

Synthesis, Characterization and Application of Karak Bentonite Clay-Graft-Poly (Acrylamide/Co- Acrylic Acid) Superabsorbent Composite and its Adsorption Study for Selected Heavy Metals

¹Shaheen Wali, ²Manzoor Iqbal Khattak, ³Mahmood Iqbal Khattak and ⁴Ashif Sjjad

^{1,2}Chemistry Department University of Balochistan, Quetta.

³PCSIR labs Complex, University Road Peshawar Pakistan.

⁴Bio-chemistry Institute University of Balochistan, Quetta.

manzoor_iqbal@yahoo.com*

(Received on 14th January 2022, accepted in revised form 17th June 2022)

Summary: A novel superabsorbent composite (SAC) based on bentonite, acrylamide and acrylic acid was synthesized. The effects of bentonite quantity, initiator content on the grafting degree and on the water absorbency for the samples were studied. Synthesis mechanism, morphology and thermal properties of the SAC were characterized. FTIR results confirmed the presence of acrylamide/ acrylic acid onto bentonite backbone while TGA showed that introduction of 70 % bentonite to polymer increases thermal stability. The SAC was also tested in the removal of heavy metal in aqueous solution where kinetics analyses were performed using Langmuir adsorption isotherm. The optimum adsorption capability of heavy metal ions onto bentonite-based SAC from solution was 92, 48 and 91 % for Pb⁺⁺, Ni⁺⁺, and Cu⁺⁺ respectively. The unique characteristics of these SAC such as its slow-release and water-retention capability, nontoxicity in soil, environmentally friendly and high capacity for the removal of heavy metals might be very valuable in agriculture and environmental studies.

Key word: Clay, Superabsorbent polymer, Graft copolymerization, Water absorbency, Heavy metal.

Introduction

Superabsorbent polymers (SAPs) are hydrophilic polymeric of three-dimensional structures with water absorption capacities of up to several hundred times their weight and the ability to hold water at high pressure. When these SAPs are left in dry air, the absorbed water is gradually released and achieve the moisture level of surrounding environment. These super absorbing polymers have a wide range of possible uses such as food packaging, towels and sanitary products as well as clothes and baby diapers. Their water retention properties in sandy soil have made them an ideal friction reduction for sewage transport in pipes and a plant growth regulator [1, 2] in the agricultural and horticultural industries.

At present, superabsorbent materials are made from petroleum-based therefore a large amount of fossil fuels is needed for their manufacture which also produce a significant environmental pollution [3]. The initial SAP was developed from acrylic acid (AA). The poor gel strength and high cost of these polymers are their major drawbacks. A number of studies on the composition of inorganic minerals like clay have been reported in order to improve their absorption rate, gel strength and capacity of these composites [4-6]. Certain inorganic elements such as Copper, Nickel and lead have to be added to these into composites to

increase their mechanical and thermal stability, swelling ability, gel strength, and lower the cost of composites for certain applications [7-11]. An increased cost-effectiveness and better efficiency have been achieved by graft-copolymerization of mica with montmorillonite and partly neutralizing AA with a water absorption capacity of 1100 times [12, 13]. Due to their cost-effectiveness and superior water absorption, SAPs gain much attention [14]. These SAPs have been synthesized and characterized in different investigations and have shown an improved water absorption capacity in distilled water [15, 16]. For water absorption in salty environments, superabsorbent may be highly useful for a variety of applications.

According to published results, clay has shown the increased thermal stability, water absorbency and gel strength apart from other usual properties [17]. The development of superabsorbent composites from clays like montmorillonite [18], attapulgite [19] and bentonite [20] has also been reported. Clays, such as bentonite, are made up of successive sheets of silicate and are widely used in the construction industry [21]. Many polymer-clay nanocomposites, such as EVA/clay nanocomposite [22], have been developed by intercalation. The

*To whom all correspondence should be addressed.

nanocomposites have received considerable attention because of their low cost, diverse application in horticulture and agriculture [23, 24]. SAPs hydrogels have also been developed to study the binding behaviour of several metal ions under varied pH and time conditions [17].

Heavy metals are highly toxic to biotic life due to their enzyme-inhibiting and harmful metabolic character. The use of heavy metals in our life have increased significantly over the past several decades and have resulted in ever growing metal contamination in the environment. According to World Health Organization copper, chromium, lead, nickel, zinc and mercury are the metals of most immediate concern owing to their toxic nature. Reverse osmosis and chemical precipitation methods are very common for removal of these toxic metals from their aqueous solutions. As complete removal of metals is not possible by these methods therefore the use of copolymeric and polymeric materials for toxin removal is preferred which are also cost-effective and safe nature [25-28].

The poly (acrylic acid-co-acrylamide)-bentonite superabsorbent composites (SAC) was synthesized. The preliminary swelling properties of SAPs in aqueous solution were studied. This composite was characterized using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Thermogravimetric Analysis (TGA). Other objective of the work was to use SAC for the removal of selected heavy metals [Pb (II), Ni (II), Cd (II) and Cu (II)] from aqueous solutions.

Experimental

Materials

The acrylamide was acquired from Daejung Chemicals & Metals Co. Ltd, Korea. Acrylic acid with 99 % purity made by Sigma-Aldrich was used for present studies. The ultrapure grade N,N-methylenebis-acrylamide, potassium persulphate and sodium sulphide are from Amresco and Applichem, the Czech Republic. The sodium bentonite clay used in present studies are being mined at Sheen Ghar Karak, Pakistan. This clay was completely dried in an oven at 110°C. The dry clay was pulverized and sieved using a 100-mesh sieve before its analysis.

The process of making Superabsorbent Polymer Composites

A graft copolymerization reaction as reported in [11, 25] was used. The right amount of clay taken

in a flask was mixed with distilled water and stirred till the formation of a homogeneous solution. The solution of acrylic acid was partially neutralized with NaOH, then with N, N – methylene-bisacrylamide and added to above. Acrylamide (AM) monomer, a solution of Potassium persulfate (KPS) and sodium sulfite were slowly added to the flask.

The shaking of the solution in the flask was carried out for 15 minutes to ensure that the graft copolymerization process has been fully completed. A steady nitrogen atmosphere was kept during the whole process to get rid of the dissolved oxygen in the solution.

FTIR Analysis

The grafting ratio was determined using FTIR spectrophotometer (Thermo Nicolet Avatar 320 spectrophotometer, USA). The Attenuated Total Reflectance (ATR) method was used for this purpose.

XRD analysis

The X-ray diffraction (XRD) spectra for given samples were obtained using X-ray diffractometer (SIEMENS D5000 with Cu anode) which worked at 40 kV and 30 mA. Samples were carefully mounted on the turn table of X-ray diffractometer and a scanning rate of 0.01 mm per second was used to cover the angles from 2° to 90°.

SEM Analysis

The SEM analysis was carried out on scanning electron microscope (Model JSM-5910 JEOL Japan) available in Centralized Resource Laboratory (CRL), University of Balochistan, Quetta.

TGA

The thermal stability of composite samples was studied by taking its TGA. Dry nitrogen at 80 mL per minute flow rate was used. The temperature was scanned over the range 30-950°C at a scanning rate of 10°C per minute.

Measurement of water absorbency

The mass of sample in dry form was determined using an electronic balance. The ability of SAC sample to soak up water at room temperature was measured in distilled water. The 500 mL of water was added to composite in powder form and left for 24 hours to ensure its uniform swelling [29]. A 100-mesh screen was used to remove excess water *i.e.*, water not used to swallow the powder. The samples in swollen

form were weighed. The water absorbency Q_{H_2O} was measured using the following equation.

$$Q_{H_2O} = (m_2 - m_1)/m_1 \quad (1)$$

where m_1 and m_2 are the mass of swollen and dry samples respectively.

Adsorption Analysis

A study was carried out on four heavy metal ions that came from single-metal aqueous solutions. The stock solutions of 100 ppm each of Pb, Ni, Cd, and Cu ions were made in water and kept in separate conical flasks. 20 mL of each absorbate solution was taken in separate flasks and 0.25g of SAC sample was added to it. The flask was placed in a rotating shaker at 150 rpm at temperature of 25°C (room temperature) for about 60 minutes. The samples with different amount of metal ions in the aqueous phases at different pH and reaction times were used. Samples are then filtered through Whatman Filter Paper 125 mm and these were analyzed using Atomic Adsorption Spectrometry. The adsorption capacity was calculated using the following formula.

$$q = \frac{(C_0 - C)V}{m} \quad (2)$$

where 'q' is the amount of metal in mg/g in the given solution of the sample that is adsorbed at equilibrium, 'C₀' is the initial or starting amount of metal 'C' is the amount of metal at a given time, 'V' the volume of the metal solution that was used (mL) and 'm' is the mass of metal.

Results and Discussion

Acrylic acid and acrylamide were grafted onto Na-Bentonite using KPS as an initiator, sodium sulfite as accelerator and MBA as crosslinker under

inert atmosphere. The effect of concentration of clay, crosslinker, initiator quantities and monomer ratios on the swelling capacity of SAC were investigated.

Decomposition of Initiator

Heating of persulfate initiator produces sulfate anion radical, which creates an active site on Na Bentonite by abstracting hydrogen. In the presence of these active centres, AA and AM undergo radical polymerization resulting in grafted copolymer. MBA facilitates these copolymers to get crosslinked together resulting in a superabsorbent polymer composite.

FTIR analysis

The FTIR spectrum of polymer (acrylamide-co-acrylic acid) is shown in Fig 2(a). The absorption maxima (i.e., the transmission minima) are observed at 3296 cm⁻¹, 2936 cm⁻¹, 1445.0 cm⁻¹, and 1114.2 cm⁻¹. These peaks are all ascribed to the stretching of the acrylamide and acrylate units. There is a correlation between AA and AM, as seen by these peaks.

The absorption peaks in FTIR spectrum of Na-Bentonite [Fig 2(b)] are observed at 3735.3 cm⁻¹, 3304.7 cm⁻¹, 1655 cm⁻¹, 1548.0 cm⁻¹ and 1404. cm⁻¹ and these are attributed to the stretching of OH, CO, C-C, and CH. Bands , 999, and 666. cm⁻¹ for layered silicates, respectively [30].

Fig 2(c) shows the FT-IR spectrum of AA/AM grafted onto Na-Bentonite. Due to the existence of CONH₂ stretching vibration of acrylamide, a new absorption band at 1658.8 cm⁻¹ has appeared. It is thought that the peaks observed at 1555 cm⁻¹ and 1408.6 cm⁻¹ are linked to -CO₂ and C-N bends respectively. Additional peaks in the Si-O stretching of layered silicates may be seen at 981 cm⁻¹.

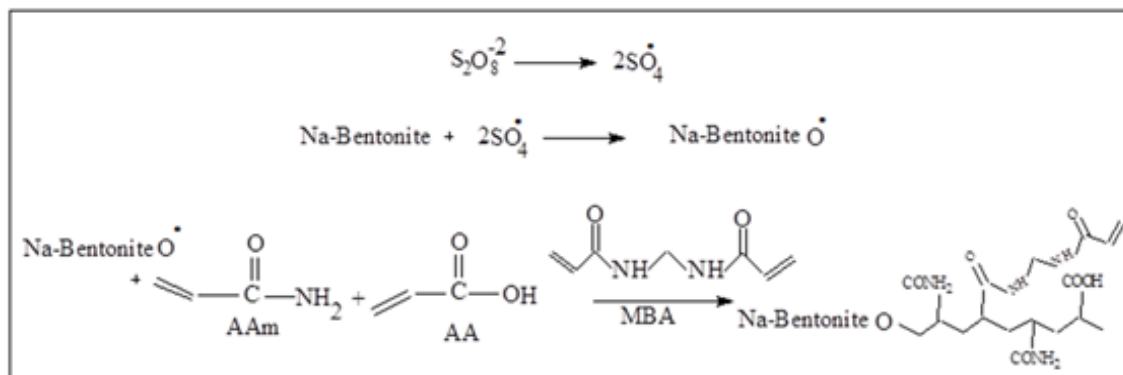


Fig. 1: Scheme of the reaction.

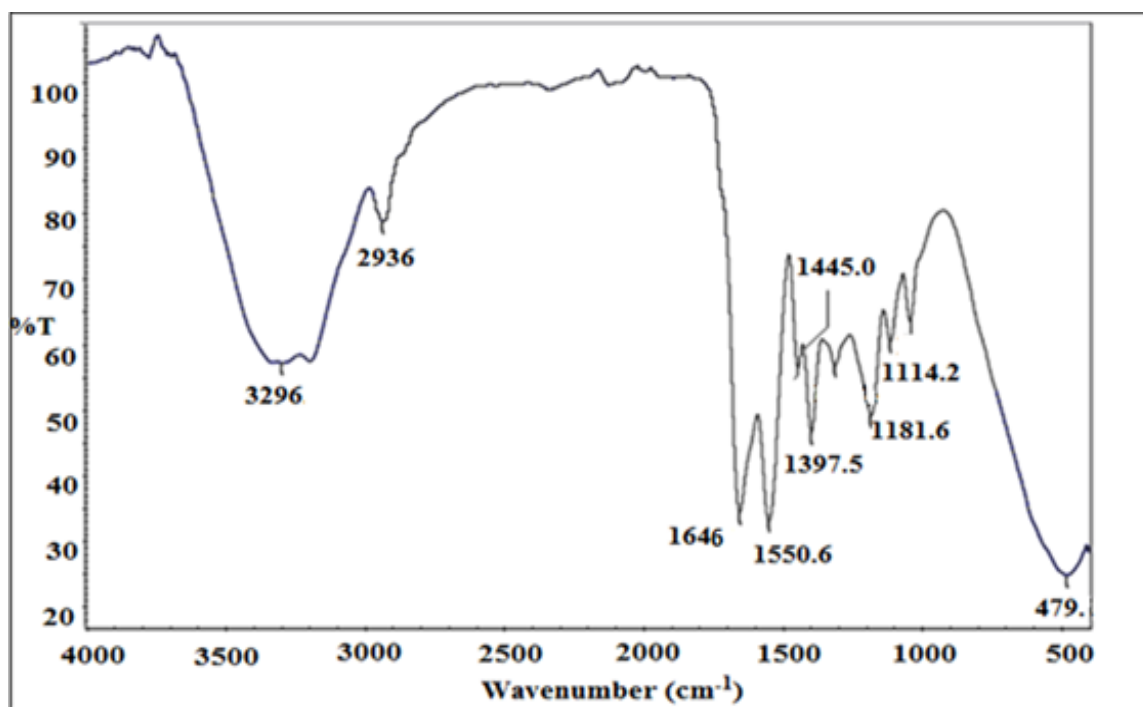


Fig. 2: (a)

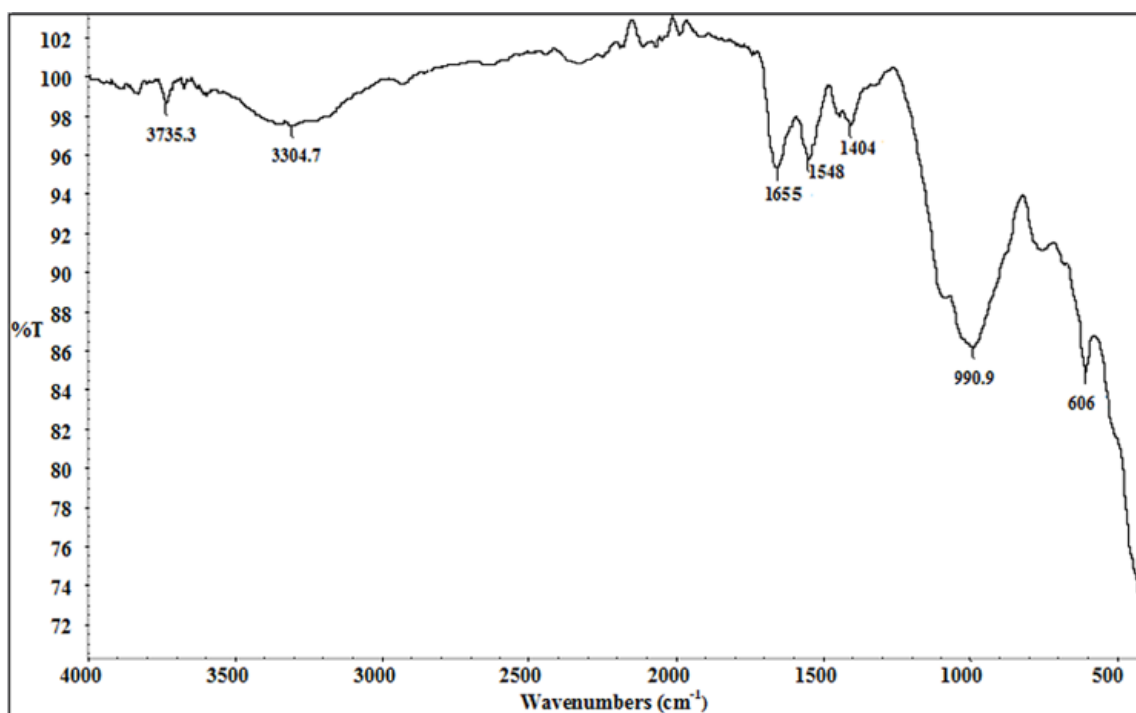
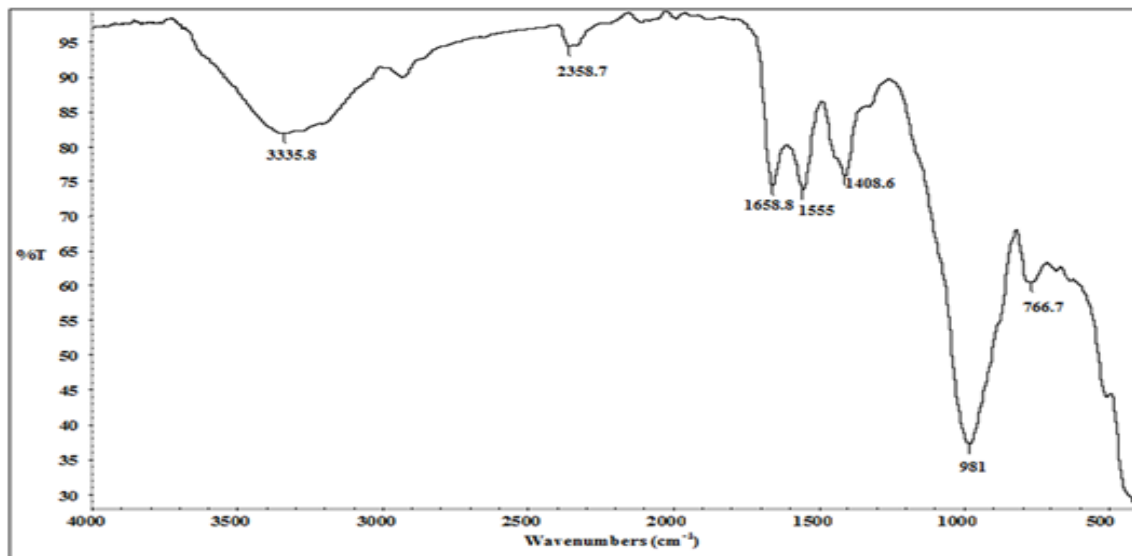


Fig. 2: (b)



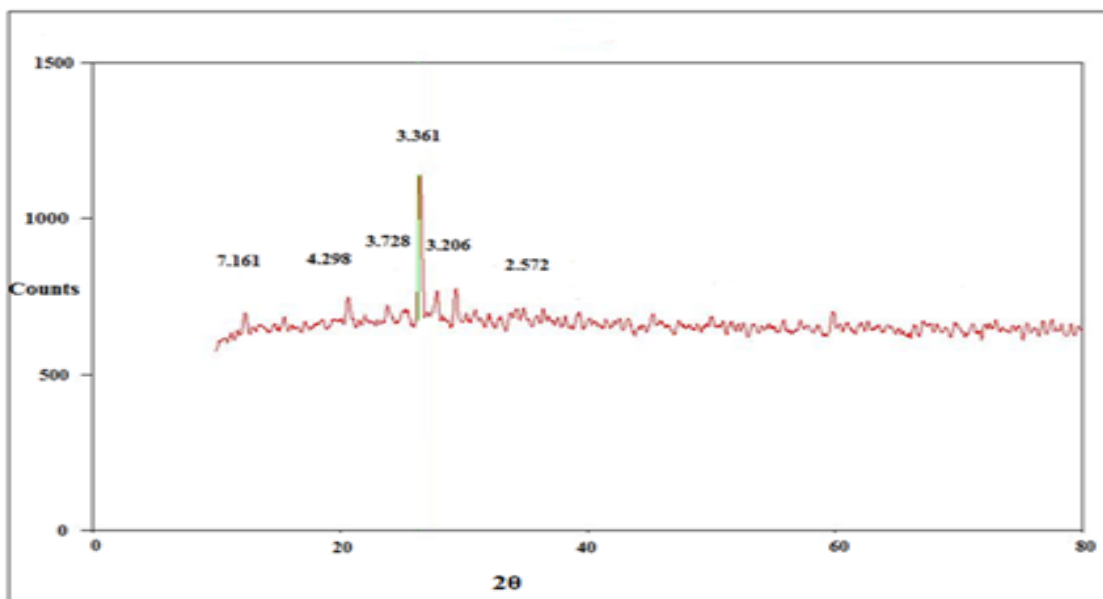
2(c)

Fig. 2: (c) poly AM/co-AA (a); sodium bentonite clay (b); and sodium bentonite/poly (AM-co-AA) composite material with exceptional absorption capacity (c).

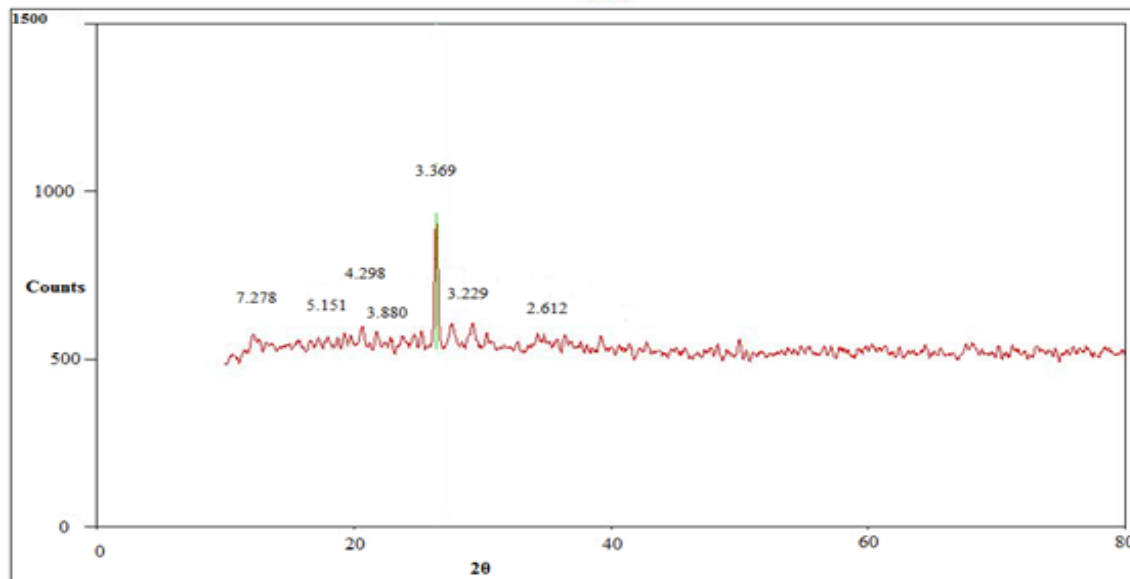
XRD Analysis

Co-K radiation, operating at 40 kV and 30 mA, was used to obtain the X-ray diffraction spectrum. All samples used were in fine powder form. XRD spectrum of Bentonite composite and its clay are displayed in Figs 3(a) and 3(b). The diffraction spectrum of bentonite [Fig 3(a)] shows six distinctive peaks at 2.572° , 3.206° ,

3.361° , 3.728° , 4.298° and 7.161° in bentonite. However, peaks at 2.612° , 3.229° , 3.369° , 3.880° , 5.151° , 4.298° , 5.151° and 7.278° are observed in XRD spectrum of Na bentonite clay sample. It is suggested that there may be interlayer penetration in acrylamide and acrylic acid solution which causes an increase in interatomic spacing *i.e.*, 'd'. Polymerization between silicate layers might expand the distance between the monomers.



(3a)



(3b)

Fig. 3: a and b are XRD spectra of Na bentonite clay.

TGA analysis

TGA spectra of five samples of the clay graft AM/ co-AA (SACs) incorporating with different amount of clay contents were obtained and results are shown in Fig. 4. It is clear that thermal stability increases as the concentration of clay is increased in the samples. However, there are three stages of thermal decomposition having well defined range of temperature. In the first stage the temperature range is

70-140 °C and rate of weight loss is relatively low. This is attributed release of moisture contents of the SAPs. In second stage the temperature range is 290–490 °C sharp decrease in weight is observed owing to thermal decomposition of Amide group in AM/AA [31]. In the third stage a gradual weight loss of SAPs is observed in the temperature range 680-750 °C and it is attributed to the decomposition of the backbone of SAPs.

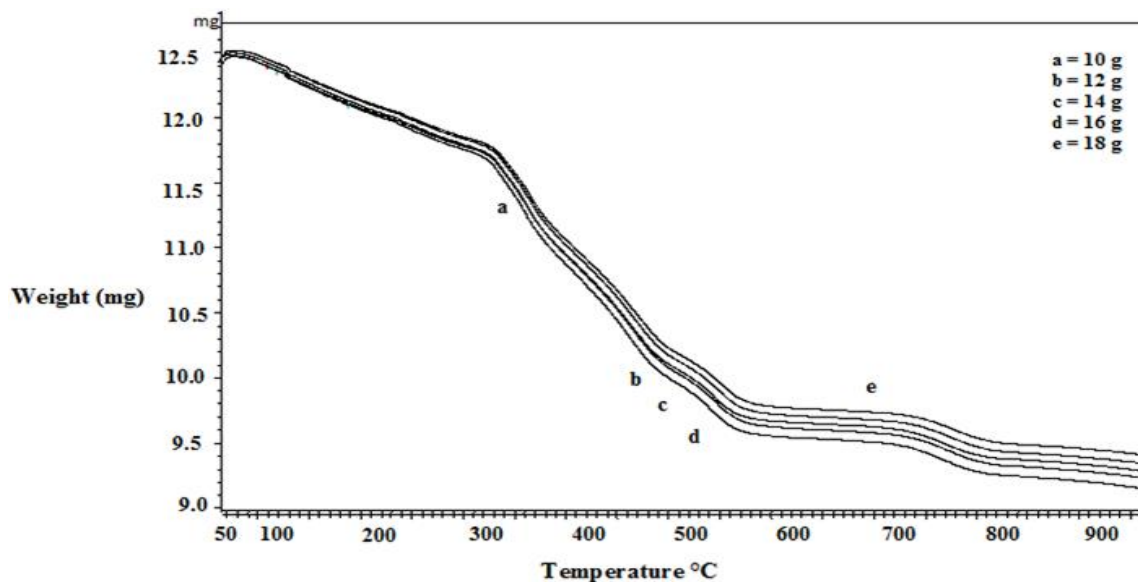


Fig. 4: TGA spectra of SAPC using different amount of clay.

Adsorption of heavy metal by SAPs and SAC

Adsorption rate

The dependence of heavy metal ions adsorption rates using single ion solution on SAPs as function of contact time is shown in Fig 5 which was calculated using Eq.2. Initially the increase in adsorption rate is high (indicated by large value of slope) then it slows down (indicated by medium slope) and finally achieves an equilibrium *i.e.*, almost negligible slope in 90–180 minutes for Pb (II), Ni (II), Cd (II), and Cu (II) [27, 32-35]. This means that 92 and 91 percent of Pb (II) and Cu (II) were removed. Apart from contact time, the absorbent rate is dependent On other parameters such as size, porosity and surface area of the absorbent. It also depends on number of metal ions present in it. In the same way, other ions in the area could also affect the results by competing with ions of interest for active adsorption sites.

Adsorption of heavy metals on SAPs is shown in Fig 6. It shows that the adsorption was at its peak at pH 4 for Ni (II), pH 2 for Pb (II), and pH 6 for Cu. This means that the adsorption of heavy metals on SAPs is best when the pH is high (II). This could be because at a low pH, there are more H⁺ ions in the solution that compete with Cu (II) ions. This makes the ion exchange reaction between Cu (II) ions and the cations in the composite very hard to do. A similar behaviour has also been observed in attapulgite clay [27].

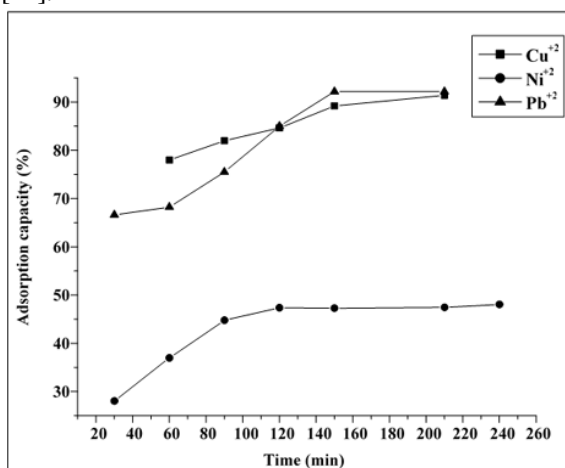


Fig. 5: Effect of time on adsorption capacity of different metals.

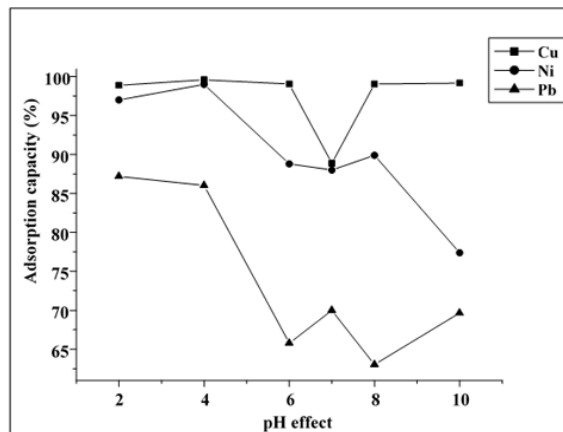


Fig. 6: Effect of pH of different metals on adsorption capacity.

Adsorption Kinetics

Different kinetic models are employed to investigate the adsorption process. The rate constant can be calculated by the following equation developed by Langmuir [36].

$$\log(q_e - q_t) = \log q_e - (k_1 t / 2.303) \quad (3)$$

where q_e and q_t , expressed in (mg/g), are the quantities of metal absorbed at equilibrium and time t (minutes) respectively. The k_1 is a first order rate constant and expressed in terms of min^{-1} . The second order equation may be stated in terms of adsorption equilibrium capacity and is given below.

$$t/q_t = (1/k_2 q_e^2) + (t/q_e) \quad (4)$$

The second-order equation's rate constant is k_2 (g/mg.min). Linear plots of $\log(q_e - q_t)$ against t and t/q_t versus t were used to assess the models' fit, as illustrated in Fig. 7 and 8. A small correlation constant precluded a complete satisfaction of the first-order rate statement in this case. To our knowledge, the q_e values estimated from these linear plots do not match with the values reported earlier [36]. A second-order model, as shown in Table 1, is the best match for the data. The second-order model's correlation coefficient is larger than 0.996, and the measured values of q_e are in close agreement with the estimated values. Based on these findings, Mishra *et al.* [28] found that metal removal by low-cost adsorbents is the best match of experimental data in the second order model.

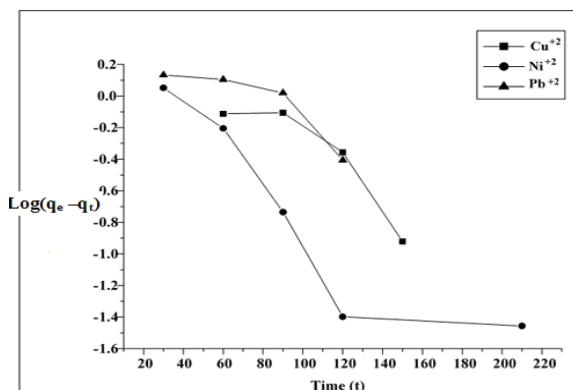


Fig. 7: Pseudo first order kinetics plot for adsorption of Cu^{+2} , Ni^{+2} , Pb^{+2} ions onto SAC.

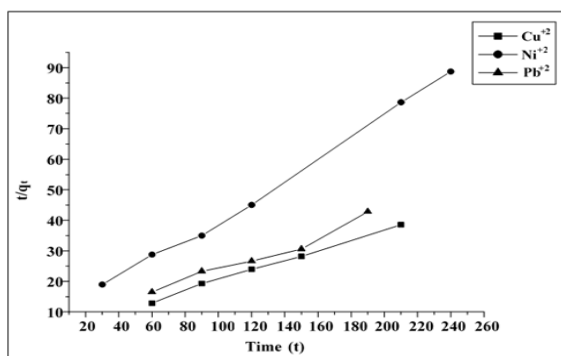


Fig. 8: Pseudo second order kinetic plot for adsorption of Cu^{+2} , Ni^{+2} , Pb^{+2} ions onto SAC.

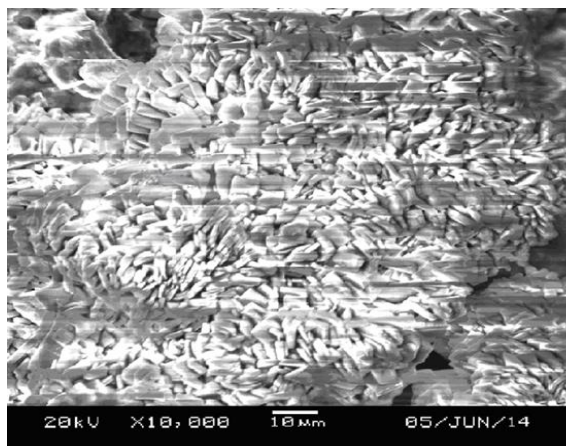
Table-1: Comparison of rate constants and difference of q_e (calculated and experimental) for pseudo-first order and second-order reaction kinetics of removal of different metals.

Metal ion concentration	Pseudo-first order		
	K_1 (1/min)	$q_e(\text{cal-exp})$	R_1^2
Cu^{+2}	0.01842	4.833	0.813
Ni^{+2}	0.0202	2.004	0.8027
Pb^{+2}	0.01312	4.4895	0.769

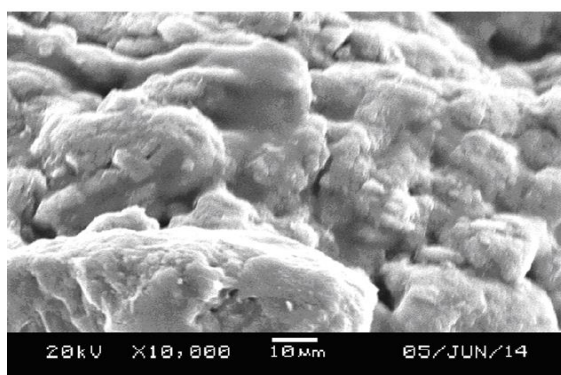
SEM analysis

The surface morphology of Na-Bentonite clay and SAP's are shown in Fig 9. (a-c). Fig 9(a) shows the morphology of the ungrafted clay which has a completely different structure than the grafted polymer. Ungrafted clay shows irregularity of particles and rough surface, while grafted Na-Bentonite has microporous appearance and fine network structure. On the other hand, SEM micrographs in Fig 9(b) and 9(c) show that Na-Bentonite clay-g-poly(acrylamide-co-acrylic acid) containing 35 wt % possess a loose and more porous morphology compared to nascent Na-Bentonite clay [38]. Moreover, the smaller particle size of the SAPs

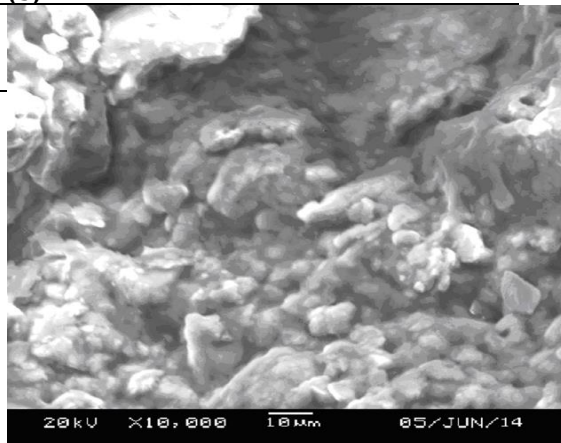
than the Na-Bentonite suggests that initially there will be more interstitial spaces which lead to its increased water absorbing capacity based on capillary action. As the size of the particle becomes extremely small, a tendency in decrease in water absorption is observed [12, 39].



(a)



(b) pseudo-second order



(c)

Fig. 9: Na bentonite clay (a), Na bentonite-g-poly (b), c) (AM-co-AA) SAPC.

Effect of Clay contents on water absorbing capacity of SAC

Table-2 depicts the dependence of Na-Bentonite clay contents on water absorbency for the SAC. It has been previously reported that amount of clay in SAC plays an important role in its water absorbency which reduces significantly with increase in clay contents in SAC [39-41]. These outcomes are in consistent with earlier study as reported by Wang *et al.* [10]. This behavior is due to the presence of more crosslinked points in polymeric network which in turn decreases the crosslinked density of the composite and leads to lower water absorbency. It is also suggested that $-OH$ moieties on the clay surface could interact with acrylic acid and acrylamide, which could enhance the polymeric network, leading to a decreased rate of water absorbency. Similarly, it is assumed that an increase in the amount of clay in composite causes the chemical interaction among AA/AM and $-OH$ groups on the clay surface, thus leading to a decrease in the water absorbency of SAC [11, 42]. In addition, the polymerization system improves the grafting ratio, but also initiation of homo-polymerization of PAA and PAM in the presence of excess initiator which plays its role in decreasing the composite water absorbency. Higher clay contents make the SAC less hydrophilic, which makes it less likely to swell, and the interaction between clay and AA/AM gets better. Eventually, chemical and physical cross-links were found to be the most common in the polymeric network. This reduced the crosslink density of the composite and the elasticity of the polymeric chains which led to a decrease in the water absorbency in SAC. Such consistent experimental results have also been reported by Wu *et al.* [12]. They found that the composite with kaolinite has maximum swelling and minimum swelling in the composite doped with sericite. The composite doped with Bentonite has moderate swelling.

Water absorption behavior of copolymer of acrylamide /acrylic acid) bentonite superabsorbent composites were compared. Table-3 shows a comparison of the water absorption behavior of the Na-Bentonite clay with different clay contents and a copolymer of acrylamide and acrylic acid. We observed that the copolymer of acrylamide and acrylic acid is better absorbent than the bentonite superabsorbent composites in distilled water at the right temperature and time.

Table-2: The water absorption capacity of clay at various concentrations is affected.

S. No	Clay content (wt %) Na bentonite clay	Water absorbency (g/g) Q_e
1	56	110.8
2	63	123.3
3	68	147.1
4	72	150.2
5	75	85.6
6	poly(acrylamide-co-acrylic acid)	179.5

Influence of initiator on grafting degree

The effect of amount of initiators in clay on how well AM/AA is grafted or water absorbency is shown in Fig 10. The results indicate peak water absorbency at 2.5 % initiator contents but it decreases with increase in initiator concentration. The water absorbency starts increasing beyond 11 % initiator contents. Clay's hydroxyl groups react with potassium persulfate to form a free radical which then damages the clay structure. When these free radicals are copolymerized, they form poly (acrylamide-co-acrylic acid) branches on the clay backbone, as seen in the illustration. Adding an initiator could also be a reason for the SAC's grafting degree getting better. Clay has more cations like Ca^{2+} , Fe^{3+} , and Na^+ which may be the reason for this observed behaviour. Besides carboxylates, $-OH$ groups (phenolic, enolic, and alcoholic) as well as amino groups, other functional groups can also affect how well the graft sticks [29, 43]. As a result, during the polymerization process, bentonite clay may chemically link with and enhance the polymer network. As a result, the grafting chemical process may be almost complete [44].

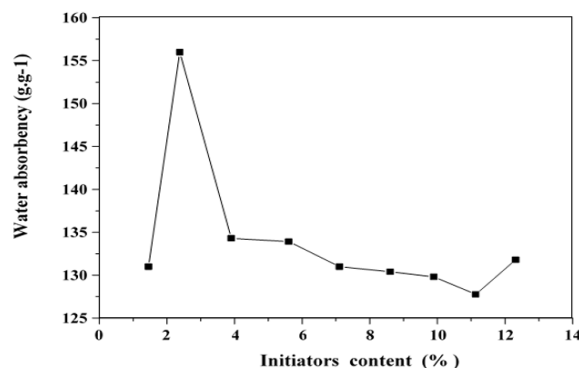


Fig. 10: Effect of initiators on water absorbency.

Conclusion

Bentonite superabsorbent composites were made by putting acylic acid and acrylamide on Bentonite and then using N,N-methylene-bisacrylamide to crosslink it and potassium persulphate to start the reaction in water. Maximum equilibrium water absorption and grafting ratio for the superabsorbent composites were found for 70% clay contents. FTIR results show that Bentonite in the form of micro powder has a lot of $-COO-$ and $-OH-$ groups on its surface. These groups react with each other. SEM results showed that clay particles were more evenly distributed into the polymer matrix when they were viewed through the scanning electron microscope. TGA curves show that the clay has a big impact on the thermal stability of the superabsorbent composites made with it. When clay is added to the

polymer network, the thermal stability of the superabsorbent composites is improved. The prepared SAC was quite efficient in removing selected heavy metals from aqueous solution. Based on the results obtained, the current SAC can be efficiently used in various industries involved in the preparation and synthesis of water absorbing materials and heavy metals removal simultaneously.

References

1. P. Wu ., Y. Wei., L. Jianming .,L. Songbai., Study on starch-graft-acrylamide/mineral powder superabsorbent composite. *Polymer*, **44**, 6513 (2003).
2. A.Pourjavadi, S. Barzegarand F. Zeidabadi, Synthesis and properties of biodegradable hydrogels of κ -carrageenan grafted acrylic acid-co-2-acrylamido-2-methylpropanesulfonic acid as candidates for drug delivery systems. *Reactive and functional Polymers*, **67**: 644(2007).
3. S.Kiatkamjornwong, K. Mongkolsawat and M. Sonsuk, Synthesis and property characterization of cassava starch grafted poly [acrylamide-co-(maleic acid)] superabsorbent via γ -irradiation. *Polymer*, **43**: 3915 (2002)
4. R.Tiwari, K. Khilar and U. Natarajan, Synthesis and characterization of novel organo-montmorillonites. *Applied Clay Science*,. **38**: 203 (2008).
5. S.Andrejkočová, I. Janotka and P. Komadel, Evaluation of geotechnical properties of bentonite from Lieskovec deposit, Slovakia. *Applied Clay Science*, . **38**: 297(2008).
6. H. El-Sherif, and M. El-Masry, Superabsorbent nanocomposite hydrogels based on intercalation of chitosan into activated bentonite. *Polymer Bulletin*,. **66**, 721 (2011).
7. G. Lagaly, M. Reese and S. Abend, Smectites as colloidal stabilizers of emulsions: I. Preparation and properties of emulsions with smectites and nonionic surfactants. *Applied Clay Science*. **14**: p. 83-(1999).
8. K. M Mostafa,, Graft polymerization of acrylic acid onto starch using potassium permanganate acid (redox system). *Journal of Applied Polymer Science*,. **56**: 263 (1995).
9. Y. Zheng, L.Ping Z.Junping and W.Aiqin , Study on superabsorbent composite XVI. Synthesis, characterization and swelling behaviors of poly (sodium acrylate)/vermiculite superabsorbent composites. *European Polymer Journal*, **43**: 1691 (2007).
10. J. Zhang, and A. Wang, Study on superabsorbent composites. IX: Synthesis, characterization and swelling behaviors of polyacrylamide/clay composites based on various clays. *Reactive and Functional Polymers*, **67**: 737 (2007).
11. A. Li, and A. Wang, Synthesis and properties of clay-based superabsorbent composite. *European Polymer Journal*, **41**: p. 1630 (2005).
12. J. Lin, W.Pard, Y. Zhengfang, P. Minli, Synthesis and properties of poly (acrylic acid)/mica superabsorbent nanocomposite. *Macromolecular Rapid Communications*, **22**: 422 (2001).
13. F.Santiago, E.Antonio . Mucientes, O. Mónica , and C. Carlos, Preparation of composites and nanocomposites based on bentonite and poly (sodium acrylate). Effect of amount of bentonite on the swelling behaviour. *European Polymer Journal*, . **43**: (2007).
14. S. S. Ray, and M. Okamoto, Polymer/layered silicate nanocomposites: a review from preparation to processing. *Progress in polymer science*, **28**: 1539 (2003).
15. W. F. Lee, and L. G. Yang, Superabsorbent polymeric materials. XII. Effect of montmorillonite on water absorbency for poly (sodium acrylate) and montmorillonite nanocomposite superabsorbents. *Journal of Applied Polymer Science*, **92**: 3422 (2004).
16. K.Kabiri. and M.J. Zohuriaan-Mehr, Porous superabsorbent hydrogel composites: synthesis, morphology and swelling rate. *Macromolecular Materials and Engineering*, **289**: 653(2004).
17. W.Li, Z.Huijun, P.R. Teasdale and J.Richard , Preparation and characterisation of a poly (acrylamidoglycolic acid-co-acrylamide) hydrogel for selective binding of Cu 2+ and application to diffusive gradients in thin films measurements. *Polymer*, **43**: 4803 (2002).
18. J.Wu, J. Lin, M. Zhou and C Wei, Synthesis and properties of starch-graft-polyacrylamide/clay superabsorbent composite. *Macromolecular Rapid Communications*,. **21**: 1032 (2000).
19. A. Li, A. Wang, and J. Chen, Studies on poly (acrylic acid)/attapulgite superabsorbent composite. I. Synthesis and characterization. *Journal of Applied Polymer Science*. **92**: 1596 (2004).
20. D. Gao, R.B. Heimann, L. Johannes, J. Seidel and G. J. Wolf, Development of a novel moisture sensor based on superabsorbent poly (acrylamide)-montmorillonite composite hydrogels. *Journal of materials science*, **36**: 4567 (2001).
21. R. Homayoonmehr, A. A.Ramezaniannpour, and M. Mirdarsoltany, Influence of metakaolin on fresh properties, mechanical properties and corrosion resistance of concrete and its sustainability issues: A review. *J. Build. Eng.* **44**, 103011(2021).
22. J. Zhang, Y. Kun, P. W. Yun. G.Sheng and Z. Sheng, Preparation and properties of polyacrylate/bentonite superabsorbent hybrid via intercalated polymerization. *Materials Letters*. **61**: 316 (2007).

23. A.Pourjavadi, and M.S. Amini-Fazl, Optimized synthesis of carrageenan-graft-poly (sodium acrylate) superabsorbent hydrogel using the Taguchi method and investigation of its metal ion absorption. *Polymer international*, **56**: 283 (2007).
24. S. S. Yilmaz, K. Dilek E. Muammer, M. Özdemir, A. Riza. Synthesis of a novel crosslinked superabsorbent copolymer with diazacyclooctadecane crown ether and its sorption capability. *European polymer journal*, **43**: 1923 (2007).
25. J. Zhang, H. Chen, and A. Wang, Study on superabsorbent composite. III. Swelling behaviors of polyacrylamide/attapulgit composite based on acidified attapulgite and organo-attapulgite. *European Polymer Journal*. **41** 2434 (2005).
26. Y.Shi. X. Zhenhua, W.Ximing, W. Aiqin and W.li Removal of methylene blue from aqueous solution by sorption on lignocellulose-g-poly (acrylic acid)/montmorillonite three-dimensional cross-linked polymeric network hydrogels. *Polymer bulletin*, **70**, 1163 (2013).
27. X.Wang, Y. Zheng, and A. Wang, Fast removal of copper ions from aqueous solution by chitosan-g-poly (acrylic acid)/attapulgit composites. *Journal of hazardous materials*, **168**, 970 (2009).
28. P.Mishra, and R. Patel, Removal of lead and zinc ions from water by low cost adsorbents. *Journal of Hazardous Materials*, **168**: 319 (2009).
29. W.Song, W.Wei, C.Ren, and S.Zhang, Effect of heat treatment or alkali treatment of veneers on the mechanical properties of eucalyptus veneer/polyethylene film plywood composites, *BioRes*. **12**, 8683 (2017).
30. H. A. Patel, S. S. Rajesh, C. B.Hari, and V. J. Raksh, Preparation and characterization of phosphonium montmorillonite with enhanced thermal stability. *Applied Clay Science*, **35**, 194 (2007).
31. I. Mathakiya, V. Vangani, and A. K. Rakshit, Terpolymerization of acrylamide, acrylic acid, and acrylonitrile: Synthesis and properties. *Journal of applied polymer science*, **69**: 217 (1998).
32. Y. Bulut, A. Gülten, E. Duygu and S. S.Ersin Synthesis of clay-based superabsorbent composite and its sorption capability. *Journal of hazardous materials*, **171**: 717 (2009).
33. S. T. Akar, Y. Yetimoglu, and T. Gedikbey, Removal of chromium (VI) ions from aqueous solutions by using Turkish montmorillonite clay: effect of activation and modification. *Desalination*, **244**, 97 (2009).
34. B. Pan, W. Zhang, L. Lu, Z. Quanxing, and S. Zheng, Development of polymeric and polymer-based hybrid adsorbents for pollutants removal from waters. *Chemical Engineering Journal*. **151**: 19 (2009).
35. G. Güçlü, A. Ebru, E. Serkan, I. Tülin, S. Özgümüş and O.Mustafa , Removal of Cu⁺and Pb²⁺ ions from aqueous solutions by starch-graft-acrylic acid/montmorillonite superabsorbent nanocomposite hydrogels. *Polymer bulletin*, **65** p. 333(2010).
36. S.Hua, and A. Wang, Synthesis, characterization and swelling behaviors of sodium alginate-g-poly (acrylic acid)/sodium humate superabsorbent. *Carbohydrate Polymers*, **75**, 79 (2009).
37. S. Azizian, A Novel and Simple Method for Finding the Heterogeneity of Adsorbents on the Basis of Adsorption Kinetic Data. *J. Colloid Interface Sci.* **302**, 76 (2006).
38. F. Bouhamed, Z. Elouear, J. Bouzid, Adsorptive removal of copper (II) from aqueous solutions on activated carbon prepared from Tunisian date stones: Equilibrium, kinetics and thermodynamics. *Journal of the Taiwan Institute of Chemical Engineers*; **43**: 741 (2012).
39. J. Zhang, L. Wang and A. Wang, Preparation and properties of chitosan-g-poly (acrylic acid)/montmorillonite superabsorbent nanocomposite via in situ intercalative polymerization. *Industrial & engineering chemistry research*, **46**: 2497 (2007).
40. J. Zhang, H. Chen, and A. Wang, Study on superabsorbent composite. IV. Effects of organification degree of attapulgite on swelling behaviors of polyacrylamide/organo-attapulgite composites. *Eur. Poly*, **42**: 101 (2006).
41. P. S. Liu, L. Li, Z. Ning, Z. Jun, and S. Jian, Waste polystyrene foam-graft-acrylic acid/montmorillonite superabsorbent nanocomposite. *Journal of Applied Polymer Science*, **104**, 2341 (2007).
42. J. Wu, L. Jianming, L. Guoqing, and W. Congrong, Influence of the COOH and COONa groups and crosslink density of poly (acrylic acid)/montmorillonite superabsorbent composite on water absorbency. *Polymer international*, **50**: p. 1050 (2001).
43. A. Saeidi, K. Ali, V. Ebrahim, and A Farhad, Formulation design, optimization, characterization and swelling behaviour of a cationic superabsorbent based on a copolymer of [3-(methacryloylamino) propyl] trimethylammonium chloride and acrylamide. *Polymer international*, **53**: 92 (2004).
44. Z. Liu, and G. Rempel, Preparation of superabsorbent polymers by crosslinking acrylic acid and acrylamide copolymers. *Journal of applied polymer science*, **64**: 1345 (1997).