Comparison between Adsorption of Copper Ions by Kaolinite and Kaolinite Composite

Diab, M. A.[1]; M. Sh. Zoromba[2]; M.A Hussien[2] and M. Sherif[2]
[1]Chemistry Department, Faculty of science, Damietta University, Egypt.
[2]Chemistry Department, Faculty of Science, Port Said University, Egypt.

Abstract: In this study, removal of toxic metal Cu (Π) from contaminated water has been investigated with the aim of detoxifying industrial effluents before their safe disposal onto land or into the river. Comparison between the two low-cost adsorbents, kaolinite and poly aniline co-anthranilic acid/kaolinite were used to remove Cu (Π) ion from synthesized waste water. Characterization study show that the composite thermally is more stable than the pure kaolinite. The effects of adsorbent amount, pH and contact time on adsorption efficiency were investigated. Generally, the result showed an increase in removal efficiency with increase in contact time and increase of pH and adsorbent dose with the both adsorbent. The modified kaolinite with PANAA is more effective than the pure kaolinite in removal of the copper ions from its solutions.

Keywords: Adsorption, Cu (II), industrial waste water, PANAA/kaolinite composite.

INTRODUCTION

The problem of removing pollutants from water is an important process and is becoming more important with the increasing of industrial activities. In order to solve heavy metal pollution in ecosystem, it is important to bring applicable solutions to the subject. It is possible to clean polluted environment only with long study requiring expensive and complex plants. Therefore, it is important to take effective precautions to prevent water, soils and air pollutions. There are several methods to treat the metal contaminated effluent such as precipitation, ion exchange and adsorption, etc., but the selection of the wastewater treatment methods is based on the concentration of waste and the cost of treatment. Adsorption is one of the more popular methods for the removal of heavy metals from the wastewater. In the purification process, low cost purificant–adsorbent systems are preferred. For this reason, industrial wastes and metallurgical by-products are used and also natural substances like zeolites particularly clays (Arthur and Gino, 1993; Brian and Garrison, 1998; Volzone and Tavani, 1996; Gonz!ales Pradas *et al.,* 1994; Jinho Jung *et al.,* 1998; Soon-Yong and Jung-Min, 1998; Baumgarten and Kirchhausen, 1997; Shukla, 2000; Rajendra *et al.,* 1997; Backes *et al.,* 1995). In our study, it is aimed to compare between the effect of removal of some heavy metals such as Cu (II) from aqueous solution by adsorption on natural kaolinite and poly aniline-co-anthranilic acid/kaolinite composite to investigate the physicochemical parameters involved during this adsorption.

MATERIALS AND METHODS

Materials:

Aniline and anthranilic acid (Aldrich), potassium dichromate (Merck), ammonia solution and hydrochloric acid (ADWIC), Kaolinite (Morgan Chemical Industry) (kaolin colloid powder, lead (Pb) = approx. 0.001%, Loss on ignition = approx. 15%. Kaolinte batch number 1097/6: maximum limits of impurities. All chemicals were used as received without any further purification.

Analytical techniques

The infrared spectroscopy of both modified and unmodified samples were obtained using a Fourier transform infrared (FT-IR) RX 1, USA. The crystallinity of the modified and unmodified samples was determined by powder X-ray diffraction (model X" Pert Pro) with filtered Cu Kα radiation operated at 40 kV and 40mA. The XRD pattern was recorded from 1.5◦ to 50◦ of 2θ with a scanning speed of 0.02◦ of 2θ per second. Solid morphology and average crystal size were determined by scanning electron microscopy (SEM) (JEOL JXA-840 Electron Probe Micro analyzer –JAPAN). The thermal characteristic was studied from TGA, Q50, TA Instruments, USA. Experiment was carried out under N2 atmosphere from 30°C to 800° C at a heating rate of 20°C/min.

Synthesis of polymer composite

The poly (aniline co-anthranilic acid) kaolinite clay composite was synthesized by the in situ chemical oxidative polymerization of aniline and anthranilic acid in presence of different percentages of kaolinite. At first, aniline and o-anthranilic acid monomers (5:1 in mass ratio, typically 9.12 ml, 100 mmol aniline: 2.74 g, 20 mmol o-anthranilic acid) were dissolved in 2M HCl. After that, the calculated amounts of kaolinite were dispersed in 10-20 ml acetone, respectively, under magnetic stirrer at 750–800 rpm. Then, the dispersed system was gradually added to the reactor with stirring at 0–5°C. At the same time, potassium dichromate (initiator) which was separately dissolved in distilled water (100 ml 1M K2Cr2O7) was slowly added into the reactor. Then, the reaction was kept for 24 h at 0°C. Ammonia solution (15 ml of 33% NH4OH diluted by 30 ml distilled water) was added drop wisely until a dark green precipitate was formed which was collected by filtration using a Bu¨chner funnel. The collected precipitates were washed several times with deionized water, washed by ethanol to remove monomer, oligomer and excess oxidant until the filtrate became almost colorless and oven dried at 60°C for 24 hr. The dark green dried powder affords (PANAA)/kaolinite clay composites.

RESULTS AND DISCUSSION

Fourier transforms infrared spectroscopy (FT-IR Spectra)

The FT-IR spectra of the kaolinite and PANAA/kaolinite composites are shown in Figures: (1 and 2) .The spectra of PANAA/kaolinite composites have two major absorptions at 1575-1589 cm^{-1} and 1501-1514 cm^{-1} due to the C=C vibrations of benzenoid and quinoid units, respectively (Shackelette *et al.,* 1988). The strong broad peak at 3330-3385 cm^{-1} may be due to the stretching vibration of N-H of secondary amines or O-H bond as was reported (Challier and Slade, 1994). The FT-IR spectrum of kaolinite is dominated by the band in Figures (2) centered on 1032–1028 cm^{-1} due to the asymmetric stretching vibration of Si-O bond. The weak absorption bands between 3670 and 3745 cm^{-1} are attributed to the OH stretching mode. The low intensities of these bonds are suggestive of the low amount of (Al-OH, Mg-OH-Al) content in kaolinite (Bhadra and Khastgir, 2007) But the stretching modes of C=N, C=C, and C-N are shifted to the lower wave numbers because of the incorporation of kaolinite composite.
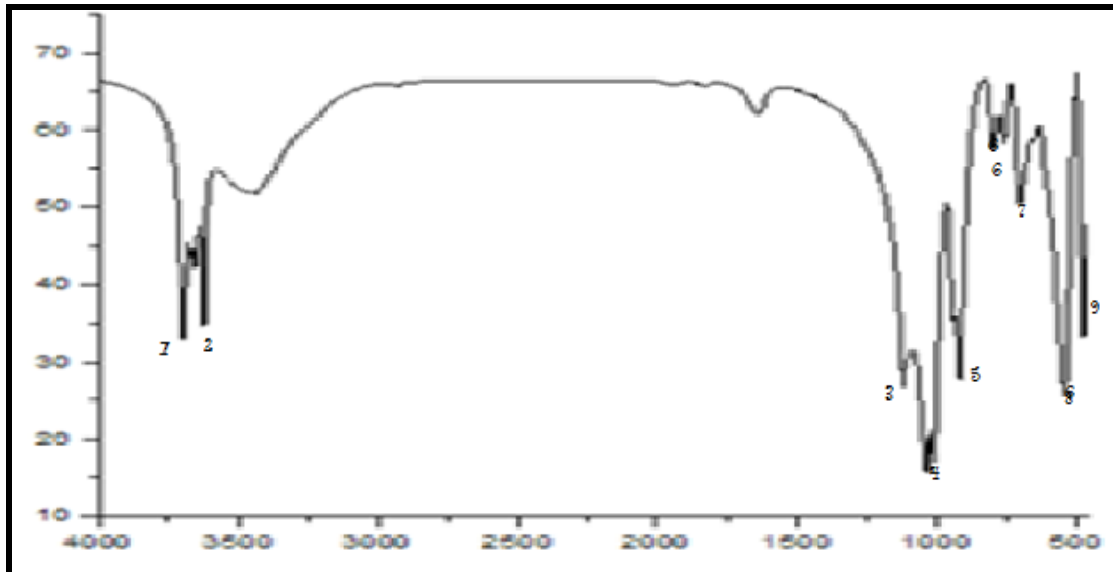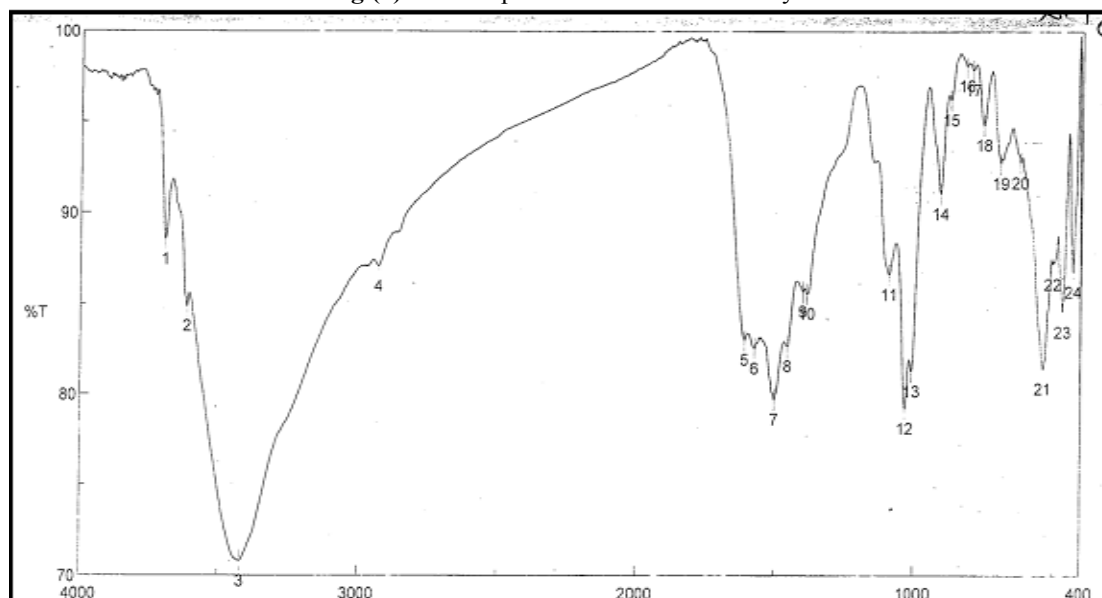

Fig (1): FT-IR spectrum Pure kaolinite clay.

Fig. (2): FT-IR spectrum of PANAA/kaolinite composites

Thermogravimetric Analysis (TGA)

Thermal stability of PANAA/kaolinite clay composite shad been analyzed and compared with that of pure kaolinite under non-oxidative (inert gases) conditions. The weight loss patterns are shown in Figures (3 and 4) and the thermal degradation data of kaolinite and PANAA/kaolinite composite are listed in Table (1). The thermo grams of the samples taken between the room temperature and 1000°C were measured. The maximum char yield at 600°C was obtained for pure kaolinite and composite 54 and 68 respectively. The TGA data are summarized in Table (1). Results showed that the incorporation of kaolinite composite has better thermal stability than the pure kaolinite with no significant unwanted effect on the thermal degradation.
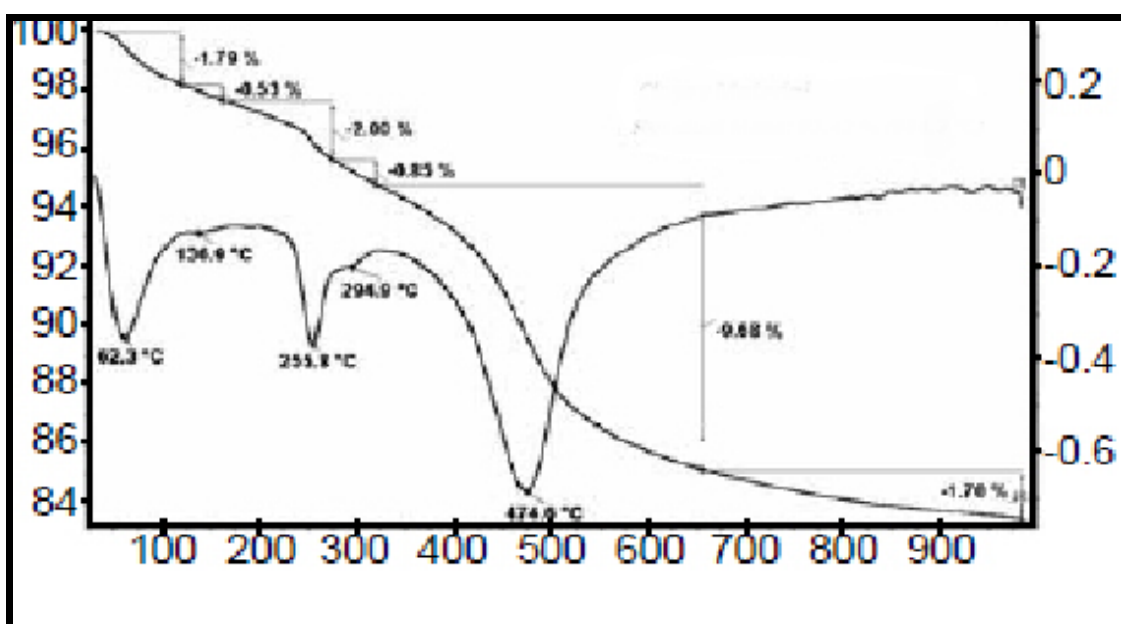
Table (1): Thermal degradation data of the kaolinite and PANAA/kaolinite composites.

Polymer code	$^aT_{15}$	Char yield at 500° C $^bW_{500}$	Char yield at 600° C $^cW_{600}$
Pure kaolinite	374	61	54
KC composite	487	73	68

$^aT_{15}$: Temperature of 15% weight loss.
$^bW_{500}$: Char yield % at 500°C, determined from TGA curve.
$^cW_{600}$: Char yield % at 600°C, determined from TGA curve.

Fig. (3): TGA and DTA curves of kaolinite composite
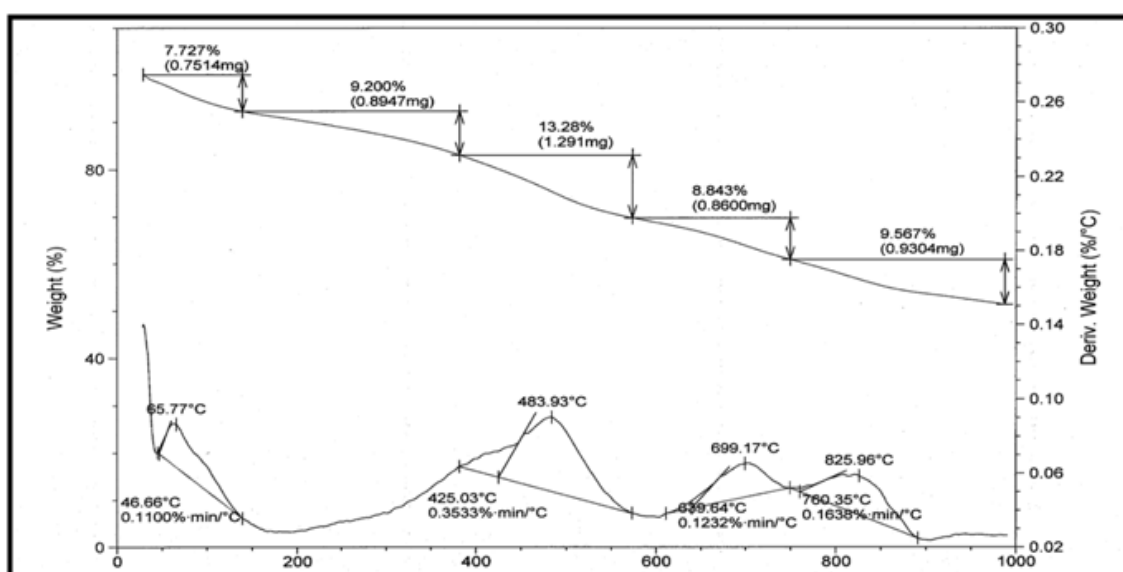
Fig. (4): TGA and DTA curves of PANAA/kaolinite composite

X-Ray Diffraction

The X-ray powder diffraction patterns for kaolinite and PANAA/kaolinite composite shown in Figures (5 and 6) are typical of fully crystalline polymers. The sharp peaks of crystallinity corresponding to kaolinite particles were recorded at 2θ angles of 24.88° and 12.46°. Consequently, PANAA/kaolinite composite exhibited three sharp peaks at 2θ angles of 44.62°, 24.88° and 12.46°. XRD pattern of PANAA/kaolinite composite containing kaolinite is similar to that of pure kaolinite. The basal spacing (24.88) of pure kaolinite does not exhibit any change indicates that PANAA EB did not intercalate into the kaolinite layers. Therefore, the kaolinite clay is just coated by PANAA EB copolymer and, it did not change the crystalline structure of kaolinite clay. Similar results have been reported (Saikia and Parthasarathy, 2010; Epstein *et al.,* 1987). Therefore, the prepared composite materials are crystalline material as shown from the X- ray diffraction patterns in Figures (5 and 6). All the spectra show crystalline structure without any amorphous character due to the absence of the broad peaks.
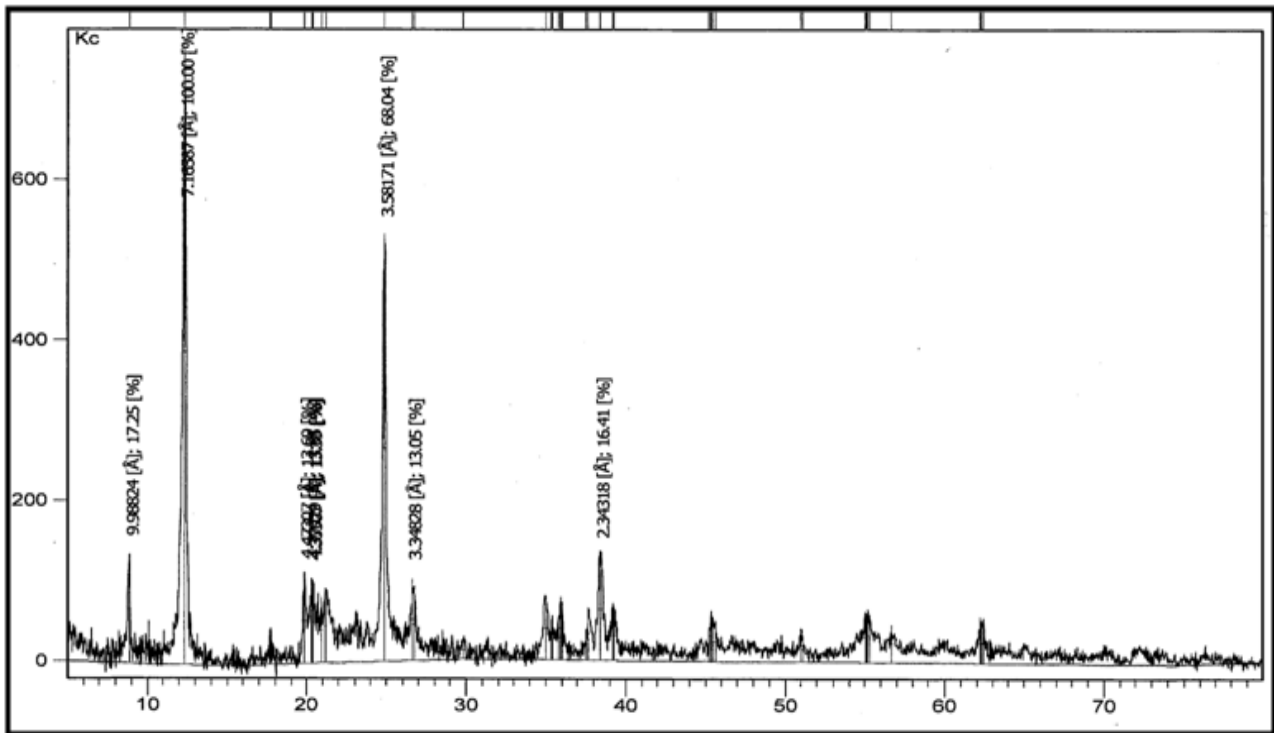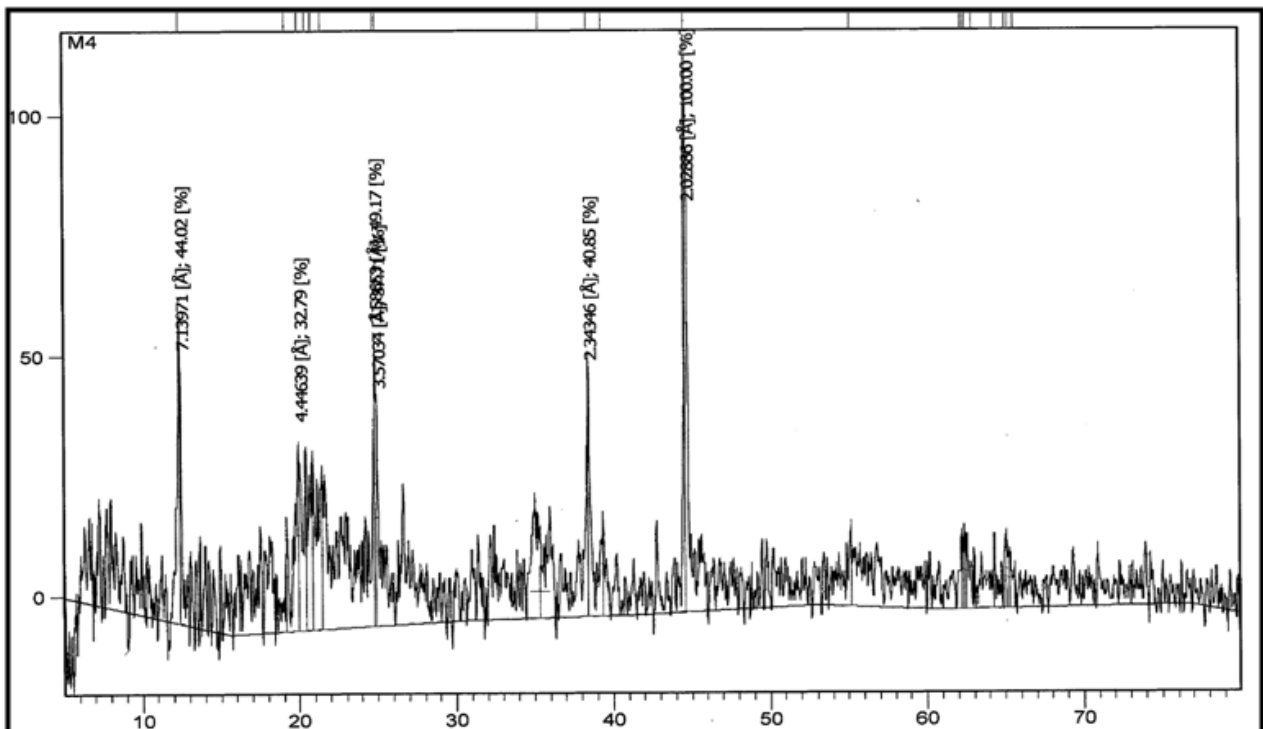

Fig. (5): XRD of kaolinite clay

Fig. (6): XRD of Poly (aniline co-anthranilic acid/kaolinite) composite

Morphology Analysis

Figures (7 and 8) showed the SEM images of pristine Kaolinite, the synthesized PANAA/kaolinite composites. These Figures showed pure kaolinite clay is flakes in shape. Scanning electron micrograph (SEM) revealed some interesting morphological differences between the pure kaolinite clay and PANAA emeraldine base-clay composites. The surface of pure clay was flaky texture reflecting its layered structure as shown. PANAA emeraldine base-clay composite has a flower petal-like appearance. It can be clearly seen in micrographs of all clay composites that the textures of both PANAA emeraldine base-clay are retained in the composites which are of different grain sizes. The micrographs of PANAA emeraldine base- Clay composites exhibit more ordered and dense structure (smaller sizes with high density of granules per unit area) comparing to both composite and the pure kaolinite clay (bigger sizes with less density per unit area). This also shows that polymerization of the copolymer occurs on the surface of kaolinite particles.
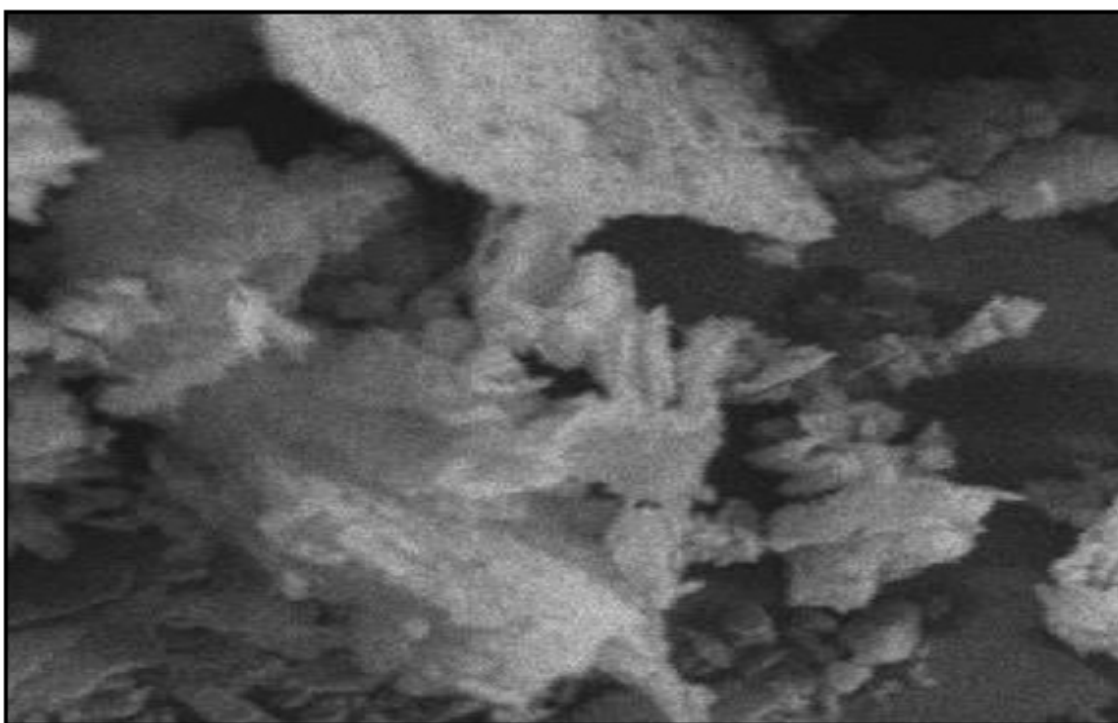

Fig. (7): SEM micrographic of Kaolinite-×2500

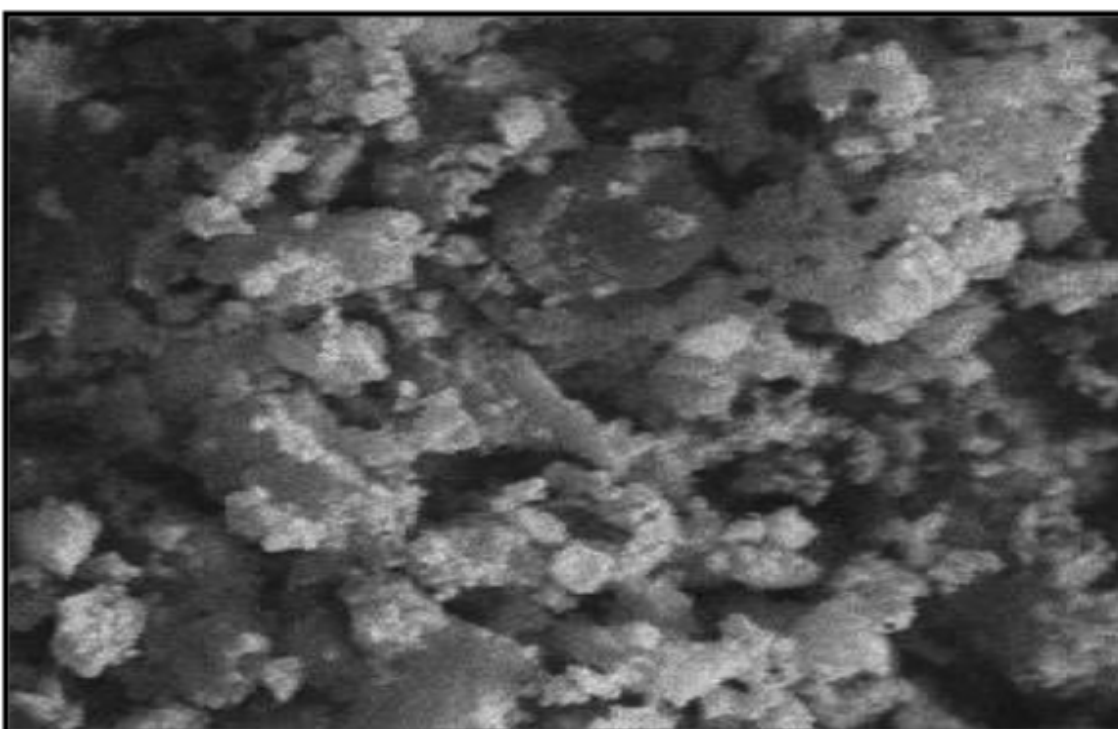**Fig. (8):** SEM micrographic of PANAA/kaolinite composite ×2500

Removal of Cu (II) ions using kaolinite and poly (aniline co-anthranilic acid)/kaolinite clay composite.

The effect of amount of sorbent on the removal of metal ions.

Effect of weight of pure kaolinite and its composite on the removal percentage of Cu (II) ions are given in Figure (9). It was found that the removal percentage reached maximum value at 0.4 gm/L for both. The removal percentage of these metal ions showed increasing trend, increased from 14.52% to 44.2% in case of pure kaolinite and from 19.85 to 73.65% in case of composite as shown in the Figure (9). The increasing of removal percentage of Copper ions with increasing kaolinite and PANAA/kaolinite Composite amount may be due to increase in surface negative charge and decrease in the electrostatic potential near the solid surface that favors sorbent-solute interactions. This result shows that the using of modified kaolinite is more effective than the pure clay.
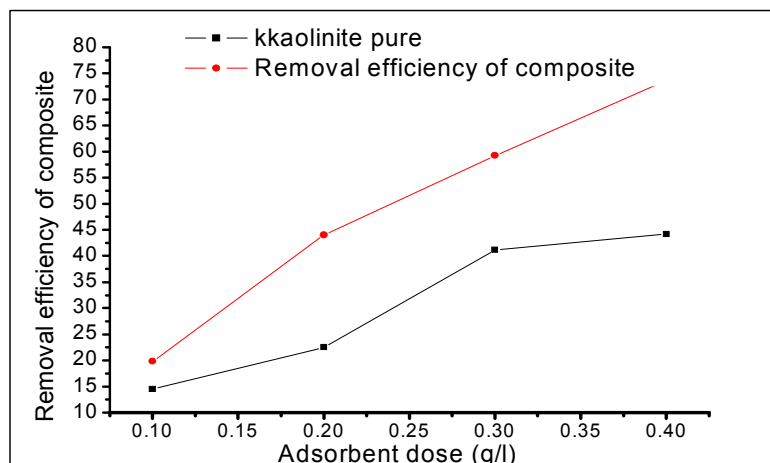

Fig. (9): Effect of adsorbent dose on the removal of Cu (II) percentage using kaolinite and PANAA/kaolinite composite.

The effect of pH on the removal of metal ions.

The pH of solutions was varied from 3 to 12 by the addition of 0.1 M nitric acid and/or 0.1 M sodium hydroxide. It was found that copper with kaolinite and its composite have almost the same trend of sorption in the pH range 3 to 12. There was an observed, increase in adsorption as pH of metal ion solution increased. But the optimal pH for Copper was 5 with the pure clay and 6.5 with the modified clay. The effect of pH on the adsorption of Cu (II) by kaolinite and PANAA/kaolinite composite is shown in Figure (10). At pH higher than 6.5 metals were precipitated due to formation of hydroxides. At low pH there is low adsorption, this may be attributed to the surface of the composite containing a large number of active sites. Consequently, it may become positively charged at low pH, leading to increase the competition between H^+ and the metal ions for available adsorption sites. However, as pH increases, this competition decreases as these surface active sites become more negatively charged, which enhances the adsorption of the positively charged metal ions through electrostatic force of attraction (Stafstrom *et al.,* 1987). In this study, the pH [5, 6.5] for the removal of Cu (II) was determined as the optimum pH in removal of copper from aqueous solution by clay and kaolinite clay composite respectively.

The effect of contact time on the removal of metal ions

The adsorption of metal ions on the modified PANAA/kaolinite composite can be described as a function of the contact time as shown in Figure (11). The adsorbent loading was kept at a constant value of 0.4 g and a contact time from 0 to 120 min was employed. The majority of metal ions in adsorption equilibrium were achieved between 10 and 25 min for all studied ions. Adsorption first followed a linear rising in which instantaneous extremely fast uptake takes place, and then a stationary state was observed. As shown in Figures (11) the removal of metal ions was attained in the first 25 min for Cu ions and the concentration became almost constant after 30 min. The fast initial uptake was due to the accumulation of metal ions on the surface of kaolinite and PANAA/kaolinite composite. It was concluded that 20 min was sufficient for sorption to attain equilibrium. This result revealed that adsorption of Cu (II) is fast and the equilibrium was achieved by 25 min of contact time. Taking into account these results, a contact time of 25 min was chosen for further experiments.

CONCLUSION

Thermal study of kaolinite and Polyanilin–Anthranic acid/kaolinite composite showed that the composite have more thermal stability than the pure kaolinite. (PANAA)/kaolinite composite was effective, for which the removal reached around 70% of copper cations. Adsorption of studied heavy metals was slightly acidic pH-dependent and the results showed that the optimum pH for the removal was found to be 6.5. The optimum time to remove the high amount of the heavy metals is 20 min then by time the removal graph showed a stationary line. Finally from the above we can conclude that (PANAA/KC) composite can be used as effective adsorbent for the copper in the industrial wastewater and it is more effective than the pure clay.
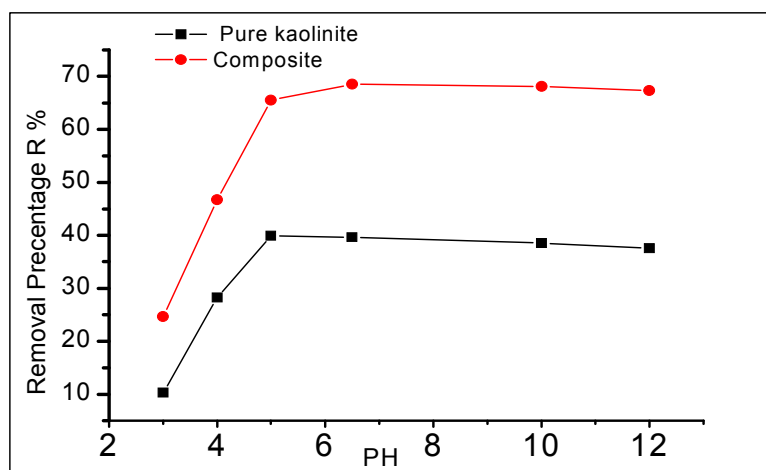
Fig. (10): Effect of pH on the removal of Cu (II) percentage using Kaolinite clay and PANAA/kaolinite composite, adsorbent dose = 0.4 g/L
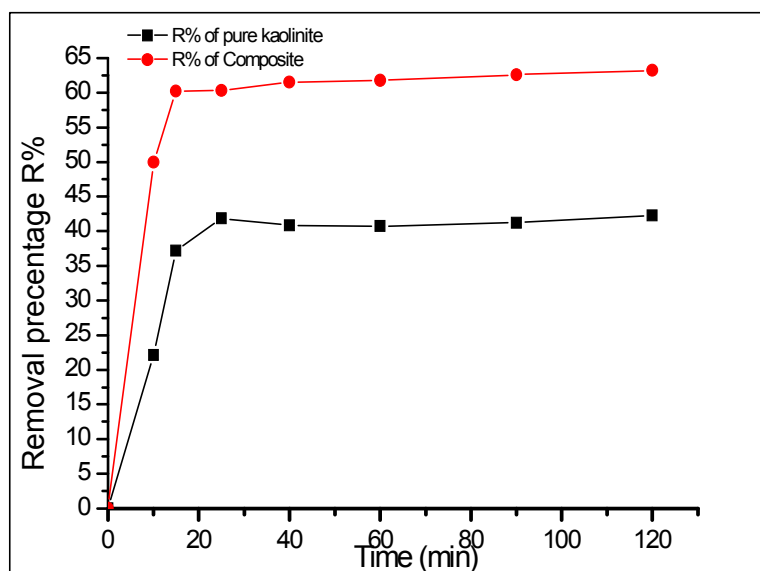

Fig. (11): Effect of Time on the removal of Cu (II) percentage using Kaolinite clay and PANAA/kaolinite composite, adsorbent dose = 0.4 g/L and pH 6

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