



Synthesis of clay-based superabsorbent composite and its sorption capability

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ABSTRACT

A novel superabsorbent composite was synthesized by copolymerization reaction of partially neutralized acrylic acid (AA) on bentonite micropowder using *N,N'*-methylenebisacrylamide as a crosslinker and ammonium persulfate as an initiator in aqueous solution. The superabsorbent composite (SAC) was characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The water retention test of SAC was also performed. The water absorbency of SAC synthesized was found to be 352 and 110 g H₂O g⁻¹ in distilled water and 0.2% NaCl, respectively. Sorption capacity of SAC was investigated for heavy metal ions (HMI) using Langmuir and Freundlich model of adsorption. The maximum adsorption capacity (Q_m) of HMI onto the bentonite-based SAC from their solution was 1666.67, 270.27, 416.67 and 222.22 mg g⁻¹ for Pb(II), Ni(II), Cd(II) and Cu(II), respectively.

All results suggested that SAC offers excellent potential for HMI removal from contaminated water.

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1. Introduction

Superabsorbent hydrogels are loosely crosslinked hydrophilic polymers that can absorb, swell and retain aqueous solutions up to hundreds of times their own weight [1]. Because of their superior properties they have hygienic, agricultural, medical and pharmaceutical applications [2,3]. In such applications, water absorbency and water retention are essential [4]. Some authors modified these absorbent polymers to enhance their absorbency, gel strength, and absorption rate [1–4]. In recent years, the preparation of organic–inorganic superabsorbent composites has attracted great attention because of their relatively low production cost, high water absorbency and their considerable range of applications in agriculture and horticulture [1,4]. The used clay in this work is bentonite because of its natural abundance and low cost. Over the last decades, a remarkable increase of heavy metal contaminant volume has posed many serious environmental problems due to their toxicity to many living forms. Heavy metals are metabolic poisons and enzyme inhibitors.

They can cause mental retardation and semipermanent brain damage [5,6]. Their concentration must be reduced to meet ever increasing legislative standards. According to World Health Organization, the metals of most immediate concern are chromium, nickel, copper, lead, mercury and zinc. Usually, when using meth-

ods such as chemical precipitation and reverse osmosis for the removal of metal ions from their aqueous solutions, metal removal is incomplete. Moreover, these processes have high reagent and energy requirement, and the toxic sludge produced requires careful disposal. The need for cost-effective and safe methods for removing toxins has resulted in the development of polymeric and co-polymeric materials, which have the ability to remove metal ions through complexation and ion-exchange mechanism. Recently, considerable interest has been generated in the development of such polymeric materials, as a tool for removing metal ions polluting surface waters [7]. Ease of handling, reusability and possibility of semi-continuous operations are other advantages which encourage the use of these materials and make them promising for water purification and in the field of hydrometallurgical applications due to their chemical stability especially hydrolytic and thermal stability [5,8]. Essawy and Ibrahim [8] prepared poly(vinylpyrrolidone-co-methylacrylate) hydrogel and studied its binding properties for a range of heavy metal ions (Cu(II), Cd(II) and Ni(II)) under varying conditions of pH, metal concentration and time. Li et al. [9] prepared poly(acrylamidoglycolic acid-coacrylamide) hydrogel and studied its binding properties for a range of metal ions (Cu(II), Cd(II), K, Na, Mg(II) and Ca(II)) under varying conditions of pH, ionic strength, metal concentration and time. The novel acrylic acid and acrylic acid grafted-cellulose based hydrogels have also been used for the removal of metal ions [7,10,11]. Recently, macroporous poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) hydrogels with different porosity parameters have been employed for the removal of Cu(II), Cd(II) and Cr(III) under noncompetitive conditions [12]. Likewise,

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Table 1
Conditions of preparation of SAC.

AA (g)	Water (mL)	Neutralization degree (%)	Clay (g)	MBA (g 10 ⁺³)	Initiator (g 10 ⁺³)	T (°C)	Time (h)
7.2	20	60	0.72	14.4	79.2	70	2

carboxymethyl chitin and carboxymethyl chitosan [13] have also been used for the removal of Cu(II) ions.

This paper deals with the synthesis of poly (AA)-bentonite superabsorbent composites (SAC). Firstly, the swelling behaviour of SAC was investigated in aqueous and salt solution. The SAC prepared was characterized by FTIR. Morphological and thermal properties of SAC were also investigated. Finally the SAC was used in adsorption studies. Adsorption of heavy metal ions (Pb(II), Ni(II), Cd(II) and Cu(II)) on SAC from aqueous solutions was also investigated. The influence of the uptake conditions, such as time and initial concentration of HMI on the SAC was also tested.

2. Experimental

2.1. Materials

Acrylic acid (AA) monomer, ammonium persulfate (I, initiator) and N,N'-methylene bisacrylamide (MBA) as a crosslinking agent were supplied by Aldrich (A.R. grade). Ethanol was of analytical reagent grade. The polymerization temperature was kept constant at 70 ± 0.1 °C, using a Heidolph (MR Hei-Standard) hot plate. Bentonite is defined as a sedimentary rock consisting of a large proportion of expandable clay minerals with three-layer structure (smectites) such as montmorillonite, beidellite and nontronite [1]. The bentonite was used as clay in this study and obtained from the town of Elazığ-Turkey. The sample was characterized by XRF. The chemical compositions of the bentonite were found to be as follows: 39.6% SiO₂, 24.2% CaO, 9.57% Al₂O₃, 5.2% Fe₂O₃, 2.4% MgO, 1.4% MnO, 0.9% K₂O, 0.7% SrO, 0.6% TiO₂, 14.0% loss on ignition. After drying at 110 °C, the sample was pulverized to pass through a 150 μm sieve. Adsorption and desorption experiments using N₂ were carried out at 77 K on a Quantochrome Autosorb-1-C/MS sorptiometer. Prior to each measurement the sample was outgassed at 10⁻³ Pa and 353 K for 3 h. The N₂ isotherms were used to determine the specific surface area (SA). The surface area was calculated using multi-point BET methods. The surface area of bentonite micropowder was determined as 67 m² g⁻¹. The cation-exchange capacity (CEC) of the bentonite sample was determined according to the ammonium acetate saturation method and was found to be 0.61 meq/g clay [14]. All the metal ion reagents (Pb(II), Ni(II), Cd(II) and Cu(II)) were of analytical grade, purchased from Aldrich, and used without any purification.

2.2. Preparation of SAC

Typical preparation conditions for samples are as follows [1]: acrylic acid monomer (7.2 g), was dissolved in distilled water (20 ml) and was partially neutralized with a sodium hydroxide solution to the degree of 60%. Clay powder (0.72 g) was dispersed in the above monomer solution. No precipitation or agglomeration of clay particles was observed. The crosslinker, MBA (14.4 mg) was added to the mixture of a clay solution under nitrogen atmosphere. The mixture was stirred at 250 rpm until the MBA was dissolved completely. The initiator (79.2 mg) was then added to the reactor. The polymerization reaction temperature was set at 70 °C for 2 h to ensure full consumption of the monomers (Table 1). The resulting rubbery gel was removed from the reaction vessel and cut into small pieces by means of scissors whose length was about 2–5 mm. The pieces were then introduced into stirred ethanol (400 ml), and the

polymer was precipitated. All samples were dried in a vacuum oven at 80 °C until constant weight, before any tests were performed.

2.3. Characterization of SAC

The IR spectra of the superabsorbent composite were recorded on Jasco model a FTIR 5300 Fourier Transform Infrared Spectrometer. Thermal stability studies of dry samples were performed on a TA, TGA Q 50 thermogravimetric analyzer with a temperature range of 30–800 °C at a heating rate of 10 °C/min by using a dry nitrogen purge at a flow rate of 50 mL min⁻¹. The morphology of the dried samples was examined by a Field Emission Scanning Electron Microscopy, JEOL, JSM-7000F SEM instrument after coating the sample with gold film.

2.4. Measurement of water absorbency

For dried polymers, a fixed amount (0.10 g) of classified (100–200 μm) product was dispersed in 100 mL of deionised water or saline solution (0.2 wt.% NaCl (aq)) and allowed to swell at constant temperature (25 °C) to reach the swelling equilibrium. Same procedure was conducted for different pH values. pH was adjusted by using HCl or NaOH. The dispersion was filtered through a wire gauze and dried carefully at room temperature. The drying process was found to be complete when the gel particles no longer slipped from the gauze when it was held vertically. Two different samples were examined for each time of swelling and averaged. The amount of water absorbency was calculated as follows [1]:

$$W_t = \frac{W_s - W_d}{W_d} \quad (1)$$

where W_t is swelling at time t , W_s is weight of the swollen SAC at time t , and W_d is weight of the dried SAC.

In order to determine the reusability of SAC, consecutive swelling–deswelling–swelling cycles were repeated five times by using the same composites. Furthermore, swelling experiments were repeated in toluene, chloroform, benzene, methyl alcohol and ethyl alcohol instead of deionised water. It was observed that the SAC did not swell in any solvent except water.

2.5. Adsorption studies

Heavy metal ion adsorption from the single metal aqueous solutions was investigated in batch experiments. In order to determine sorption rate of SAC, 250 mL of the solutions containing 100 mg/L of Pb(II), Ni(II), Cd(II) and Cu(II) ions were separately prepared with deionised water. Then, 0.025 g SAC was added to the solutions. The solutions were stirred at 25 °C, with an agitation speed of 150 rpm. The concentration of the metal ions in the aqueous phases at certain times (5–240 min) was determined by using AAS (Unicam model Atomic Absorption Spectrometer) and deuterium background correction was used. The instrument response was periodically checked with known heavy metal solution standards. For each sample, the mean of twice AAS measurements was recorded. The amount of adsorbed heavy metal ions was calculated by the following equation [3,6]:

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

where q is the amount of metal ions adsorbed onto unit amount of the composites (mg g⁻¹); C_0 and C_e are the concentrations of metal ions in the initial solution and in the aqueous phase after adsorption, respectively (mg mL⁻¹); V is the volume of the aqueous phase (mL), and m is the weight of SAC (g).

The effects of the initial HMI concentration on the adsorption capacity were studied. In all experiments, SAC concentration was

kept constant at 0.01 g/50 mL. The concentration of the metal ions in aqueous phases after the desired treatment periods was measured by using AAS.

Competitive adsorption of heavy metal ions from their mixture was also investigated in a batch wise form. A solution (200 mL) containing 100 and 250 mg L⁻¹ from each metal ion was treated with the 0.2 g SAC at 25 °C, in the flask stirred magnetically at 150 rpm. After adsorption equilibrium, the concentration of metal ions in the remaining solution was measured by an AAS system.

Desorption of HMI was achieved by metal ions loaded (89.96 Pb(II), 27.11 Ni(II), 61.12 Cd(II) and 24.26 Cu(II) mg g⁻¹) SAC (0.01 g) were stirred with HNO₃ solution (50 mL, 0.1 N) at 25 °C for 150 min. The final metal ion concentration in the aqueous phase was determined by using an AAS. The desorption ratio was calculated from the amount of metal ions initially loaded on the composites and the final metal ion concentrations in the desorption medium and by the following equation [3]:

$$\text{Desorption ratio (\%)} = \frac{\text{Amount metal ions desorbed into the elution medium (mg)}}{\text{Amount of metal ions adsorbed onto the SAC (mg)}} \times 100 \quad (3)$$

3. Results and discussion

3.1. Structure characterization of SAC

The surface morphology of SAC was examined using scanning electron microscopy (SEM). The dried specimens were coated with a platinum metal layer to provide proper surface conduction. Fig. 1 shows the photographs obtained from SEM of the microstructure polymer nanocomposite. The SEM results show a well dispersion of the clay particles in polymer matrix. The FTIR spectrum of SAC is shown in Fig. 2. The C–H stretching bands of alkylammonium molecules occur in the 3000–2850 cm⁻¹. Two intense bands at 2988 and 2901 cm⁻¹ show the antisymmetric and symmetric CH₂ stretching modes, respectively. At the same time, N–H stretching of NH groups and O–H stretching of OH groups are shown at 3432 and 3675 cm⁻¹, respectively. Also, alkylammonium molecules give strong bands near 1457 cm⁻¹ attributed to antisymmetric C–H bonding of CH₂ groups. C=C stretching of CH₂ groups and stretching C=O of CO groups are shown at 1581 and 1735 cm⁻¹, respectively. In addition, a band at 1407 cm⁻¹ is assigned to symmetric C–N. The strong absorption band at 1284 cm⁻¹ is attributed to C–O groups indicated. TGA curve is seen in Fig. 3, showing that polymer nanocomposite is a thermally stable material.

3.2. Swelling rate

The swelling rate of SAC was determined [15] and is shown in Fig. 4. The swelling increases with time, but with further increase in time, reaches a limiting value which is the equilibrium value. Fig. 4 indicates that the swelling rate of superabsorbent composite is high in 0–60 min and that the water absorbency of superabsorbent composite reaches 286.20 g g⁻¹ within 60 min. After 60 min, the swelling rate becomes low and the maximum swelling capacity (352 g g⁻¹) of SAC was reached within 180 min. Fig. 4 outlines the result obtained from the experiment carried out using 0.2% NaCl solution. As can be seen from figure SAC holds 76 g of water in the first 15 min and after 45 min reaching the equilibrium it holds 110 g of water. Effect of pH on water absorbency capacity of SAC was examined both for distilled water and 0.2% NaCl solution. Fig. 5 shows that water absorbency capacity was enhanced by increasing pH for distilled water. Moreover SAC was dissolved at pH 2 and no water absorbency was observed. Although pH was not considerably affected the water absorbency capacity in the case of 0.2% NaCl solution, water absorbency was maximum in the neutral region.

The SAC was not soluble in toluene, chloroform, benzene, methyl alcohol and ethyl alcohol.

3.3. Water retention test

Water retention of the swollen SAC was determined by centrifuging it at 5000 rpm for 90 min. The swollen superabsorbent composite samples show good ability of water retention and can keep approximately 97% of the distilled water. However, water retention of the swollen superabsorbent composites was determined by a heating oven test at different temperatures. Fig. 5 shows the water retention capacity of swollen superabsorbent composite (SAC, 40 g) as a function of time at 60 and 100 °C. The swollen sample had a decreasing tendency of water retention with prolonging the time. About 83% and 57% of distilled water could be held after 10 h of water retention test at 60 and 100 °C, respectively. In the case

of 60 and 100 °C water retention test, the water loss of SAC almost reached 99.9% after 72 and 24 h, respectively. After the swollen sample thoroughly lost its adsorption water, the resulting dry sample (SAC) still retained good water absorbing ability and could keep approximately 90% of initial water absorbency even after repeating 3 times of heating oven as seen in Fig. 6. Water absorbing ability diminished down to 24% in the fifth use (82.5 g g⁻¹).

3.4. Sorption results

3.4.1. Sorption rate and kinetic

Fig. 7 exemplifies adsorption rates of heavy metal ions by SAC as a function of time. The figure shows the changes in the metal ions adsorbed over time, which were calculated by using the expression given in Eq. (2). Note that these batch experiments were performed by using single (not multiple) solutions of the ions of interest. Adsorption conditions are given in the figure legend. As seen from Fig. 7 high adsorption rates were observed at the beginning and then plateau values (i.e., adsorption equilibrium) were gradually reached within 90–180 min for Pb(II), Ni(II), Cd(II) and Cu(II).

Various experimental data on the adsorption kinetics of heavy-metal ions by various sorbents have shown a wide range of adsorption rates [3,8,16–18]. For example, Apohan et al. considered 3 h to be a short equilibrium time in their metal ions (Cd(II), Cu(II) and Fe(II)) adsorption kinetics studies, in which hydrogels were used [16]. Essawy and Ibrahim investigated Cd(II), Cu(II), Cd(II) and Ni(II) adsorption on poly(vinylpyrrolidone-co-methylacrylate) hydrogel and reported that the adsorption was able to use a 1–2 h equilibrium time [8]. Pan et al. studied lead removal from aqueous solution by polymer-based zirconium phosphate and reported an equilibrium time of 150 min [17]. Say et al. investigated Pb(II), Cd(II) and Cr(III) adsorption on dithiocarbamate-anchored polymer/organosmectite composites and reported 15–25 min equilibrium adsorption time [18]. Yılmaz et al. investigated Pb(II), Cd(II), Cu(II), Cr(III), Mn(II), Zn(II) and Ni(II) adsorption on a novel crosslinked superabsorbent copolymer and reporting that the adsorption was able to use a 45–75 min equilibrium time [3].

Note that in such an adsorption process, there are several parameters which determine the adsorption rate: agitation rate in aqueous phase, sorbent structural properties (e.g., size, porosity, surface area), amount of sorbent, metal ion properties (e.g., hydrated ionic radius), initial concentration of metal ions, pH, temperature and of course, the existence of other ions which may compete with the ions of interest for active adsorption sites. All individual experimental studies published in the literature have

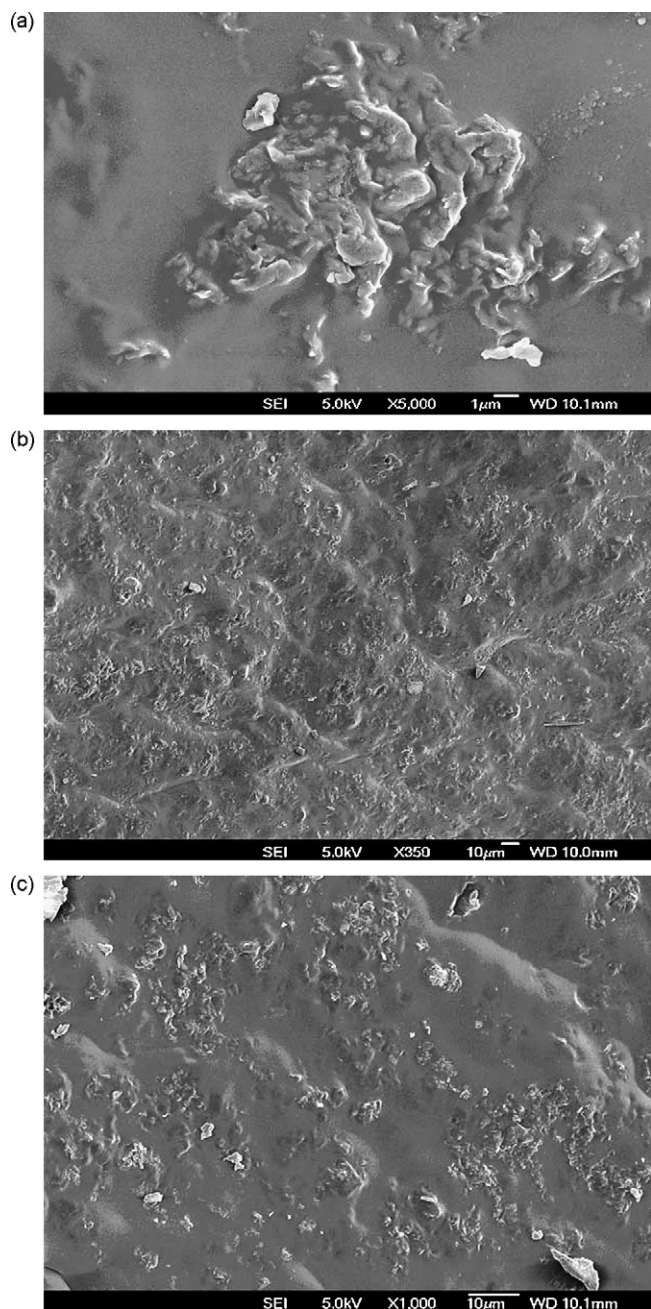


Fig. 1. Scanning electron micrographs for dried SAC.

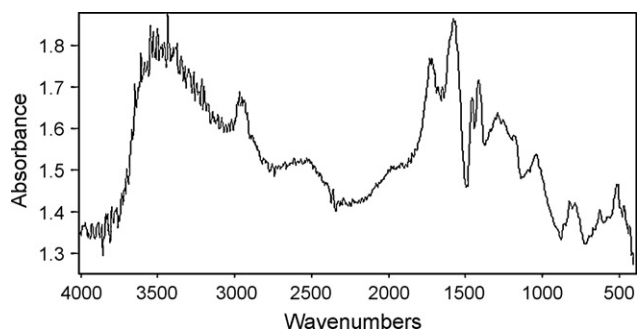


Fig. 2. FTIR spectra of SAC.

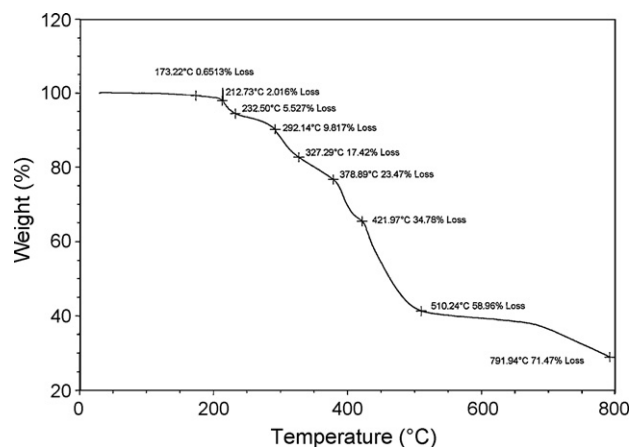


Fig. 3. TGA curves of SAC.

been performed under different conditions. Consequently, it is not possible to make a reasonable comparison of the adsorption rates reported. However, it can be said that, considering the above results, we have relatively good equilibrium time.

Kinetic data for HMI were then represented by the pseudo-first-order model (3) and pseudo-second-order model (4) [17,19]

$$\log(q_e - q_t) = \frac{\log q_e - k_f}{2.303t} \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e t} \quad (4)$$

where q_e and q_t are the amount sorbed in equilibrium and at time t , respectively, k_f and k_s are the sorption kinetic constants. Higher correlation coefficients and the calculated q_e values (Table 2) close to the experimental data indicated that HMI uptake onto SAC could be estimated more favorably by the pseudo-second-order model than the pseudo-first-order one.

3.4.2. Adsorption isotherms

The heavy metal ion adsorption capacities of SAC are given in Fig. 8 as a function of initial concentration of heavy metal ions within the aqueous phase. It was observed that the amount of adsorption was significantly increased with initial heavy metal concentration especially in the case of Pb(II) and also for Cd(II) in the studied initial concentration range (50–500 mg L⁻¹). During the batch experiments, adsorption isotherms were used to evaluate adsorption properties. For the systems considered, the Langmuir and Freundlich adsorption model were found to be applicable in interpreting Pb(II), Ni(II), Cd(II) and Cu(II) adsorption by the SAC.

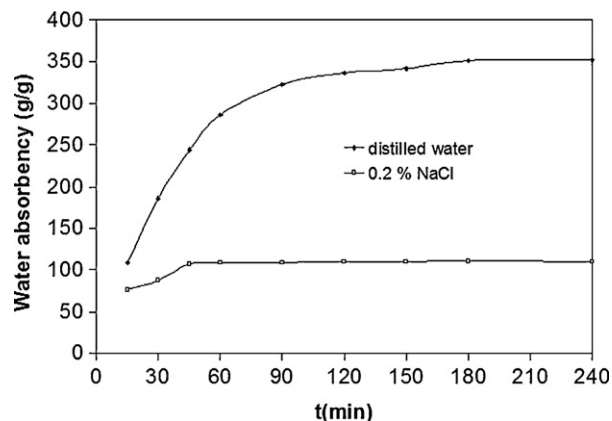


Fig. 4. Variation of the water absorbency with time for SAC.

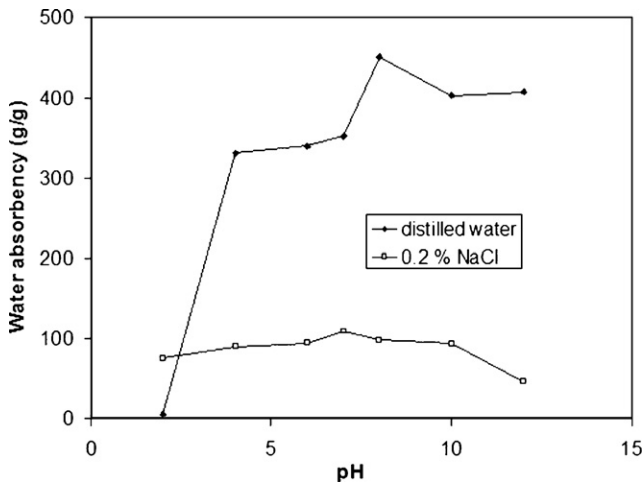


Fig. 5. Effect of pH on water absorbency capacity for SAC.

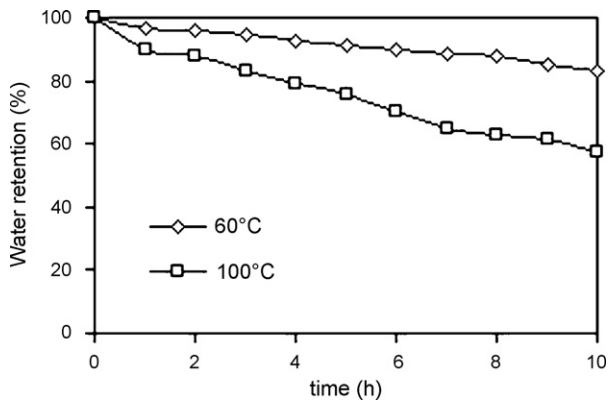


Fig. 6. Water retention of swollen samples (SAC, 40 g) as a function of time at 60 and 100 °C.

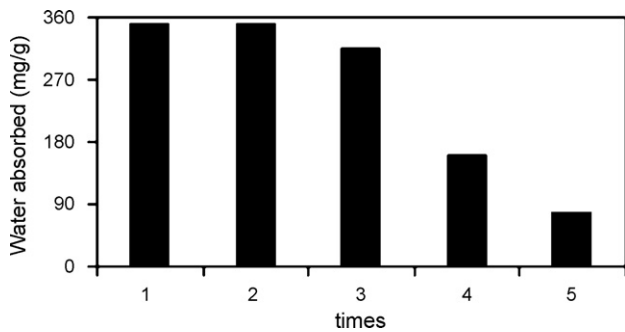


Fig. 7. Water absorbency of SAC as a function of swelling–deswelling–swelling times.

The Langmuir adsorption isotherm is expressed by Eq. (5). The corresponding transformations of the equilibrium adsorption data for Pb(II), Ni(II), Cd(II) and Cu(II) ions gave rise to a linear plot, indicating that the Langmuir model should be applied in this system and described by Eq. (5) [19]

$$\frac{C_{eq}}{q} = \frac{1}{bQ_{max}} + \frac{C_{eq}}{Q_{max}} \quad (5)$$

where q is the concentration of the adsorbed HMI on the adsorbent (mg g^{-1}), C_{eq} is the equilibrium HMI concentration in solution (mg L^{-1}), b is the Langmuir constant (L mg^{-1}), and Q_{max} is the maximum adsorption capacity (mg g^{-1}) (Fig. 9).

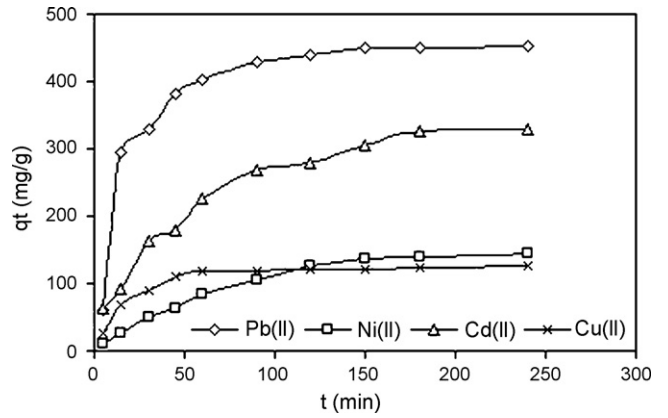


Fig. 8. Percent removal of HMI versus time.

The Freundlich isotherm is given in logarithmic form as (6) [19]:

$$\log q = \log K_F + \frac{1}{n} \log C_{eq} \quad (6)$$

where K_F is roughly an indicator of the adsorption and $(1/n)$ of the adsorption intensity, K_F and n can be determined from the linear plot of $\log q_e$ versus $\log C_e$.

Adsorption isotherms were obtained in view of Eqs. (5) and (6) by using experimental adsorption results in these equations. The values Q_{max} , b , K_F , and n are summarised in Table 3. The isotherm data were calculated from the least square method, and the related correlation coefficients (R^2 values) are given in the same table. As seen from Table 3, the Langmuir equation represents the adsorption process very well; the R^2 values were all higher than 0.97, indicating a very good mathematical fit. The maximum adsorption capacities of SAC at 25 °C in the studied range are 1666.67, 270.27, 416.67 and 222.22 mg g^{-1} for Pb(II), Ni(II), Cd(II) and Cu(II), respectively. The affinity order (weight basis) is Pb(II) > Cd(II) > Ni(II) > Cu(III) from the Langmuir model. It should be noted that the maximum adsorption capacities (molar basis) of SAC are 8.04, 4.60, 3.71 and 3.50 mmol g^{-1} of SAC for Pb(II), Ni(II), Cd(II) and Cu(II), respectively. The order of affinity based on millimole uptake by the sorbent differs according to weight base and is as follows: Pb(II) > Ni(II) > Cd(II) > Cu(III).

A brief comparison of metal ion sorption capacity of SAC and some composites recently reported are given in Table 4. The values of free energy change (ΔG°) for the sorption process were calculated, using the following Eq. (7) [19]

$$\Delta G^\circ = -RT \ln b \quad (7)$$

The estimated values of ΔG° for adsorption of HMI onto SAC were -20.52 , -13.28 , -18.86 and -13.12 kJ mol^{-1} for Pb(II), Ni(II),

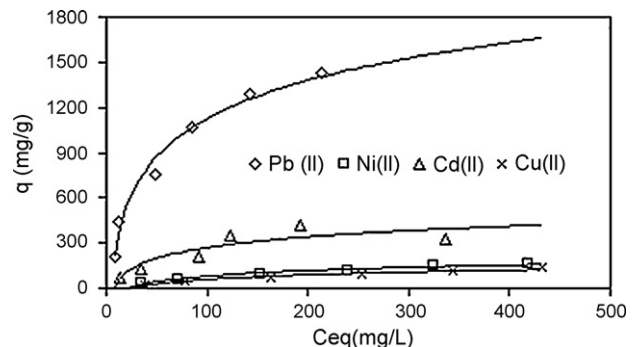


Fig. 9. Adsorption isotherms of Pb(II), Ni(II), Cd(II) and Cu(II).

Table 2
Adsorption kinetic parameters of Pb(II), Ni(II), Cd(II) and Cu(II) on SAC.

HMI	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	k_f (min ⁻¹)	q_e (mg g ⁻¹)	R_1^2	k_s (g mg ⁻¹ min ⁻¹) 10 ⁴	q_e (mg g ⁻¹)	R_2^2
Pb(II)	0.0299	309.74	0.9748	724.64	500.00	0.9987
Ni(II)	0.0214	161.36	0.9600	10.01	208.33	0.9995
Cd(II)	0.0205	310.24	0.9438	136.84	384.62	0.9997
Cu(II)	0.0214	154.33	0.5502	16.01	135.14	0.9987

Co = 100 mg L⁻¹, $m = 0.025$ g, $V = 250$ mL, $T = 25$ °C, stirred speed = 150 rpm.

Table 3
Adsorption constants for the sorption of Pb(II), Ni(II), Cd(II) and Cu(II) on SAC.

HMI	Freundlich constants			Langmuir constants				ΔG (kJ mol ⁻¹)
	K_F	n	R_F^2	Q_m (mg g ⁻¹)	b (L mg ⁻¹)	b (L mol ⁻¹)	R_L^2	
Pb(II)	83.17	0.45	0.9183	1666.67	0.0190	3946.67	0.9854	20.52
Ni(II)	3.09	0.33	0.9708	270.27	0.0036	212.34	0.9905	13.28
Cd(II)	19.95	0.46	0.8576	416.67	0.0179	2022.37	0.9714	18.86
Cu(II)	2.26	0.33	0.9876	222.22	0.0032	199.62	0.9743	13.12

$m = 0.01$ g, $V = 50$ mL, $T = 25$ °C, stirred speed = 150 rpm, time = 180 min.

Table 4
Adsorption capacities for some reported in the literatures.

Adsorbent	Pb(II)	Ni(II)	Cd(II)	Cu(II)	Reference
SAC (mg g ⁻¹)	1666.66	270.27	416.67	222.22	Present study
Hydrogel (mg g ⁻¹)	–	–	74.12	62.74	[16]
A novel crosslinked copolymer (mg g ⁻¹)	215.49	27.00	213.57	–	[3]
Dithiocarbamate-anchored polymer/organosmectite composites (mg g ⁻¹)	170.70	–	82.20	–	[18]
Poly(ethylene glycol dimethacrylate- <i>n</i> -vinyl imidazole) beads (mg g ⁻¹)	117.60	–	71.40	–	[6]

Cd(II) and Cu(II), respectively. Negative ΔG° values indicate the spontaneous nature of the adsorption process.

3.4.3. Competitive adsorption

Competitive adsorption capacities of SAC for metal ions under competitive conditions (adsorption from solutions containing all heavy metal ions) for Pb(II), Ni(II), Cd(II) and Cu(II) are given in Table 5. The SAC exhibits the following metal ion affinity sequence (weight basis) under competitive adsorption conditions: Pb(II) > Cd(II) > Cu(II) > Ni(II) at 100 and 250 mg L⁻¹ initial concentration. The order of affinity based on millimole uptake

Table 5
Competitive adsorption of heavy metal ions on SAC.

Ions	Concentration of each metal ions (mg L ⁻¹)			
	100		250	
	q (mg g ⁻¹)	q (mmol g ⁻¹)	q (mg g ⁻¹)	q (mmol g ⁻¹)
Pb(II)	85.68	413.51	201.60	972.97
Ni(II)	19.06	324.65	8.40	143.08
Cd(II)	67.68	602.08	118.68	1055.78
Cu(II)	64.13	1009.13	96.20	1513.77

$m = 0.02$ g, $V = 200$ mL, $T = 25$ °C, stirred speed = 150 rpm, time = 180 min.

Table 6
Desorption ratios of heavy metal ions from SAC and ionic diameters of the metal ions (ID) [3].

Metal ion	ID (Å)	Amount of the sorbed metal ion (mg)	Amount of the desorbed metal ion (mg)	Desorption ratio (%)
Pb(II)	2.42	89.96	72.40	80.48
Ni(II)	1.34	27.11	26.00	95.91
Cd(II)	1.82	61.12	48.39	79.17
Cu(II)	1.44	24.26	23.85	98.31

$m = 0.01$ g, $V = 50$ mL, $T = 25$ °C, stirred speed = 150 rpm, time = 180 min.

by the sorbent differs according to weight base is as follows: Cu(II) > Cd(II) > Pb(II) > Ni(II) at 100 and 250 mg L⁻¹ initial concentration.

The removal of some of heavy metal ions on a novel crosslinked copolymer was investigated and affinity order under competitive Pb(II) > Cu(II) > Cd(II) > Zn(II) (weight basis) was reported [3]. Also, Say et al. [18] investigated and found that the dithiocarbamate-anchored polymer/organosmectite composites exhibit the following metal ion affinity sequence (weight basis) under non-competitive and competitive conditions: Cr(III) > Pb(II) > Cd(II).

3.4.4. Desorption and reusability of SAC

Desorption experiments were performed with 0.1 M HNO₃ as the desorption agent. The SAC loaded the maximum amounts of the respective metal ions when placed within the desorption medium, the amount of metal ions desorbed in 150 min was measured. Table 6 shows the adsorption–desorption values of heavy metal ions by SAC after several cycles of consecutive adsorption and desorption. The desorption ratios were between 98.31% (for Cu(II)) and 79.17% (for Cd(II)). This table clearly shows that the SAC can be used repeatedly without losing their adsorption capacities for all metal ions studied here.

4. Conclusions

Novel poly AA-bentonite superabsorbent composite was synthesized by a solution polymerization technique. The swelling behaviour of this superabsorbent composite was investigated in deionised water and saline solution. However, superabsorbent composite synthesized was used for adsorption of Pb(II), Ni(II), Cd(II) and Cu(II) from aqueous solutions. The following conclusions are drawn from the present investigation.

A maximum value of 352 and 110 g water (g dried SAC)⁻¹ were achieved at 180 and 45 min distilled water and 0.2% NaCl solution, respectively. Furthermore, effect of pH on water absorbency capac-

ity for SAC was investigated. The SAC was not soluble in toluene, chloroform, benzene, methyl alcohol and ethyl alcohol. However, it could swell in water. The water retention test of SAC was also carried out and the results obtained from this study show that the SAC has a good water retention capacity. Thus this superabsorbent can also be used to remove water from the organic solvents as well as the usage of a good heavy metal removing agent. Also, this novel superabsorbent with excellent water absorbency and water retention under load could be especially useful in agricultural and horticultural applications.

It successfully sorbed heavy metal ions (Pb(II), Ni(II), Cd(II) and Cu(II)) and desorbed them in an acidic media. The maximum binding capacity (Q_m) of SAC for different metal ions was in the order Pb(II) > Cd(II) > Ni(II) > Cu(II). Considering the above results, it can be concluded that the method applied here is a cheap and highly selective for the removal of heavy metal ions.

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