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Preparation and Characterization of Poly (Anilinco-Anthranilic Acid)/Kaolinite Composite and Use It in Removal of CU (II) and CD (II)

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Abstract:
Copolymers of aniline and o-anthranilic acid (PANAA)/ kaolinite clay composites were synthesized by 5:1 molar ratios of the respective monomers with different percentages of kaolinite clay particles via in situ chemical co-polymerization. The spectral characteristics of the resulting copolymers were investigated. The composite was characteristic by measuring the UV-Vis, FT-IR,TGA , and SEM .Chemically synthesized polyaniline-anthranilic acid/kaolinite (PANAA/kaolinite) composites were used as adsorbent materials for the removal of Cu (II) and Cd (II) from aqueous solutions. The effects of initial kaolinite concentration, temperature, pH, adsorbent dose and contact time parameters onto the adsorption of cadmium and copper ions from aqueous solutions were investigated.

Keywords: *Adsorotion- Heavy metal -composite materials/kaolinite clay- poly aniline co-anthranilic acid*

1. Introduction

Fresh water is already a limiting resource in Egypt and many parts of the world. In the next decades, it will become even more limiting due to increased population, urbanization, and climate change. This limitation is caused not just by increased demand for water, but also by pollution in freshwater ecosystems. Pollution decreases the supply of usable water and increases the cost of purifying it. Major water pollutants include a variety of organic and inorganic chemicals such as heavy metals, dyes and industrial compounds. They can affect human health and/or interfere with industrial or agricultural water use. If the level of a pollutant in the water supply exceeds an acceptable level for given water use, the water is considered unsafe or too degraded for that use. Solutions to such pollution problems, therefore, usually focus on reduction of pollution at the source and/or treatment of the polluted water prior to use [i-v]. We can use the adsorption process to remove the heavy metals and dyes from waste water. The adsorption process can be either physical or chemical in nature, and frequently involves both. Physical adsorption involves the electrostatic forces between the different electric charges on the adsorbent and adsorbate. on the other hand, Chemical adsorption is the product of a reaction between the adsorbent and the adsorbate [vi]. In recent years, stringent government regulations have made it mandatory to stop such effluents, unless they are treated properly; hence, the removal of color from the effluent discharge has become environmentally important [vii, viii].

2. Experimental

2.1. 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.

2.2. Preparation of (PANAA)\Kaolinite

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 (0.0%, 1%, 5%, 10%, 20%, 30%, 40% and 50%) 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 $K_2Cr_2O_7$) was slowly added into the reactor. Then, the reaction was kept for 24 h at 0°C. Ammonia solution (15 ml of 33% NH_4OH 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 h. The dark green dried powder affords (PANAA EB) (Ao) and (PANAA)/ kaolinite clay composites (A1, A2, A3, A4, A5, A6 and A7), respectively. The copolymer yield was calculated using the following relationship:

$$\text{Polymer yield} = \frac{100 \times \text{Amount of polymer (g) produced}}{\text{Amount of aniline and antharanilic acid}}$$

3. Result and Discussions

3.1. Fourier Transforms Infrared Spectroscopy (FT-IR Spectra)

The FT-IR spectra of the copolymers PANAA/kaolinite composites (A0-A7) are shown in Figures: [(3.1) to (3.8)]. The spectra of either PANAA EB or PANAA /kaolinite composites (A0-A7) 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 (ix).The number of quinoid units was almost higher than the number of benzenoid units in PANAA and PANAA /kaolinite composites (A0-A7) as there were apparent differences in the relative intensity of quinoid to benzenoid band which is a measure of the degree of the oxidation of the polymer chain (155). The band appeared at 1375–1384 cm-1 is due to C-N stretching vibrations of benzenoid-quinoid-benzenoid sequence [x]. The strong band at 1159 cm^{-1} is the characteristic band of the charged defects [xi]. The spectra of copolymers showed similar bands as those reported for PANI in absence of anthranilic acid AA with exception of C=O absorption band at ca. 1702–1790 cm^{-1}. Therefore, we can distinguish the copolymer with homo polymer by this characteristic band. It can be inferred that the AA had been introduced into the polymer chain successfully. The weak C=O absorption band is due to low intensity of this band which is suggestive of the low amount of AA content. This result is compatible with the spectra published elsewhere [ix]. 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 [xii]. The FT-IR spectrum of kaolinite is dominated by the band in Figures [(3.1) to (3.8)] 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 [xiii] 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.

3.2.Ultraviolet-visible absorption spectra measurement (UV-Vis)

The UV-Vis absorption spectra of copolymers PANAA and PANAA/kaolinite composites (A0-A6) in DMF are shown in Figure (3.9). It can be seen that, the copolymers showed two major absorptions appeared at about 292 and 335 nm, which are attributed to л ►л* transition at higher energy side. Therefore, it is a measure of the extent of conjugation between the adjacent phenyl rings and benzenoid to quinoid exciton transitions at lower energy side[xiv, xv]. Moreover, the complete disappearance of the peak at 590 nm in the UV-Vis spectra of PANAA/kaolinite composites was detected. Obviously, it indicates that insertion of PANAA EB has this effect due to an interaction at the interface of kaolinite clay particles.

3.3. Thermo gravimetric Analysis (TGA)

Thermal stability of PANAA /kaolinite clay composite shad been analyzed and compared with that of pure polymer under non-oxidative (inert gases) conditions. The weight loss patterns are shown in Figures [(3.10) to (3.17)] and the thermal degradation data of PANAA and PANAA/kaolinite composite are listed in Table 1. The thermo grams of the polymer samples taken between the room temperature and 1000°C were measured. In case of absence of kaolinite particles, the first weight loss (~11.43%) at 120°C of PANAA (A0), is attributed to the loss of water molecules. The second stage within the temperature range of 120–300°C is related to removal of CO2 molecules from the PANAA EB copolymer as was reported (xvi). However, in case of presence of kaolinite particles in A5, A6 and A7, it is obvious that the weight loss due to the loss of water molecules (~9.43, ~9.02, and ~8.19%) respectively, occurred at ~150°C. The weight loss observed in A0, A1, A2, A3, A4, A5, A6 and A7 between 300 and 900°C corresponds to the thermo oxidative degradation of the polymer chain similar results were reported (xvii). The present results suggest that the use of PANAA/kaolinite (A5, A6 and A7) offers some advantages in terms of thermal stability over PANAA (A0) at temperature >300°C, under this experimental concentration and conditions. DTA curves illustrated endothermic peaks around 65, 135 and 586°C, while the exothermic peaks were observed. The temperature of 15% weight loss of pure PANAA (A0) was 315°C, but that of the PANAA/kaolinite composite (A5, A6 and A7) was 487, 510, and 560°C respectively. The 50% degradation temperature of bare PANAA (A0) was 770°C, but that of the PANAA/kaolinite composite (A5, A6 and A7) was over 900°C. Char yield is an easy and important measurement which correlates to the ability to sustain combustion[xviii]. The maximum char yield at 600°C was obtained for polymer A7 (74%) and the minimum was obtained for polymer A0 (58%) in nitrogen. The TGA data are summarized in Table 1. Results showed that the incorporation of kaolinite composite has better thermal stability than the bare copolymer PANAA with no significant unwanted effect on the thermal degradation.

3.4. Morphology Analysis

Figures [(3.18) to (3.21)] showed the SEM images of pristine Kaolinite, the synthesized PANAA and PANAA /kaolinite composites. This 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 in Figure [(3.18) to (3.30)]. PANAA EB has a rod like network texture and 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 20% composites exhibit more ordered and dense structure (smaller sizes with high density of granules per unit area) comparing to both PANAA EB 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.

4.Removal of CU(II) and CD(II) from Aqueous Solutions Using Different Percentage from Kaolinite at Poly(Aniline Co-Anthranilic Acid)/ Kaolinite Clay Composite

By using 100 ppm Cu (II) and Cd (II) solutions with different kaolinite percentage (A2, A3, A5, A6, A7) the removal % reaches maximum at A5 as the result in table (4.1), (4.2) and figures (4.1), (4.2) show. There for A5 could be used for all the other effects. The sorption of Cu (II) and Cd (II) ions on modified PANAA/kaolinite Composite was studied by batch method. The general method used for this study is described as follows: 0.4 g from A5 (PANAA/kaolinite clay) with kaolinite 30% was equilibrated with 50 ml of the metal solution of known concentration in a stoppered glass flask at a fixed temperature and the stirring speed was 500 rpm. The pH of solution was adjusted with diluted 0.1 M NaOH or 0.1 M HNO_3 until the equilibrium was achieved. A known volume of the solution was removed and filtered for metal analysis by atomic absorption. The effect of pH on adsorption of Cu (II Cd (II) ions onto the modified PANAA/kaolinite was investigated by varying the solution pH from 3 to 12. The effect of temperature and adsorbent concentration on uptake of metals were then examined. The Cu (II) and Cd (II) percent Removal (R %) was calculate using the following equation:

$$\text{Removal percentage (R\%)} = \frac{C_i - C_e \times 100}{C_i}$$

Where C_i(mg/l) = 100 ppmand Ce (mg/l) are the initial and equilibrium metal concentration, respectively (mg/l).

4.1. The Effect of Amount of Sorbent on the Removal of Metal Ions

Effect of weight of composite on the removal percentage of Cu (II) and Cd(II) solution are given in table [(4.3) , (4.4)]respectively and figures [(4.3) ,(4.4)] represented the effect of weight of composites on the removal percentage of Cu(II)and Cd (II) solution, respectively it was found that the removal % reached maximum at 0.4 gm/L the percentage removal of these metal ions showed increasing trend, increased from 19.85 to 73.65 %in Cu (II) and 12.8 to 66.8 % for Cd (II)as shown in the figures : [(4.3) , (4.4)]. The increased Removal percentage of these studied metal ions with increasing PANAA/kaolinite Composite may be due to increase in surface negative charge and decrease in the electrostatic potential near the solid surface that favors sorbent-solute interactions.

4.2. 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 and cadmium have almost the same sorption in the pH range 3 to 12. The optimal pH for Copper and cadmium was 6.5. At pH higher than 6.5 metals were precipitated due to formation of hydroxides. The effect of pH on the adsorption of Cu (II) and Cd (II) by PANAA/kaolinite Composite is shown in Figure [(4.5), (4.6)] There was an observed increase in adsorption as pH of metal ion solution increased. At pH of 6.5 Removal percentage of Cu(II) and Cd(II) on PANAA/kaolinite Composite were 68.6% and 59.4%, respectively. 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 [23] In this study, the pH at 6.5 for the removal of Cd(II) and Cu(II) was determined as the optimum point in removal of copper and cadmium in aqueous solution by modified kaolinite clay. Table [(4.5), (4.6)] show the result of the effect of pH on the Removal percentage (R%) of the Cu(II) and Cd(II).

4.3. 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 [(4.7), (4.8)].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 20 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

[(4.7), (4.8)] the removal of metal ions was attained in the first 20 min for Cu, and Cd and the concentration became almost constant after 30 min. The fast initial uptake was due to the accumulation of metal ions on surface of PANAA/kaolinite Composite clay adsorbent which is a rapid step. It was concluded that 20 min was sufficient for sorption to attain equilibrium. This result revealed that adsorption of Cu (II), Cd (II) is fast and the equilibrium was achieved by 20 min of contact time. Taking into account these results, a contact time of 20 min was chosen for further experiments.

4.4. Effect of Temperature

The adsorption of Copper and cadmium onto by PANAA /kaolinite composite. at different temperatures showed an increase in the removal percentage R% with increase in temperature. For example, with increase in temperature from 25 to 45°C, the adsorption capacity increased for Cu(II) from 46.75 to 59.75 mg/g, and for Cd (II) from 37.12to 49.26 mg/g, as shown in Table [(4.9), (4.10)] and figures [(4.9), (4.10)]. This indicates that the adsorption reaction was endothermic in nature. The increase in the adsorption capacity reflects the chemical interactions between adsorbent and adsorbate.

5. Table and Figures

polymer code	**$^{a}T_{15}$**	**char yield at 500° C bW_{500}**	**char yield at 600° C $^{c}W_{600}$**
A0	315	61	58
A1	340	63	60
A2	379	65	62
A3	429	68	63
A4	454	71	66
A5	487	73	68
A6	510	75	70
A7	560	76	74

Table 1: Thermal degradation data of the PANAA EB and PANAA EB/kaolinite composites, based on the TGA results in nitrogen atmosphere.

$^{a}T_{15}$: Temperature of 15% weight loss.

$^{b}W_{500}$: char yield % at 500°C, determined from TGA curve.

$^{c}W_{600}$: char yield % at 600°C, determined from TGA curve.

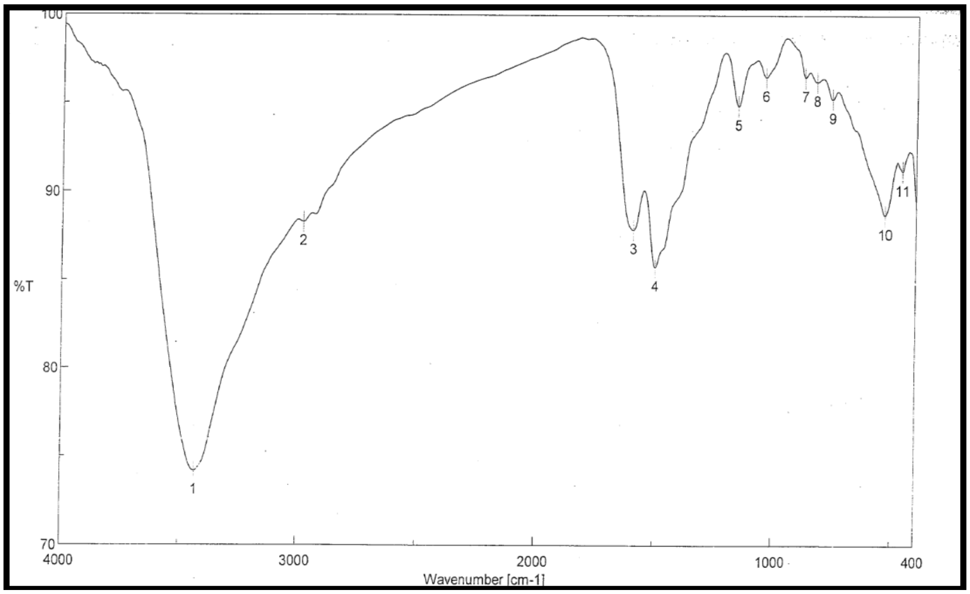

Figure 1: FT-IR spectra of PANAA EB A0 composites)

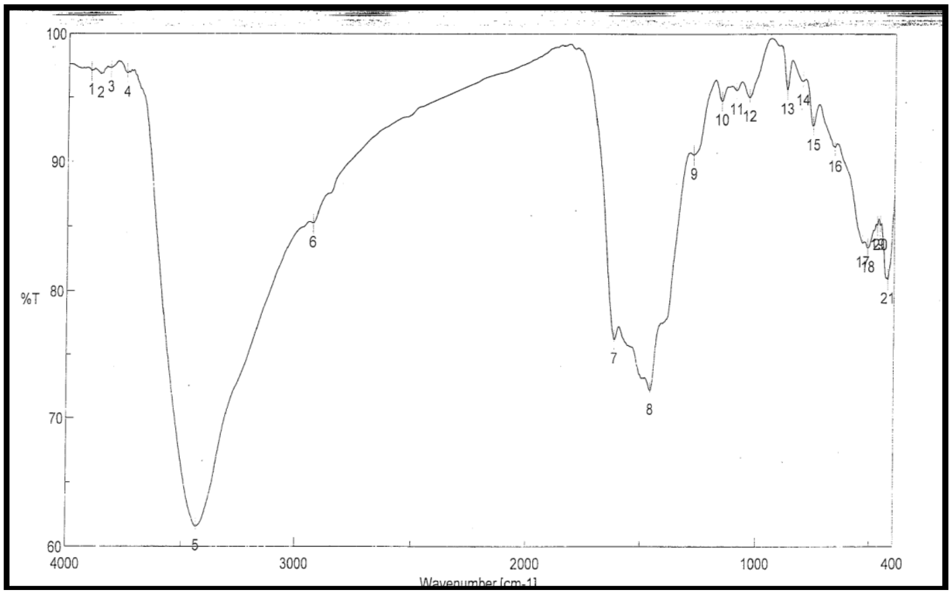

Figure 2: FT-IR spectra of PANAA EB / kaolinite A1 composites)

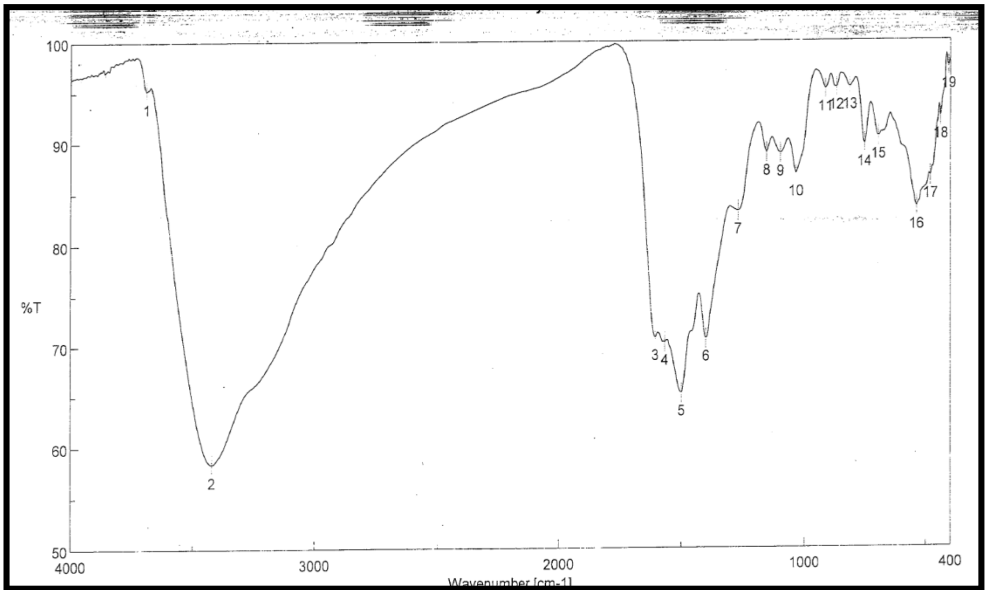

Figure 3: FT-IR spectra of PANAA EB / kaolinite A2 composites)

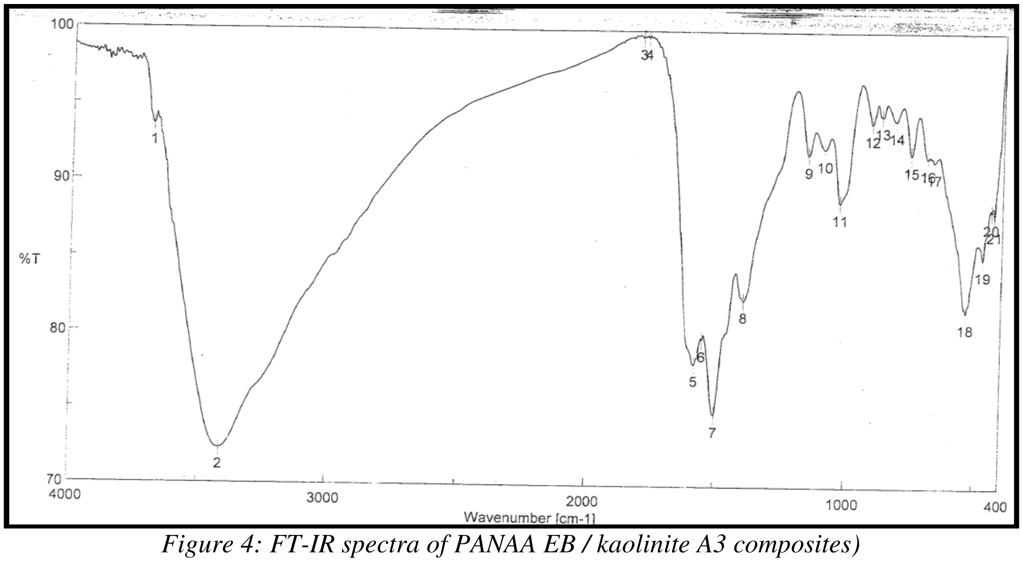

Figure 4: FT-IR spectra of PANAA EB / kaolinite A3 composites)

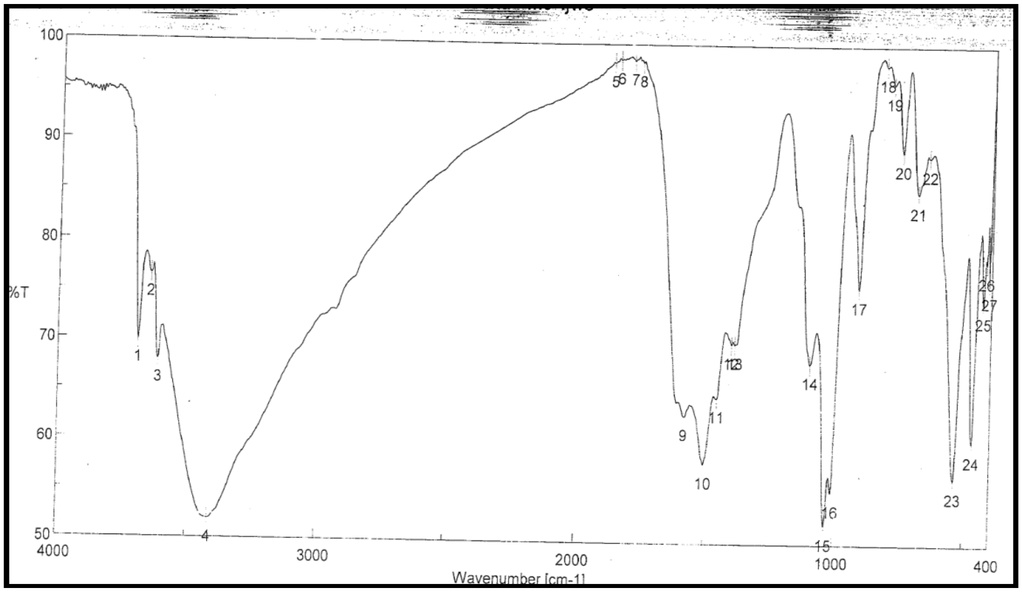

Figure 5: FT-IR spectra of PANAA EB / kaolinite A4 composites)

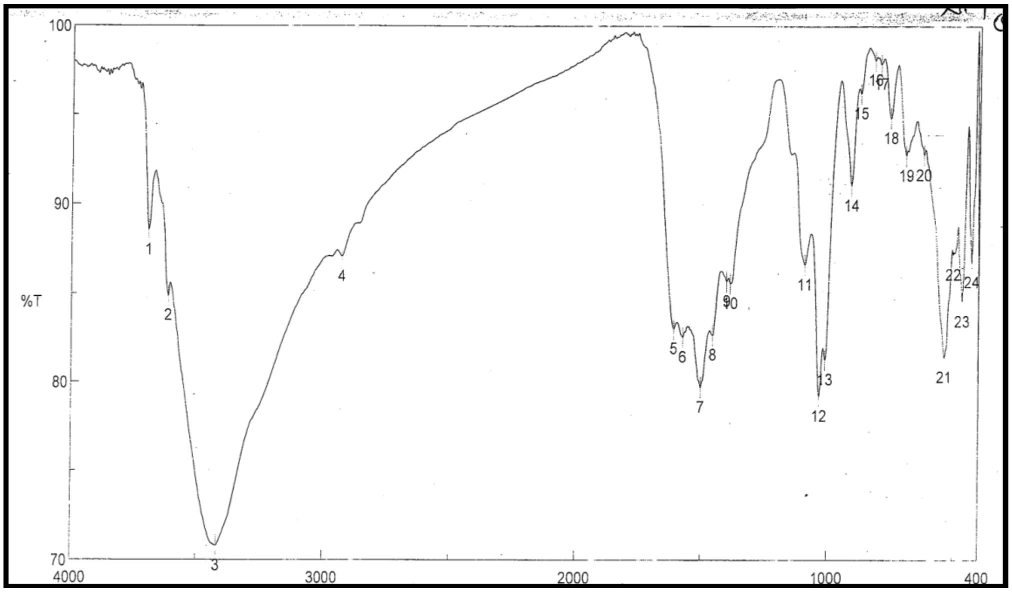

Figure 6: FT-IR spectra of PANAA EB / kaolinite A5 composites)

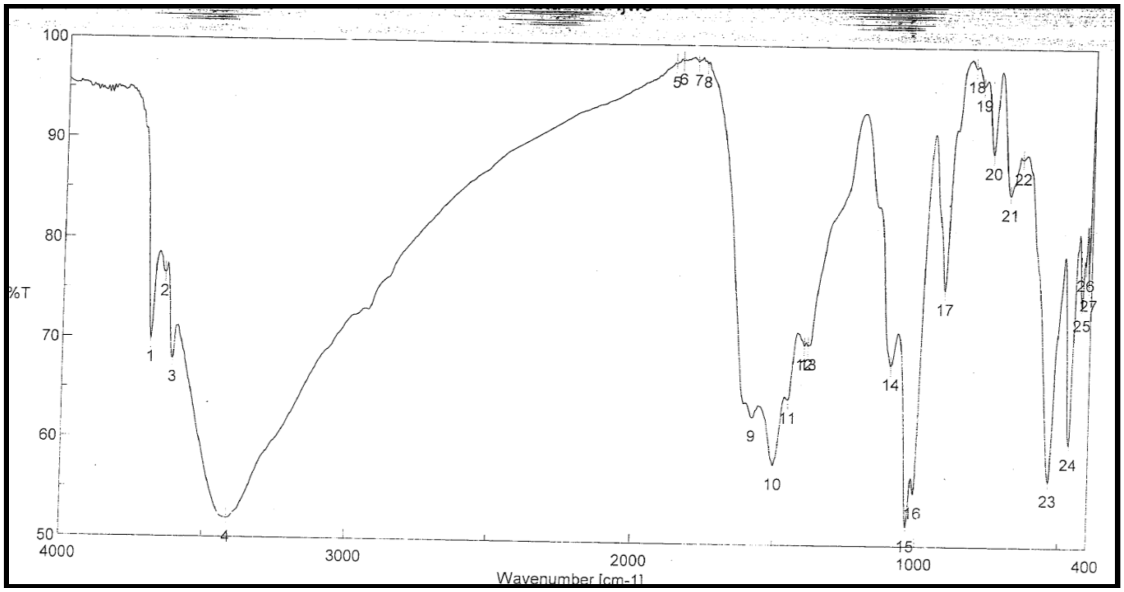

Figure 7: FT-IR spectra of PANAA EB / kaolinite A6 composites)

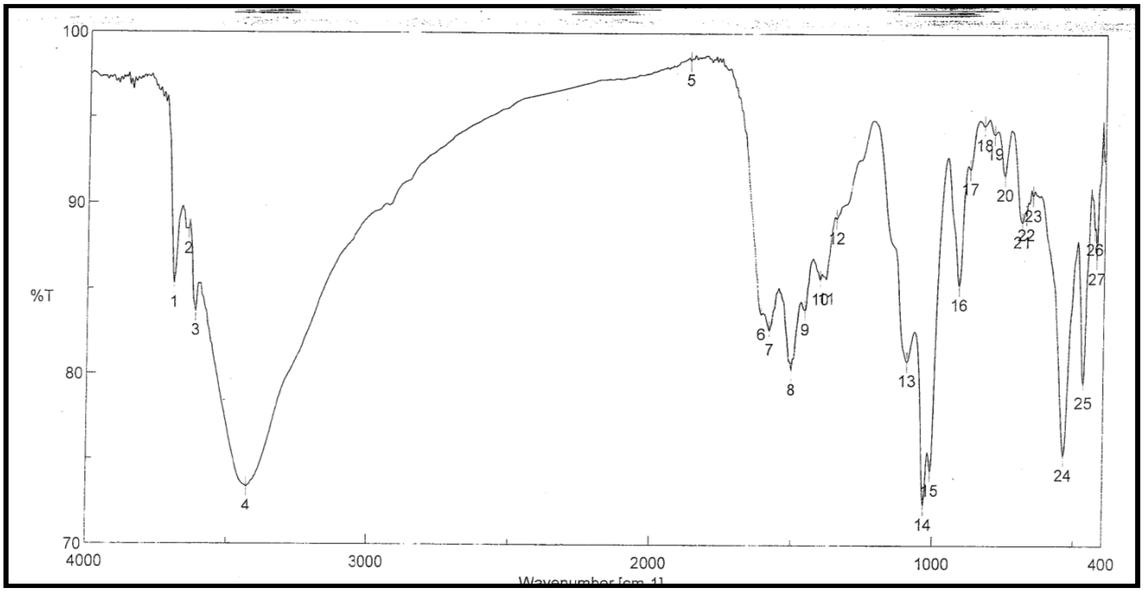

Figure 8: FT-IR spectra of PANAA EB / kaolinite A7 composites)

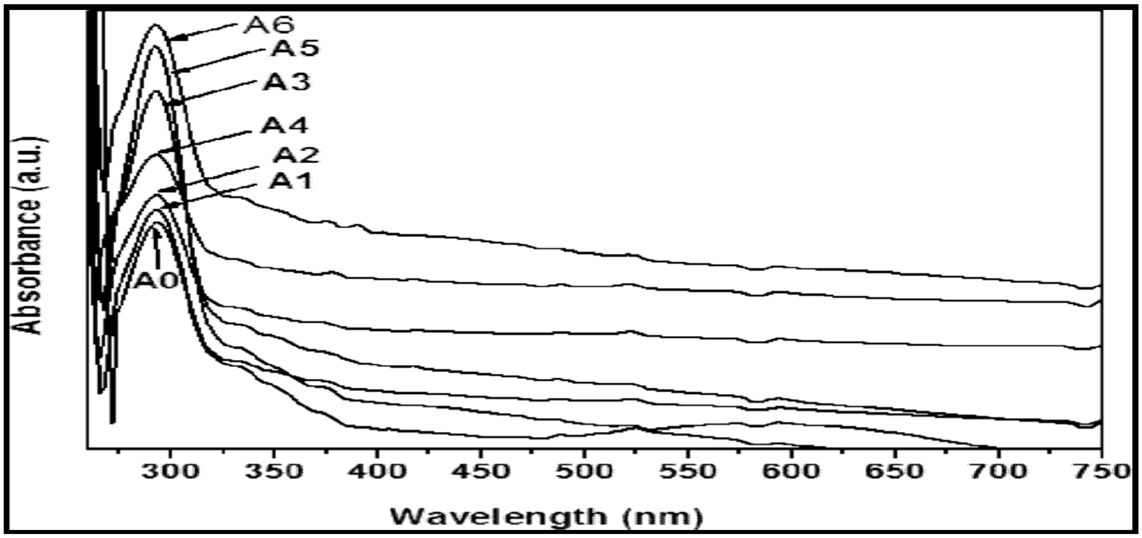

Figure 9: UV-Vis Spectra of PANAA EB and PANAA EB/kaolinitecomposites (A0-A6) in DMF.

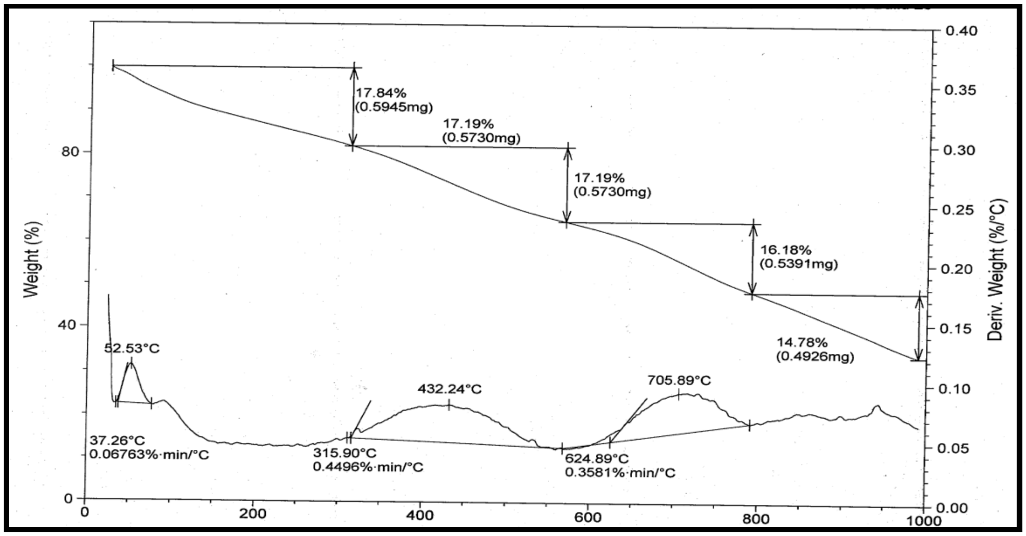

Figure 10 : Thermal analysis curves of (Ao) PANAA in nitrogen, (Heating rate=20C°/min.)

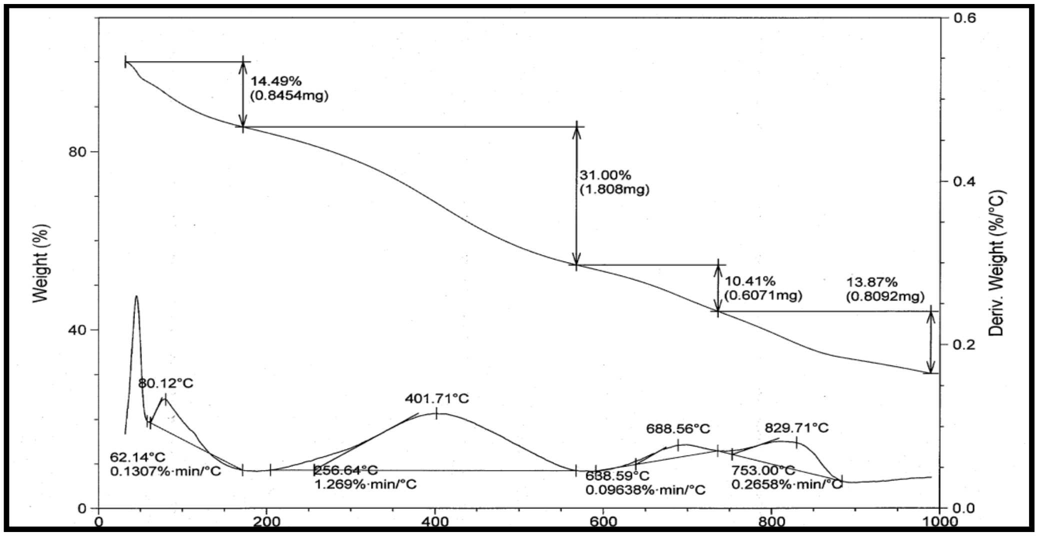

Figure 11: TGA=DTA curves of (A1) PANAA/kaolinite at nitrogen medium (at a heating rate of 20°C min^{-}1)

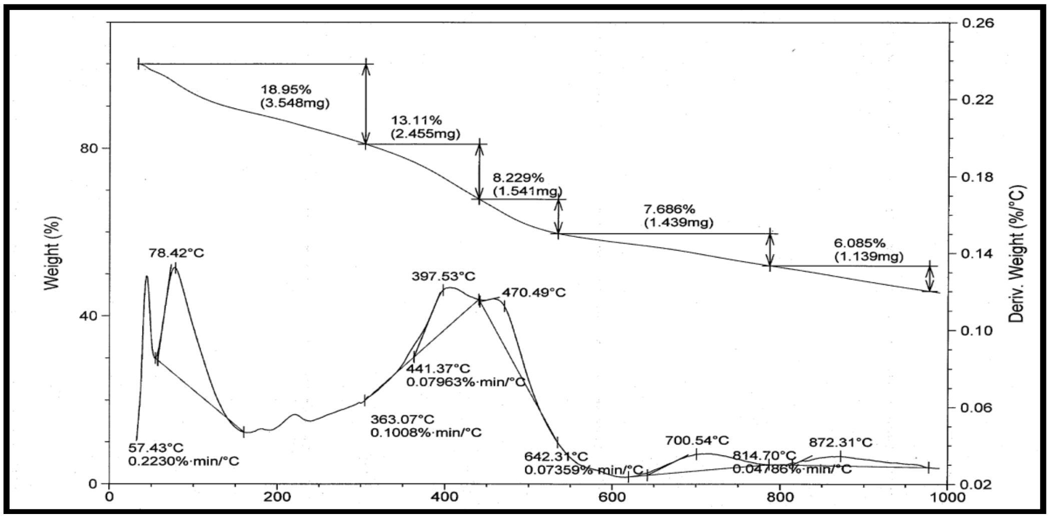

Figure 12: TGA=DTA curves of (A2) PANAA/kaolinite at nitrogen medium (at a heating rate of 20°C min^{-}1)

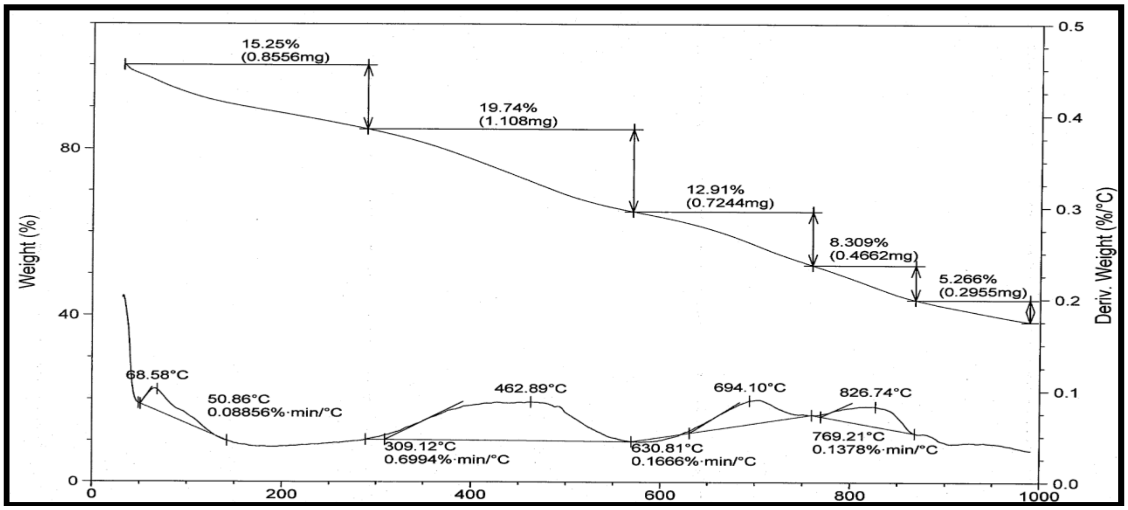

Figure 13: TGA=DTA curves of (A3) PANAA/kaolinite at nitrogen medium (at a heating rate of 20°C min-1)

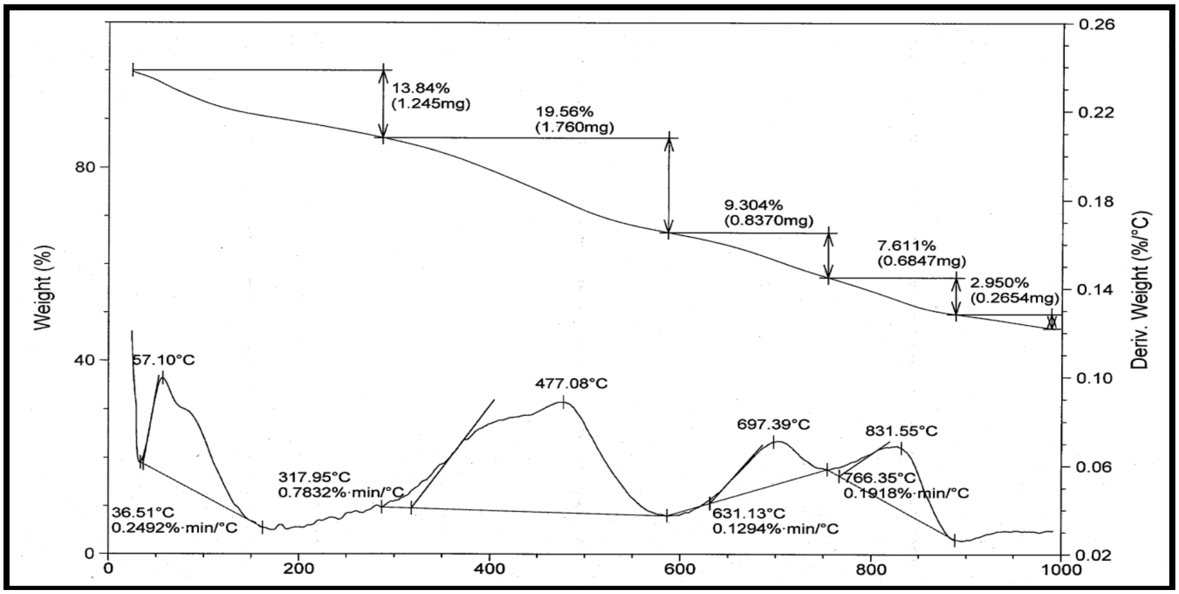

Figure 14: TGA=DTA curves of (A4) PANAA/kaolinite at nitrogen medium (at a heating rate of 20°C min-1)

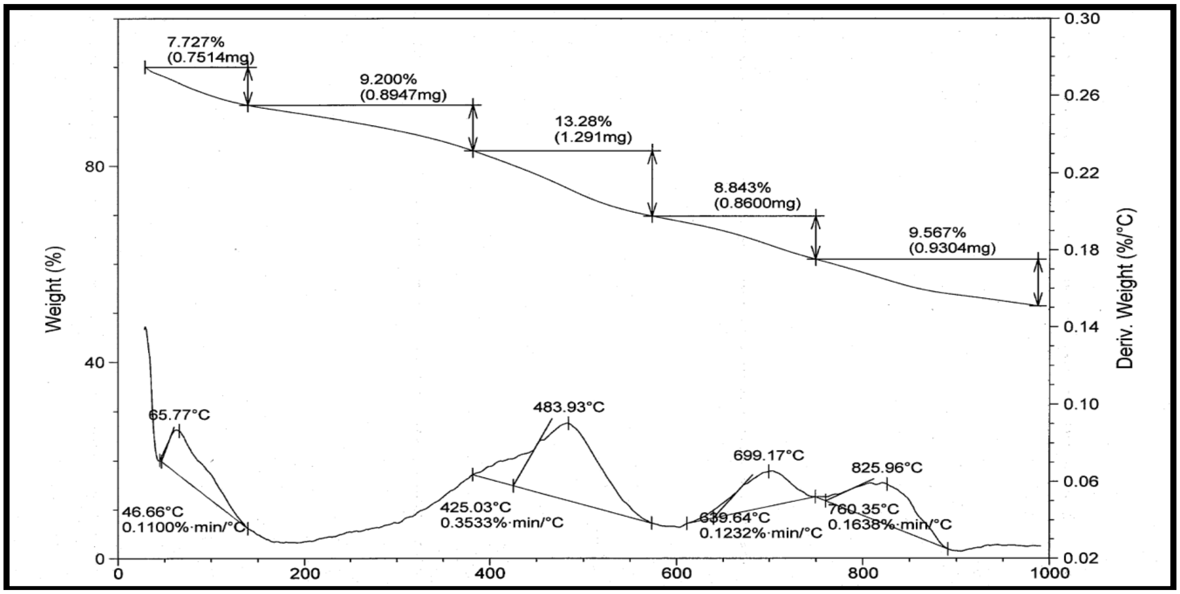

Figure 15: TGA=DTA curves of (A5) PANAA/kaolinite at nitrogen medium (at a heating rate of 20°C min-1)

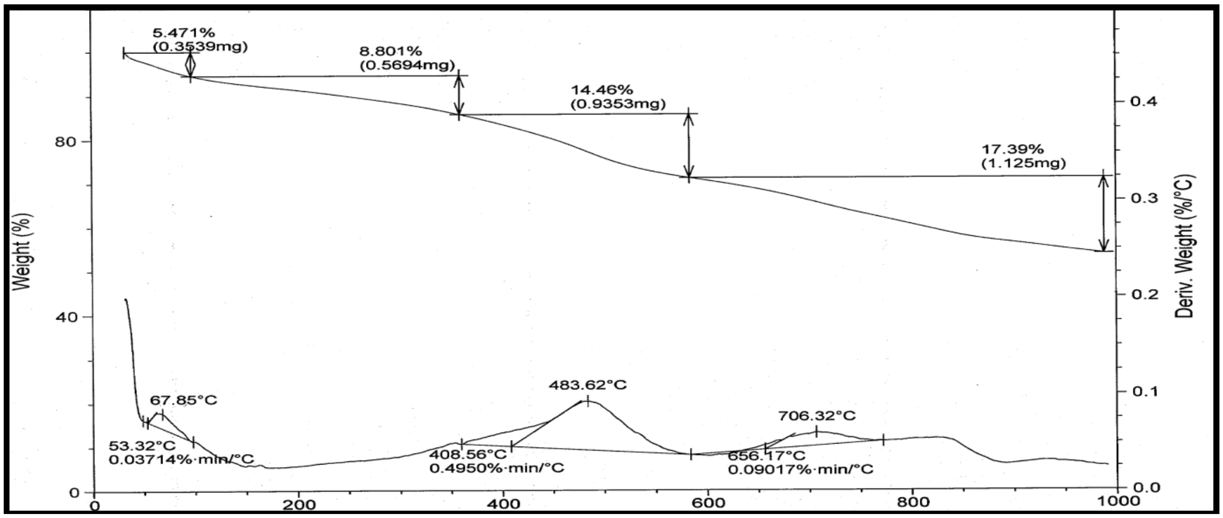

Figure 16: TGA=DTA curves of (A6) PANAA/kaolinite at nitrogen medium (at a heating rate of 20°C min^{-}1)

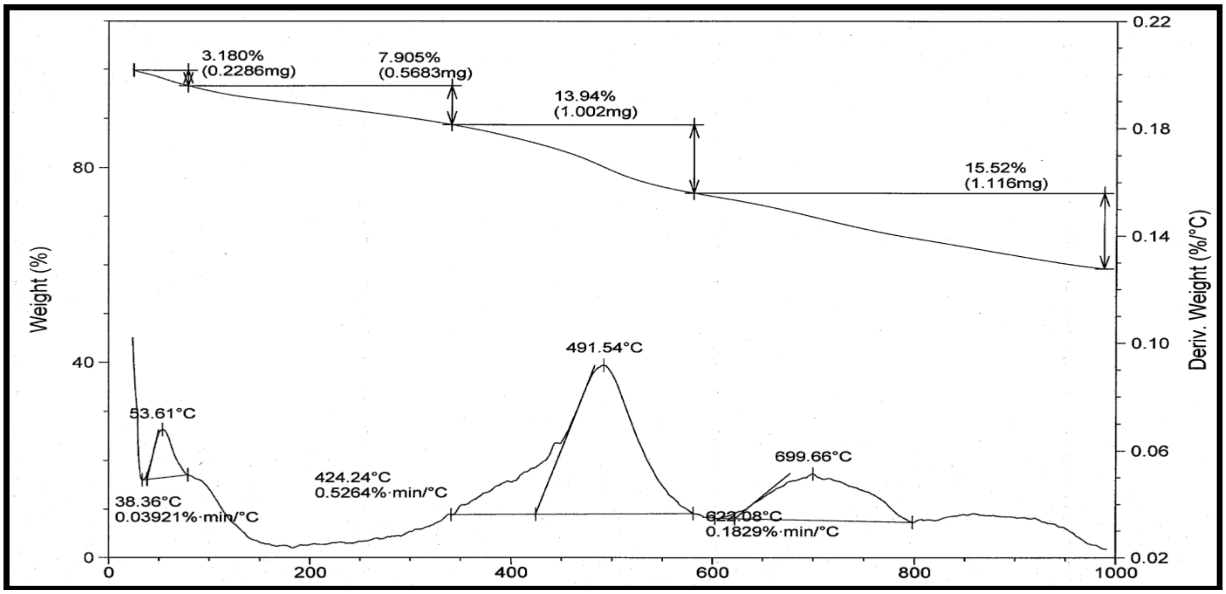

Figure 17: TGA=DTA curves of (A7) PANAA/kaolinite at nitrogen medium (at a heating rate of 20°C min^{-}1)

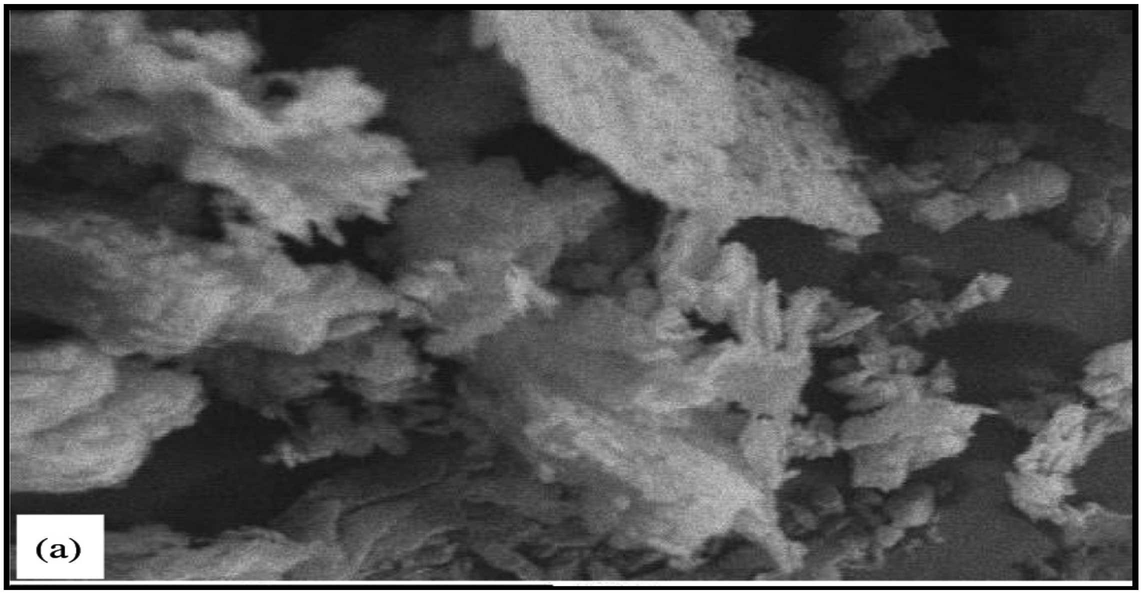

Figure 18: SEM micrographic of (a) pristine Kaolinite-2500×

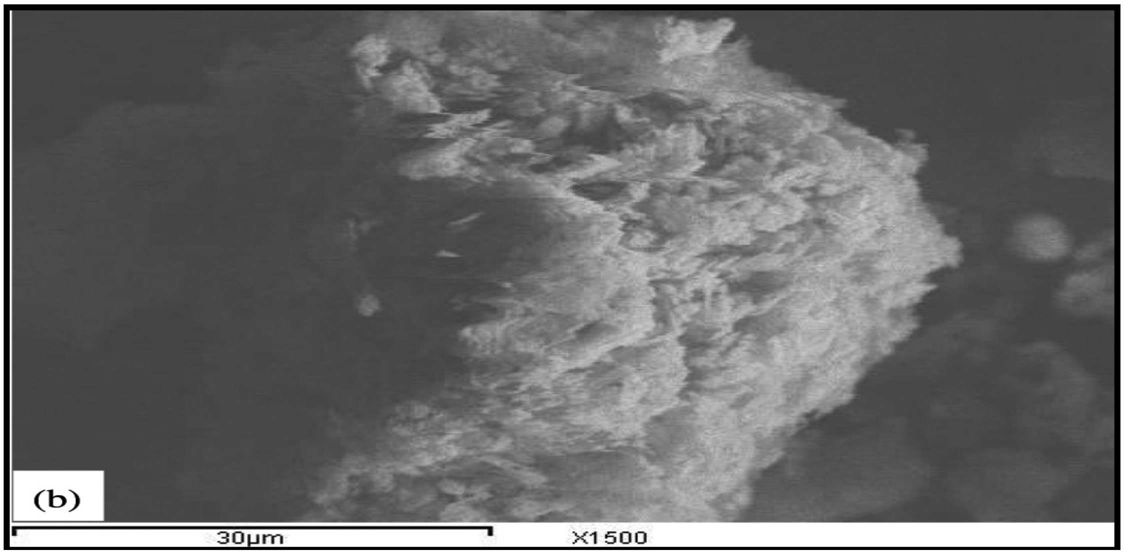

Figure 19: SEM micrographic of (b) pristine Kaolinite-1500×

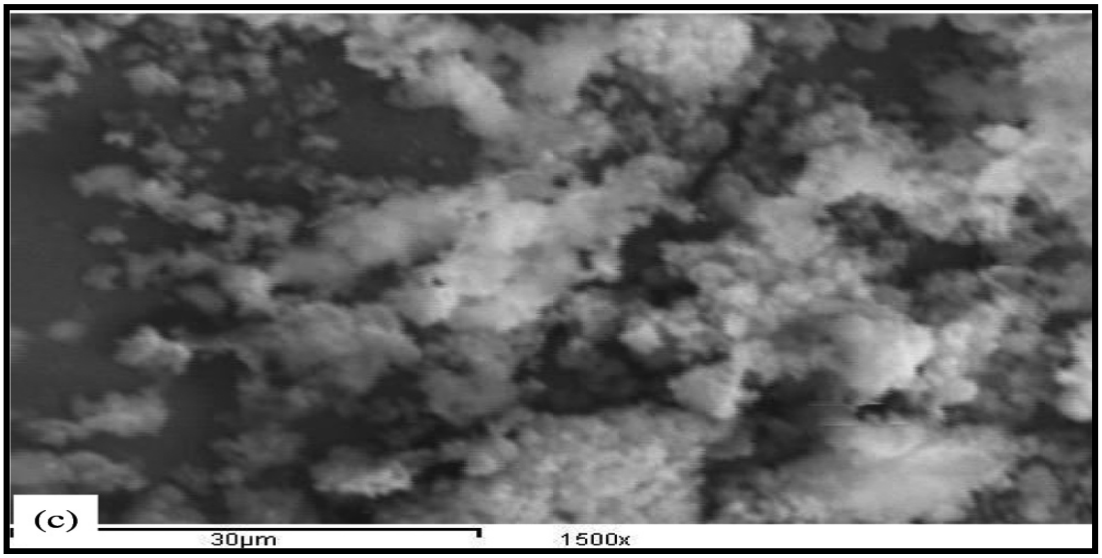

Figure 20: SEM micrographic of (c) pure PANAA EB-1500×

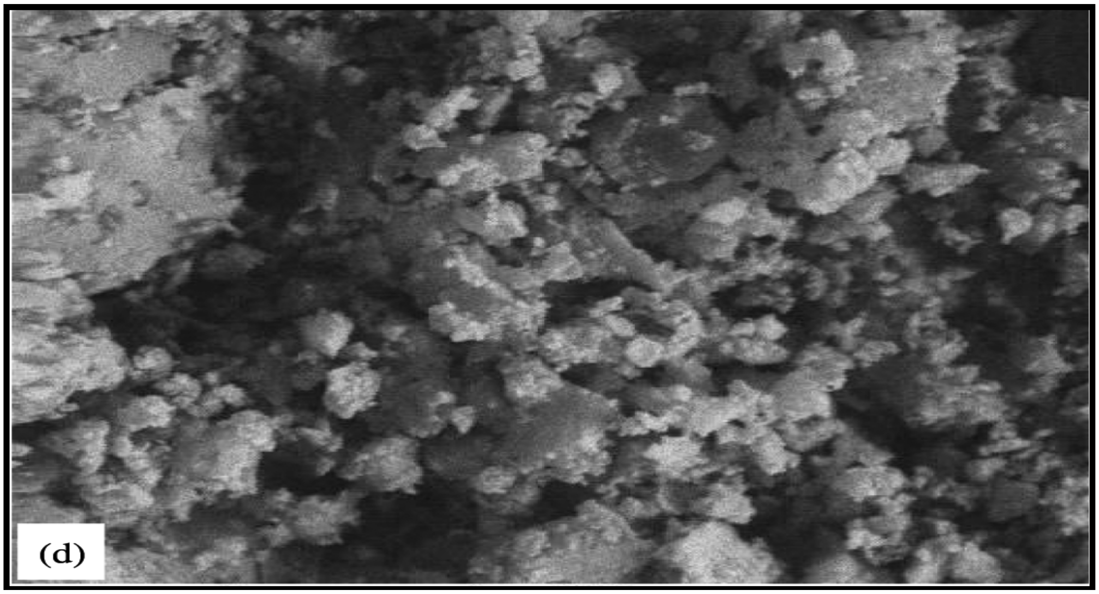

Figure 21: SEM micrographic of (d) pure PANAA EB/kaolinite at 1500×

Sample Code	[Cu(II)]ppm	Removal Percentage R %
A2	85	15
A3	65	35
A5	52	48
A6	59	41
A7	76	24

Table 2: The Removal percentage of Cu (II) with composites which have the different ratio of kaolinite clay.

Sample code	[Cd(II)]ppm	Removal Percentage R %
A2	72	28
A3	66	34
A5	61	39
A6	68	32
A7	69	31

Table 3: The Removal percentage of Cd (II) with composites which have the different ratio of kaolinite clay.

pH	Contact time (min)	Adsorbent dose (g/l)	[Cu(II)] ppm	Removal Percentage R %
6.5	120	0.1	80.15	19.85
		0.2	55.98	44.02
		0.3	40.7	59.3
		0.4	26.35	73.65

Table 4: Effect of adsorbent dose on adsorption of Cu (II) ions by PANAA /kaolinite . composite

pH	Contact time (min)	Adsorbent dose (g/l)	[Cd(II)] ppm	Removal Percentage R %
6.5	120	0.1	87.2	12.8
		0.2	64.35	35.65
		0.3	44.9	55.1
		0.4	33.2	66.8

Table 5: Effect of adsorbent dose on adsorption of Cd (II) ions by PANAA /kaolinite composite .

Adsorbent dose (g/l)	pH	[Cu(II)] ppm	Removal Percentage R %
0.4	3	75.32	24.68
	4	53.3	46.7
	6	34.5	65.5
	6.5	31.4	68.6
	10	31.9	68.1
	12	32.7	67.3

Table 6: Effect of pH on adsorption of Cu(II) ions by poly(aniline co-anthranilic acid)/ kaolinite clay composite:

Adsorbent dose (g/l)	pH	[Cd(II)]ppm	Removal Percentage R %
0.4	3	79.7	20.3
	4	62.8	37.2
	6	44.8	55.2
	6.5	40.6	59.4
	10	41.3	58.7
	12	41.8	58.2

Table 7: Effect of pH on adsorption of Cd(II) ions by poly (aniline co-anthranilic acid)/ kaolinite clay composite.

pH	Adsorbent dose (g/l)	Contact time (min)	[Cu(II)] ppm	Removal Percentage R %
6.5	0.4	10	49.7	50.2
		15	41.4	60.22
		25	41.07	60.35
		40	40.55	61.55
		60	40.4	61.78
		90	40.22	62.55
		120	40.11	62.25

Table 8: Effect of pH on adsorption of Cd(II) ions by poly (aniline co-anthranilic acid)/ kaolinite clay composite

pH	Adsorbent dose (g/l)	Contact time (min)	[Cd(II)]ppm	Removal Percentage R %
6.5	0.4	10	54.7	45.3
		15	41.4	58.6
		20	41.07	58.93
		40	40.55	59.45
		60	40.4	59.6
		90	40.22	59.78
		120	40.11	59.89

Table 9: Effect of contact time on adsorption of Cd(II)ions by PANAA /Kaolinite composite .

pH	Adsorbent dose (g/l)	Temperature C°	[Cu(II)] ppm	Removal Percentage R %
6.5	0.4	25	53.25	46.75
		30	52.47	47.53
		35	50.98	49.02
		40	48.65	51.35
		45	40.25	59.75

Table 10: Effect of Temperature on adsorption of Cu(II) ions by PANAA/Kaolinite composite.

pH	Adsorbent dose (g/l)	Temperature C°	[Cd(II)] ppm	Removal Percentage R %
6.5	0.4	25	62.88	37.12
		30	62.25	37.75
		35	60.56	39.44
		40	57.78	42.22
		45	50.74	49.26

Table 11: Effect of Temperature on adsorption of Cd(II)ions by PAAN/Kaolinite composite.

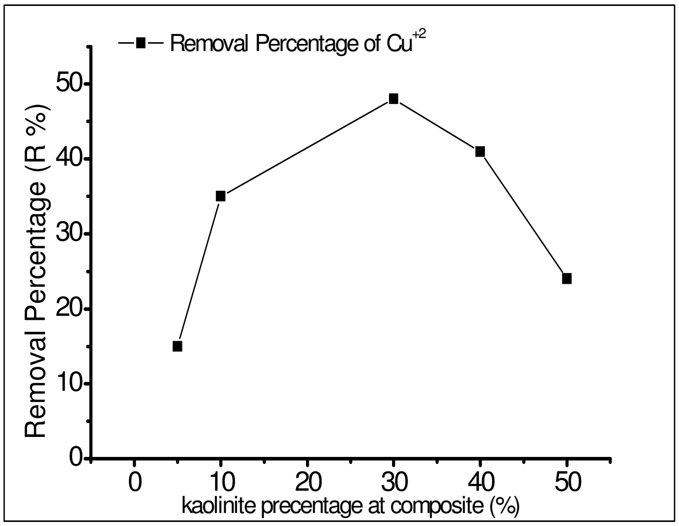

Figure 22: Effect of Kaolinite clay ratio on the percentage of Cu (II) removal using PANAA composites.

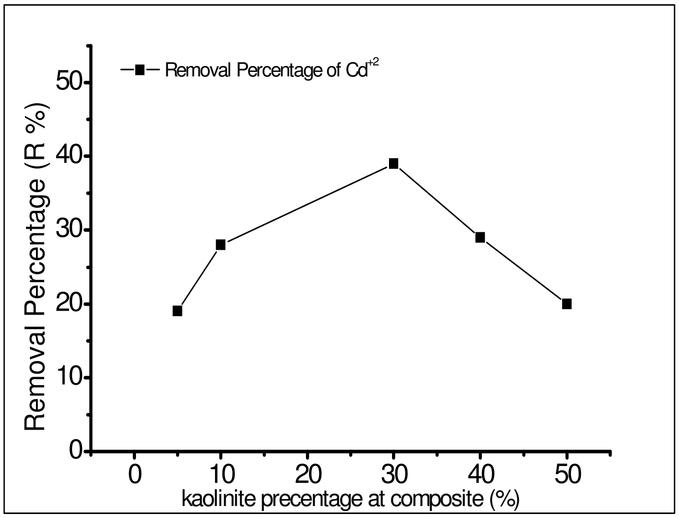

Figure 23: Effect of Kaolinite clay ratio on the percentage of Cd (II) removal using PANAA composites

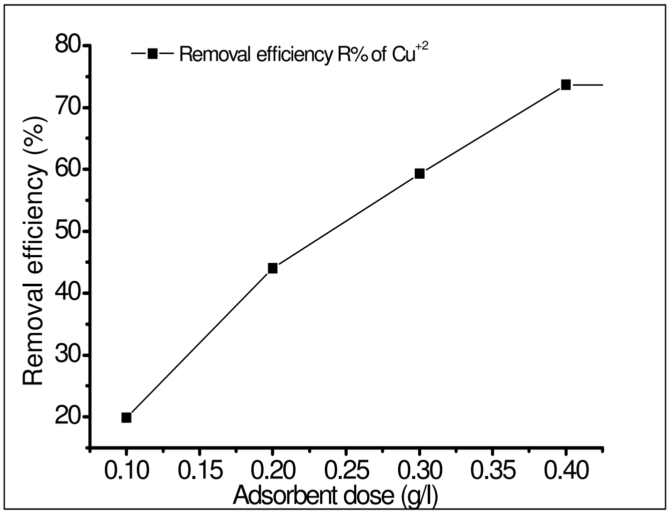

Figure 24: Effect of adsorbent dose of PANAA (30% Kaolinite) on the percentage of Cu(II) removal

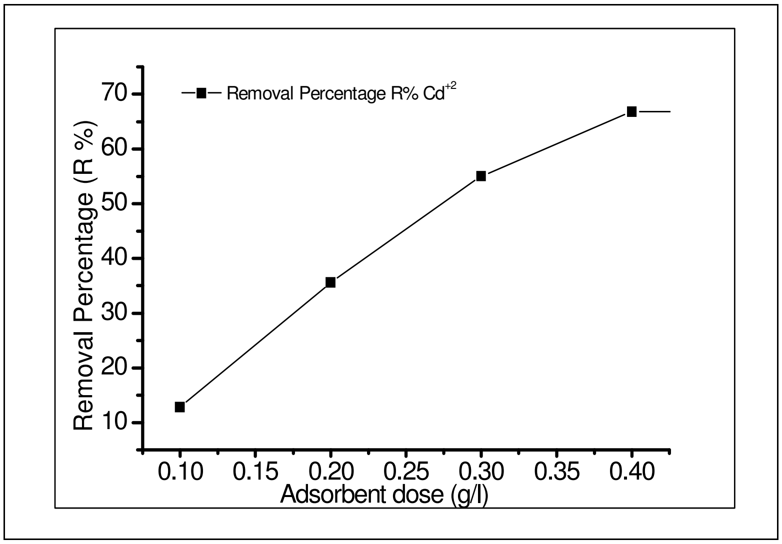

Figure 25: Effect of adsorbent dose of PANAA (30% Kaolinite) on the percentage of Cd(II) removal

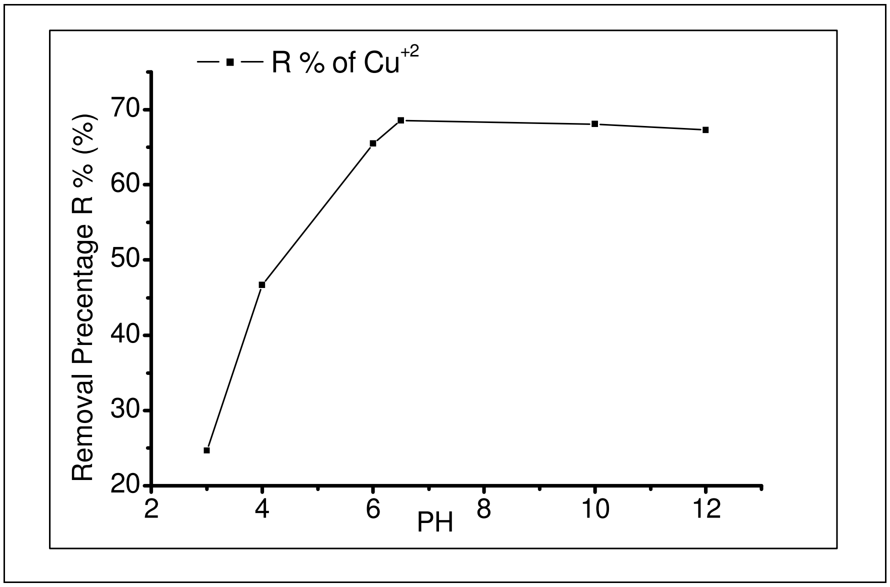

Figure 26: Effect of pH on the removal of Cu(II) percentage using PANAA composite (30% Kaolinite), adsorbent dose = 0.4 g/L

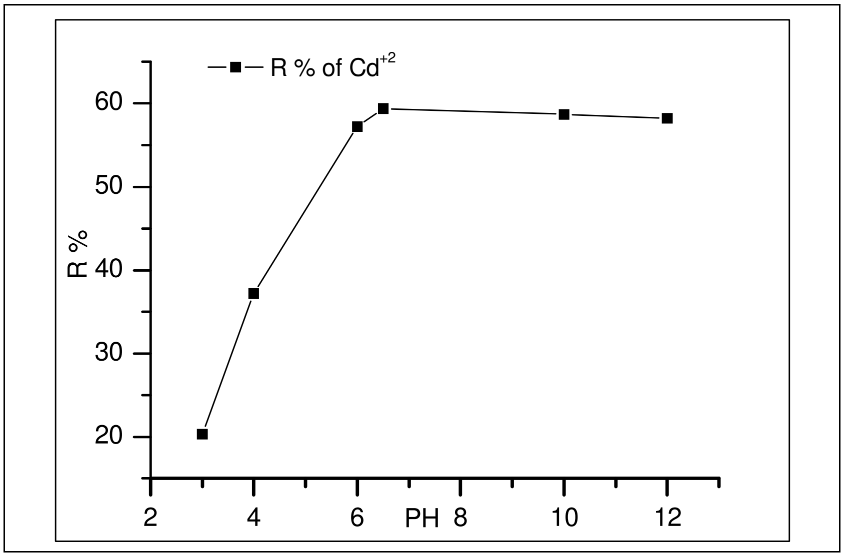

Figure 27: Effect of pH on the removal of Cd(II) percentage using PANAA composite. (30% Kaolinite), adsorbent dose = 0.4g/L

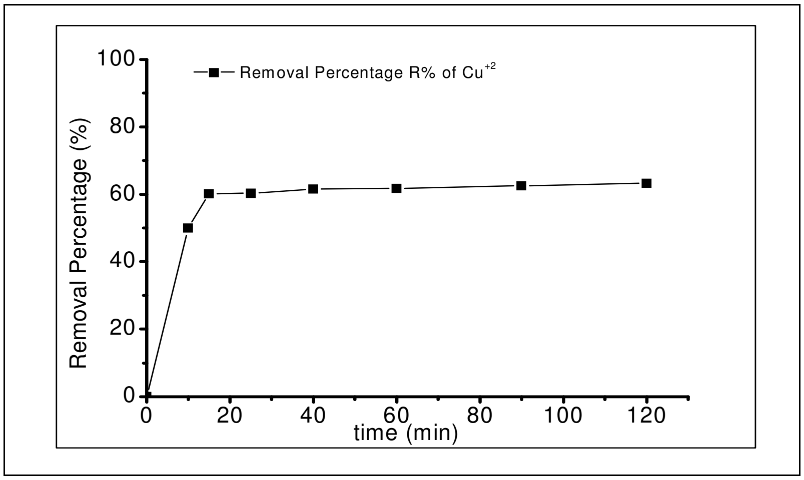

Figure 28: Effect of contact time on the removal percentage of Cu(II) using PANAA composite. (30% Kaolinite), adsorbent dose = 0.4g/L and pH=6.5

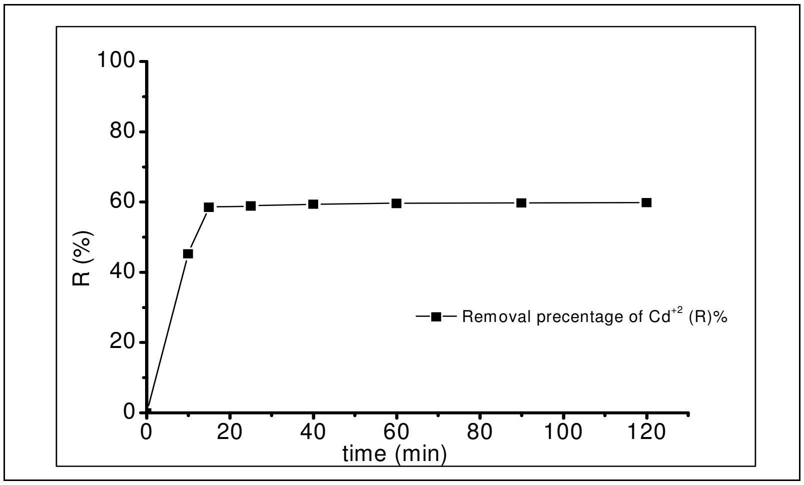

Figure 29: Effect of contact time on the removal percentage of Cd(II) using PANAA composite (30% Kaolinite), adsorbent dose = 0.4g/L and pH=6.5

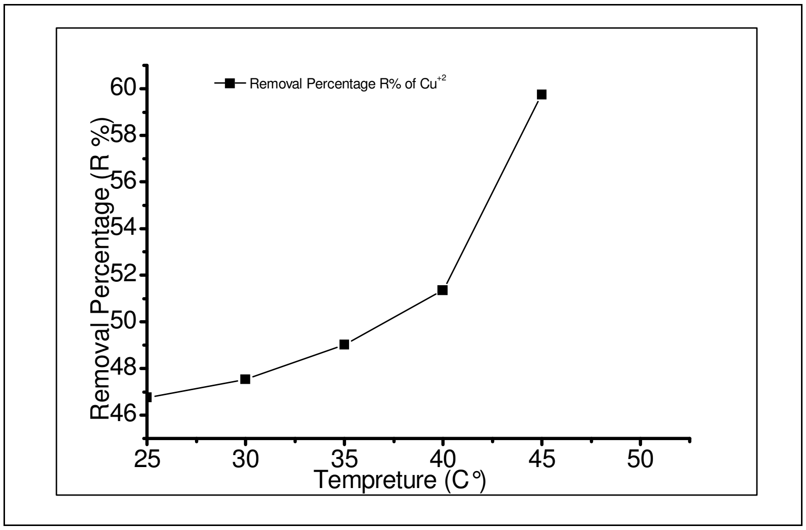

Figure 30: Effect of temperature on the removal percentage of Cu(II) using PANAA composite (30% Kaolinite) with adsorbent dose = 0.4g/L, pH=6.5, contact time= 20min.

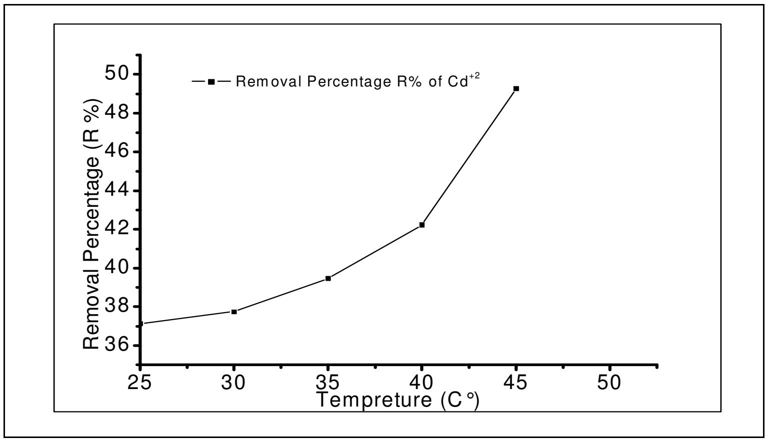

Figure 31: Effect of temperature on the removal percentage of Cd(II) using PANAA composite (30% Kaolinite) with adsorbent dose =0.4g/L, pH=6.5, contact time=20min.

6. Conclusions

Thermal study of Polyanilin–Anthranic acid /kaolinite composite showed that the composite has more thermal stability than the kaolinite and poly aniline-anthranilic acid. PANAA/kaolinite composite which have 30% kaolinite showed the highest removal percentage of copper and cadmium. (PANAA)/kaolinite composite was effective, for which the removal reached around 70 % of copper and cadmium cations. Adsorption of studied heavy metals was 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 stationary line. Temperature has high effect on the adsorption of studied heavy metals onto the surface of (PANAA/kaolinite) composite. Adsorption of studied heavy metals increases as the composite dosage increases. (PANAA/kaolinite) composite can be used in adsorption of heavy metals several times by regeneration with Sodium hydroxide solution. Finally, from the above we can conclude that (PAN–AC) composite can be used as effective adsorbent for the dyes in the industrial wastewater.

7. References

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