, b is the Langmuir constant (indicates the nature of sorption and the shape of the isotherm accordingly) and C_o is the initial concentration of analyte. The R_L value indicates the type of the isotherm as follows:

R_L Value Type of isotherm	Results
$R_L>1$	Unfavorable
$R_L=1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The R_L for Cu(II) sorption (0.6) supports a highly favorable sorption process based on Langmuir model.

3.3.7. Influence of medium on the stability of the kaolin sorbent

The study of medium effect on the stability of the kaolin sorbent is important from practical application point of view. It was performed in different buffer solutions pH 1.0-10.0 for 10 h contact time in order to assess the possible leaching or hydrolysis processes (Ahmed, 2008). The results showed that the kaolin is stable after long time of contact in the pH range from 1.0 to 10.0 especially at basic medium. So, a decomposition or hydrolysis of kaolin was found at high hydrogen ion concentration judging from the percentage decrease of efficiency of Cu(II) uptake as found to be about 37% at pH ≤ 5.0, 5.5% at pH=6.0. On the other hand, at pH range 8.0-10.0 the percentage of hydrolysis did not exceed 4%.

3.3.8. Distribution coefficient (K_d) of Cu(II) ions to kaolin sorbent

The value of distribution coefficient K_d of Cu(II) ions was calculated as:

$$K_d = q_e / C_e$$

Where, q_e is the amount of the Cu(II) ion sorbed by the kaolin in mmol g^{-1} and C_e is the amount of the Cu(II) ion unsorbed in solution in mmol ml^{-1}. It was found that, $K_d$calculated to be 8.406×10^4 mL g^{-1}. This parameter (K_d) reflects the overall Cu-surface affinity (Wang et al., 2009).

3.3.9. Influence of ionic strength

The effect of NaCl electrolyte concentration on the adsorption of Cu(II) onto the kaolin sorbent was investigated. It was obtained that there was decrease in percentage of extraction of the kaolin sorbent for the Cu(II) ions (4.0-10.0%) with increasing concentration of NaCl from 0.02×10^{-2} - 1.0×10^{-2}M. The percentage extraction was 13.0 % when the electrolyte concentration increased to 2×10^{-2}M. The effect of NaCl ionic strength on Cu(II) ion adsorption is often attributed to the competition between cations of the electrolyte and metal ion for the surface sites, where the Na^+ cations compete much more effectively for permanent negatively charged sites (silanol sites, Si–O) on the kaolinite faces than on the aluminol sites (Al–OH) (Jiang et al. 2011).Therefore, a little decrease in adsorption of Cu(II) ion with increasing ionic strength of NaCl implies that increasing ionic strength is making the potential of the sorbent surface less negative and thus would decrease metal ion adsorption (Unuabonah et al., 2008).

Table (1): The chemical composition in weight % of kaolin heated at 750°C for 5 h and de-aluminated kaolin

Element	Element %
Al	34.96
Si	50.965
P	5.54
S	-
K	0.765
Ca	0.235
Ti	1.62
Fe	1.945
Cu	2.13
Zn	1.845

Table (2): Energy dispersive X-ray (EDX) analysis of kaolin

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	L.O.I	TiO_2	Total
Kaolin	51.33	42.125	1.82	0.574	0.303	0.228	0.222	0.502	1.4	1.268	98.37
Dealuminated Kaolin	75.13	9.11	0.89	0.00	0.155	1.47	0.113	0.052	9.18	3.72	99.82

Table (3): Parameters of First order and second order kinetic constants for binding of Cu(II) using kaolin at room temperature.

Sorbent	Metal ion	First order			Second order			
		K_1	q_e	r^2	K_2	q_e	ν_o	r^2
Kaolin	Cu(II)	0.142	4.462	0.892	0.948	0.241	0.055	0.994

Table (4): Parameters of Freundlich and Langmuir isotherms constants for binding of Cu(II) using kaolin at room temperature.

Sorbent	Metal ion	Freundlich constants			Langmuir constants			
		K_f	n	r^2	Q_o^a	b^b	R_L	r^2
Kaolin	Cu (II)	0.079	0.272	0.978	0.279	650.96	0.60	0.986

^{a} mmol g^{-1} , ^{b} ml / mmol

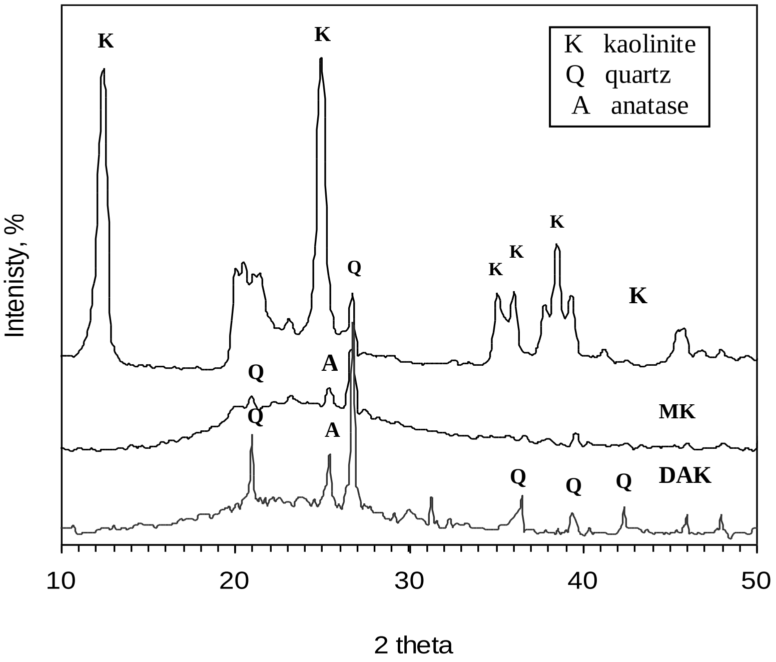
Table (5): Recovery % of Cu(II) ions spiked natural water samples with Kaolin using batch technique

Sample	Spiked Cu(II) ions (ppm)	Recovery %
NRW (Nile river water)	1.0 2.0 5.0	97.30 96.60 98.18
GW (Ground water)	1.0 2.0 5.0	90.0 90.0 97.0
TW (Tap water)	1.0 2.0 5.0	95.70 99.10 99.69
MW (Mineral water)	1.0 2.0 5.0	100.0 100.0 100.0

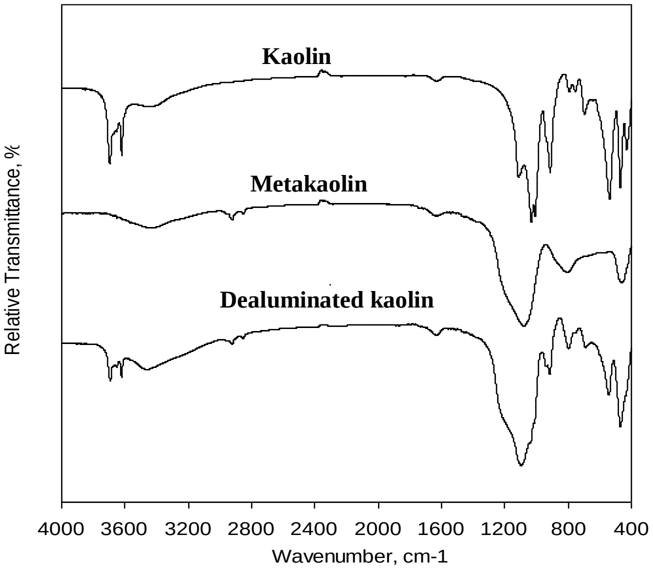
For N= 3, RSD % = 0.001-0.017

Table (6): Comparison of our studied natural kaolin with other natural and modified kaolinite samples

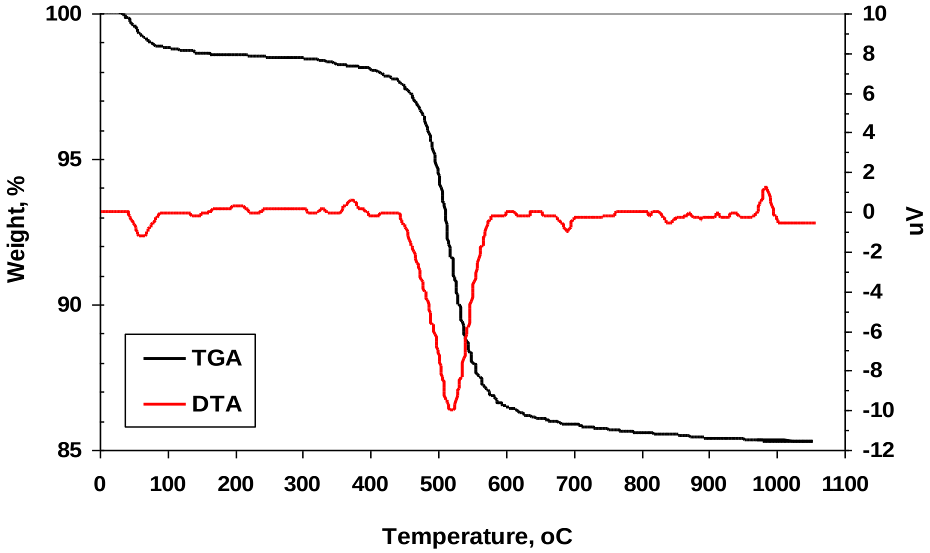
Sorbent	Copper uptake	time of equilibrium or particle size	models of characterization	Application
Zeolite prepared from Egyptian kaolin (Jamil and Ibrahim, 2010)	99%	30 min	XRD, SEM, FT-IR, ESR	No application
Natural and acid activated clays (Bhattacharyya and Gupta, 2011)	37.1%,38.8%	360 min	XRD, FT-IR, particle size	No application
Natural kaolinite clay (Jiang *et al.*, 2011)	98%	30 min	XRD, SEM	Removal of Cu(II) from wastewater
Natural, sulfate and phosphate modified kaolin (Adebowale *et al*., 2005)	71.95%, 80.94%, 77.09%	Non detectable	No characterization	No application
Natural and modified kaolinite (Bhattacharyya and Gupta, 2008)	24.7%, 28.1%, 20.5%, 21.3%	Non detectable	No characterization	No application
Natural kaolinite [our work]	100%	60 min	XRD, FT-IR, SEM/EDX, TGA, XRF, particle size	Removal of Cu(II) from NRW, GW, DTW, and MW



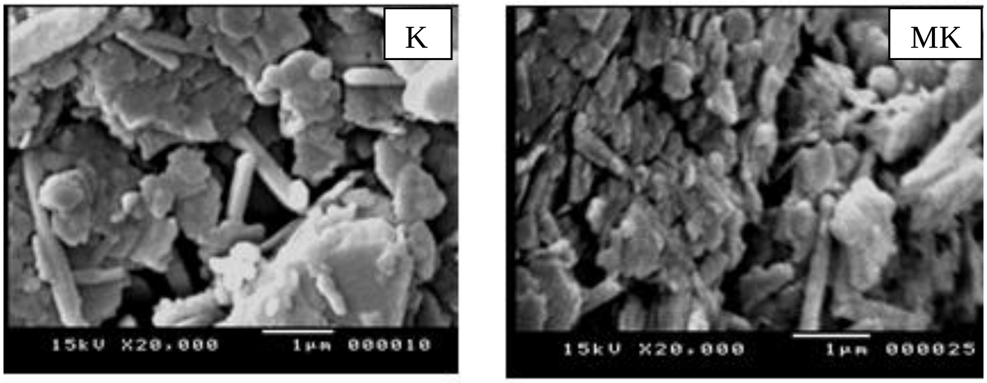
Fig(1): XRD patterns of kaolin, metakaolin and dealuminated kaolin



Fig(2): FTIR spectra of kaolin, metakaolin and dealuminated kaolin

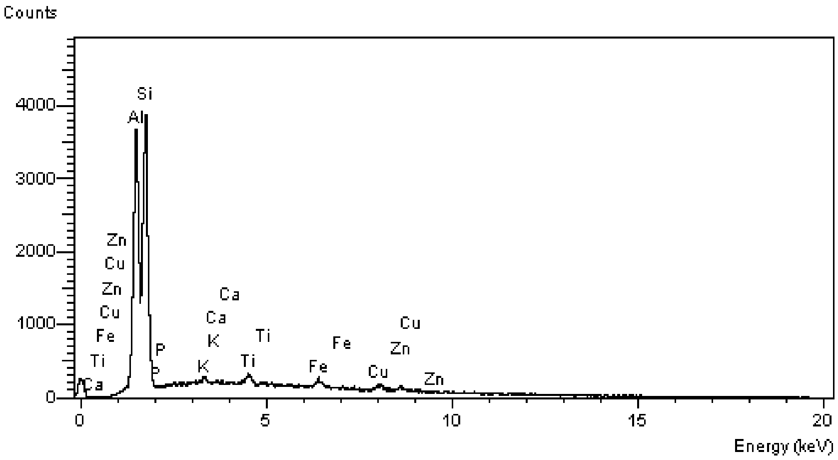


Fig(3): TGA and DTA thermograms of kaolin

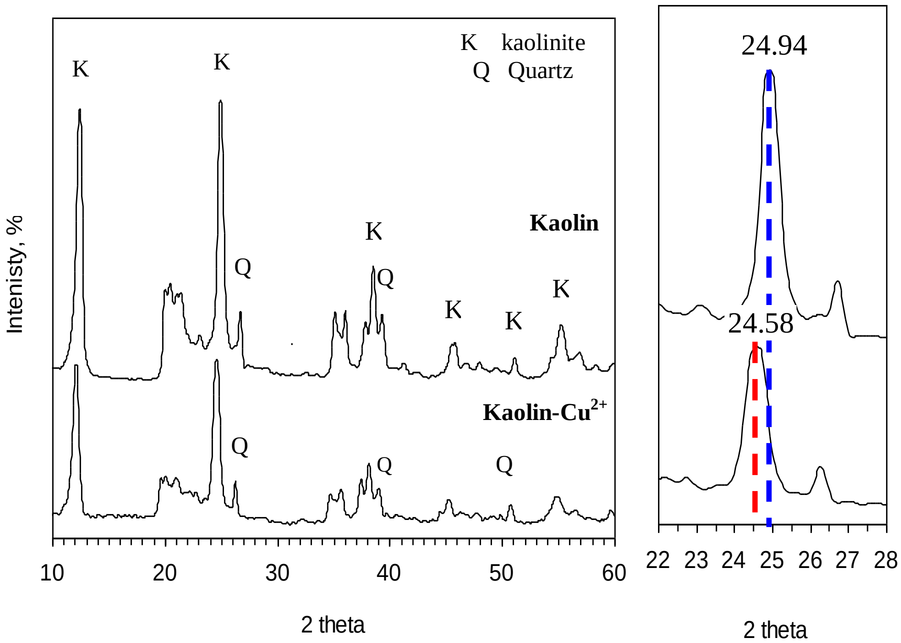


Kaolin **Metakaolin**

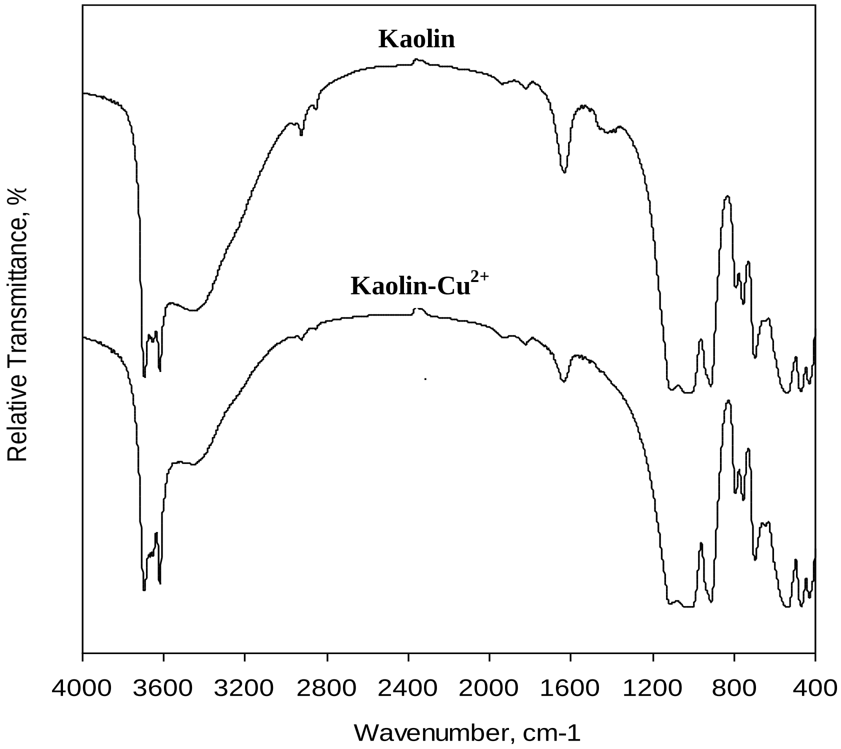
Fig(4): SEM micrographs of kaolin and metakaolin



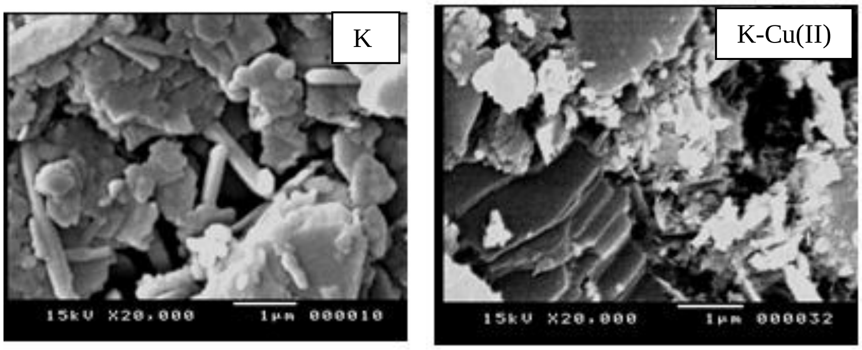
Fig(5): Energy dispersive X-ray (EDX) pattern of kaolin sorbent



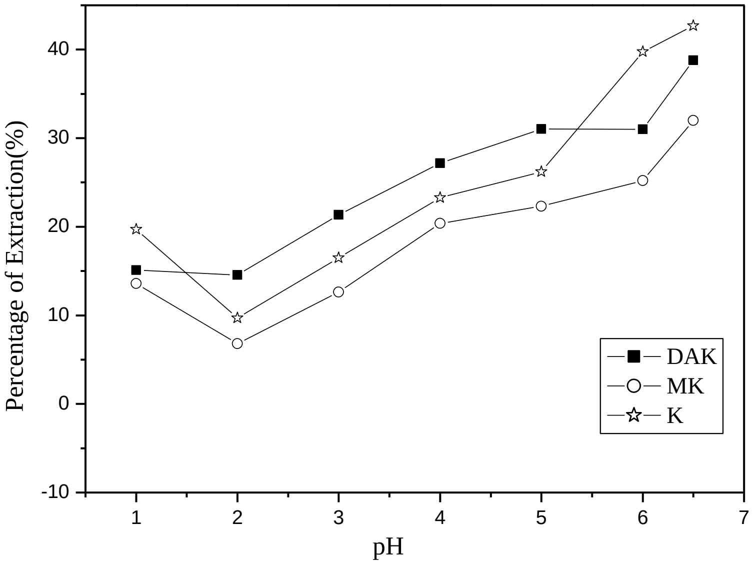
Fig(6): XRD patterns of kaolin before and after copper adsorption



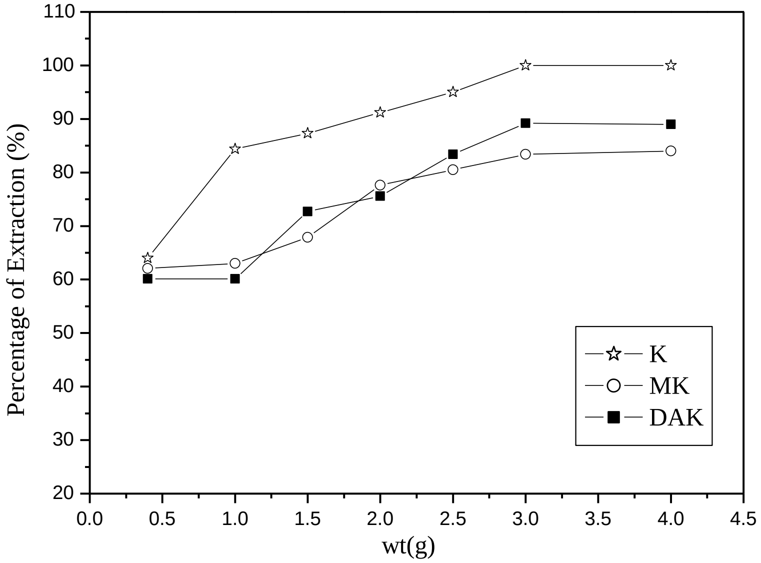
Fig(7): FTIR spectra of kaolin before and after copper adsorption



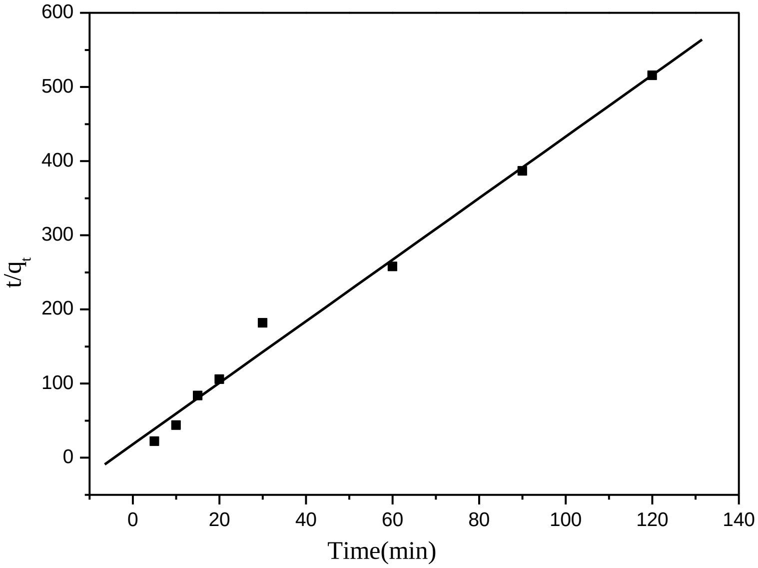
Fig(8): SEM micrographs of kaolin before and after copper adsorption



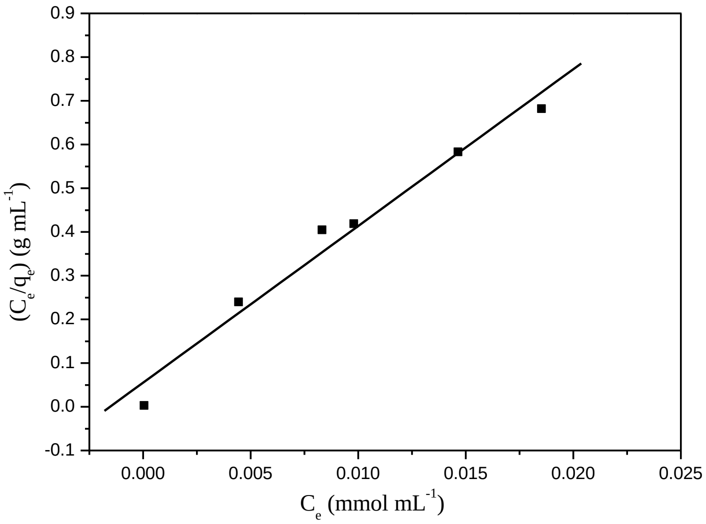
Fig(9): Percentage of extraction of Cu(II) as a function of pH using (K,MK,DAK)



Fig(10): Effect of (K,MK,DAK) weight on percentage extraction (%) of Cu(II)



Fig(11):Pseudo-second-order kinetic plot for the sorption of Cu(II) on kaolin



Fig(12): Langmuir plot for the sorption of Cu(II) on kaolin at constant temperature

4. Applications

4.1. Effect of interfering ions

The same batch procedures were also used to evaluate the effect of foreign ions on percentage extraction values of Cu(II) by kaolin sorbent. A sample of dry sorbent, 50.0 mg, was added to a mixture of 5.0 ppm of Cu(II) and 2.0, 1.0 and 2.0 ppm of the selected foreign solutions $NiCl_2$, $ZnCl_2$ and $CdCl_2$, respectively at the optimum pH justified using HCl and NaOH solutions. This mixture was shaken for 60 min, filtered, washed with DDW and the un-extracted Cu(II) was determined by AAS analysis. Evaluation of the possible interference of foreign ions was performed on the basis of constant concentration of Cu(II) ions versus different concentrations of other interfering species. The determined percentage extraction of Cu(II) in presence of these coexisting cations and anions is 96.0% (N=3, RSD%=0.007) (Mahmoud et al., 2011).

4.2. Effect of binary mixture

The effect of binary mixtures of: Cu(II)-Ni(II), Cu(II)-Zn(II) and Cu(II)-Cd(II) in aqueous solutions was investigated. It was found that, the percentage extraction of Cu(II) in these mixtures were 97.0% (RSD%=0.008), 97.6% (RSD%=0.006) and 95.0% (RSD%=0.006) for Cu(II)-Ni(II), Cu(II)-Zn(II) and Cu(II)-Cd(II), respectively. It may be represented by the ratio of the percentage extraction (%E) for one metal ion in the presence of the other metal, $\% E_{mix}$, to the percentage extraction for the same metal ion when it is present alone in the solution, E_o, so that for:

$$\%E_{mix}/ \%E_o > 1,$$

the sorption is promoted by the presence of other metal ion,

$$\%E_{mix}/ \%E_o = 1,$$

there is no observable net interaction, and

$$\%E_{mix}/ \%E_o < 1,$$

sorption is suppressed by the presence of other metal ion (Unuabonah et al., 2007).

The values of $\%E_{mix}/\ \%E_o$ for Cu(II)-Ni(II), Cu(II)-Zn(II) and Cu(II)-Cd(II) are found to be ≅ 1, suggesting that the simultaneous presence of Ni(II), Zn(II) and Cd(II) not affect the sorption of Cu(II) ions through competition for adsorption sites on kaolin sorbent.

4.3. Removal of Cu(II) from environmental water samples using batch technique

Removal experiments were carried out using different environmental water samples: MW, DTW, NRW, GW and SW. A weight of 1.5g of kaolin was conditioned with 50.0 ml of water sample spiked Cu(II) at concentration of 1.0, 2.0 and 5.0 ppm (adjusted at pH 6.5) with shaking for 60 min. 20.0 ml of the solution (free from the suspended solid phase) were taken at the end of the experiment where the residual concentration of metal ion was determined via AAS. The percentage recovery values of Cu(II) were combined in Table (5).

5. Comparison of uptake of Cu(II) using kaolin sorbent with alternative sorbents

The proposed method was compared to a variety of recent kaolin sorbents reported in literature for the determination and removal of Cu(II). The distinct features are summarized in Table (6). The kaolin sorbent described in this comparison showed high affinity and selectivity of Cu(II) compared to other modified and unmodified kaolin sorbents (values of equilibrating time, 60 min; type of sorbent, unmodified kaolin; percentage removal of Cu(II), 100.0% and method of applications, removal from different environmental water samples).

6. Conclusion

Kaolin sorbents as native solid phase extractors have the following advantages: i) benign natural polymeric material ii) inexpensive iii) rich in oxygen containing functional groups iv) have pronounced capability for the Cu(II) removal from aqueous solution at the pH 6.5 v) their sorption performance were fitted well with Langmuir model (r^2 =0.986 for and 0 < RL< 1), along with fast kinetics obeying pseudo-second-order type (r^2 =0.994) vi) they were successfully applied for determine of Cu(II) in presence of different coexisting ions **:** interfering ions and binary mixture vii) it was also applicable for selective removal of Cu(II) from different environmental water samples (percentage recovery 90.0-100.0%, RSD%=0.001-0.017%) using batch technique.

Acknowledgment:

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

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