Novel thermally stable poly(vinyl chloride) composites for sulfate removal

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ABSTRACT

$BaCO_3$ dispersed PVC composites were prepared through a polymer re-precipitation method. The composites were tested for sulfate removal using rapid small scale column test (RSSCT) and found to significantly reduce sulfate concentration. The method was extended to synthesize barium carbonate-loaded silica aero-gels-polyvinyl chloride (PVC) polymer composites. The PVC composites were characterized using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray mapping, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and inductively coupled plasma mass spectrometry (ICP-MS) analysis. The method has advantages over conventional sulfate precipitation (sulfate removal process) using $BaCO_3$ wherein clogging of the filter can be avoided. The method is environmentally friendly and does not interfere with natural organic matter as the conventional resin does. Some of the composites were thermally more stable as compared with the pure PVC discussed in the literature.

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1. Introducton

Organic and inorganic nanocomposites have received a large amount of attention because these materials often exhibit unexpected properties [1–8]. One of the most promising composite systems is polymer nanocomposites where clays are dispersed in a polyvinyl chloride (PVC) polymer matrix [1–8]. Among other polymers, PVC is one of the major thermoplastics used today (worldwide production is thought to be 36 million tons per year) [9]. Due to its interesting properties, various PVC composites have been prepared by dispersing double hydroxides [10], $CaCO_3$ [11,12], metal oxides [12], multiwall carbon nanotubes [13], C-60 [14], polyaniline, a conducting polymer [15], and silica [16,17]. Soong et al. have reported the feasibility of using copper nanoparticle-dispersed PVC nanocomposites toward environmental remediation techniques, such as antifungal and bacteriostatic applications [18].

Organic and inorganic composites can find various applications including an environmental remediation such as water purification. Recently, there has been great interest in the removal of sulfate from drinking water [19,20]. People unaccustomed to drinking water with elevated levels of sulfate can experience diarrhea and dehydration. Infants are often more sensitive to sulfate than adults. As a precaution, water with a sulfate level exceeding 400 mg/L should not be used in the preparation of infant formula. Older children and adults become accustomed to high sulfate levels after a

few days. Animals are also sensitive to high levels of sulfate. In young animals, high levels may be associated with severe, chronic diarrhea, and in a few instances, death. As with humans, animals tend to become accustomed to sulfate over the time.

In addition to health concerns, high sulfate levels may also corrode plumbing, particularly copper piping. In areas with high sulfate levels, plumbing materials which are more resistant to corrosion, such as plastic pipes, are commonly used. The most common method of sulfate removal is precipitation of sulfate with $BaCO_3$ and/or use of polymer ion exchange resins. The former methods have high capacity of sulfate removal but have several drawbacks. Furthermore, clogging problems while $BaSO_4$ filtration and direct exposure of barium sulfate. The later polymer resin process leads to removal of natural organic materials other than sulfate. In order to address the above drawbacks, we report a facile one-pot synthesis of PVC composites that removes sulfate without eliminating other natural organic matter. The method also allows to create a porosity thus by avoiding column clogging problems and direct exposure to barium salts. The obtained barium entrapped PVC composites were tested for sulfate removal using rapid small scale column test (RSSCT) and found to significantly reduce sulfate concentration compared to the control pure PVC. The method is extended to make other composites such as silica-aerogel-PVC composites wherein silica aero-gels preloaded with barium carbonate.

2. Experimental

Preparation of $BaCO_3$ loaded polyvinyl chloride (PVC) polymer composites. Predetermined amounts of PVC (43.27 g) were

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Table 1
BaCO$_3$ and or silica aero-gel loaded PVC polymer composites composition.

Serial Number	Composition[a]	Code given
1	2 g of silica aero-gel loaded BaCO$_3$ + 1 mL of PVC	BA-1
2	2 g of silica aero-gel loaded BaCO$_3$ + 5 mL of PVC	BA-2
3	2 g of silica aero-gel loaded BaCO$_3$ + 15 mL PVC	BA-3
4	3 g of BaCO$_3$ + 10 mL PVC	BA-4
5	5 g of BaCO$_3$ + 50 mL of PVC	BA-5
6	50 g of BaCO$_3$ + 50 mL of PVC	BA-6
7	10 g of BaCO$_3$ + 10 mL of PVC	BA-7

[a] Predetermined amounts of PVC (43.27 g) were dissolved in a THF solvent (1000 mL), and the stoichiometric amount of BaCO$_3$ was added.

dissolved in a THF solvent (1000 mL), and the stoichiometric amount of BaCO$_3$ was added (as shown in Table 1) and the mixture was stirred using a magnetic stirrer. The polymer mixture containing BaCO$_3$ was re-precipitated by adding water. The BaCO$_3$-loaded PVC was washed several times with water, and then dried at room temperature. The EDS spectra and elemental compositions are shown in supplemental Figures S1–S6 and Table S1–S6. This method ensures that no thermal degradation occurs due to low room temperature synthesis, as compared with the melt blending technique found in the literature and, which operates at a higher temperature.

Similarly, the barium-loaded silica aero-gels were prepared by hydrolyzing a stoichiometric amount of tetraethyl orthosilicate (TEOS) in ethanol with barium hydroxide at room temperature. Then the barium-loaded silica aero-gels composites with PVC were prepared as described above. The samples were then characterized with scanning electron microscopy (SEM) (JEOL-6490LV with an Oxford X-Act EDS system was used for imaging and elemental analysis generally following ASTM E1508 procedures). XRD was used to identify crystalline phases of barium composites. PANalytical Xpert

Pro theta-two theta diffractometer using a Cu Kα radiation at 45 kV and 40 mA was used. Scans were typically over the range of 5–90° 2θ, with 0.02° step sizes that were held for 2 s each. Pattern analysis was performed using the Jade+ software v.7 or later (MDI, Inc., Livermore, CA), which generally followed the ASTM D934-80 procedure. Reference patterns were from 2002 PDF-2 release from the ICDD (International Center for Diffraction Data, Newtown Square, PA).

For sulfate removal, the glass column was 20 cm in height, had an inner diameter of ∼0.8 cm, and was filled to 10.5 cm of composites. The flow rate through the column was kept at 1.0 ± 0.1 mL/min for each of the experiments. A 1075 mg/L sulfate solution was pass through the column and 1 mL/min effluent solution was collected and tested with Hach spectrometer using sulfate powder pillows manufactured by Hach. TGA curves were obtained using a Perkin–Elmer Thermal Analyzer with a heating rate of 10 °C/min under air.

3. Results and discussion

The barium carbonate loaded PVC composites were prepared by dissolving PVC in tetrahydrofuran (THF), followed by dispersion of the BaCO$_3$ and re-precipitation of PVC with water. The synthesis can be accomplished at room temperature and no need of melting PVC at higher temperatures. The other advantages of the method are that during re-precipitation, the barium carbonate and or barium carbonate-loaded silica gels can encapsulate into the PVC matrix and thus create porosity in the PVC matrix. Since PVC is a thermoplastic polymer, the re-precipitation does not yield any gelatinous precipitate like many other polymers do. The advantages of using pre-loaded silica aero-gels are: (1) barium is part of the silica matrix in the hydrolysis process, eliminating solubility issues of BaCO$_3$ in water, thus reducing waste of BaCO$_3$ and environmental issues,
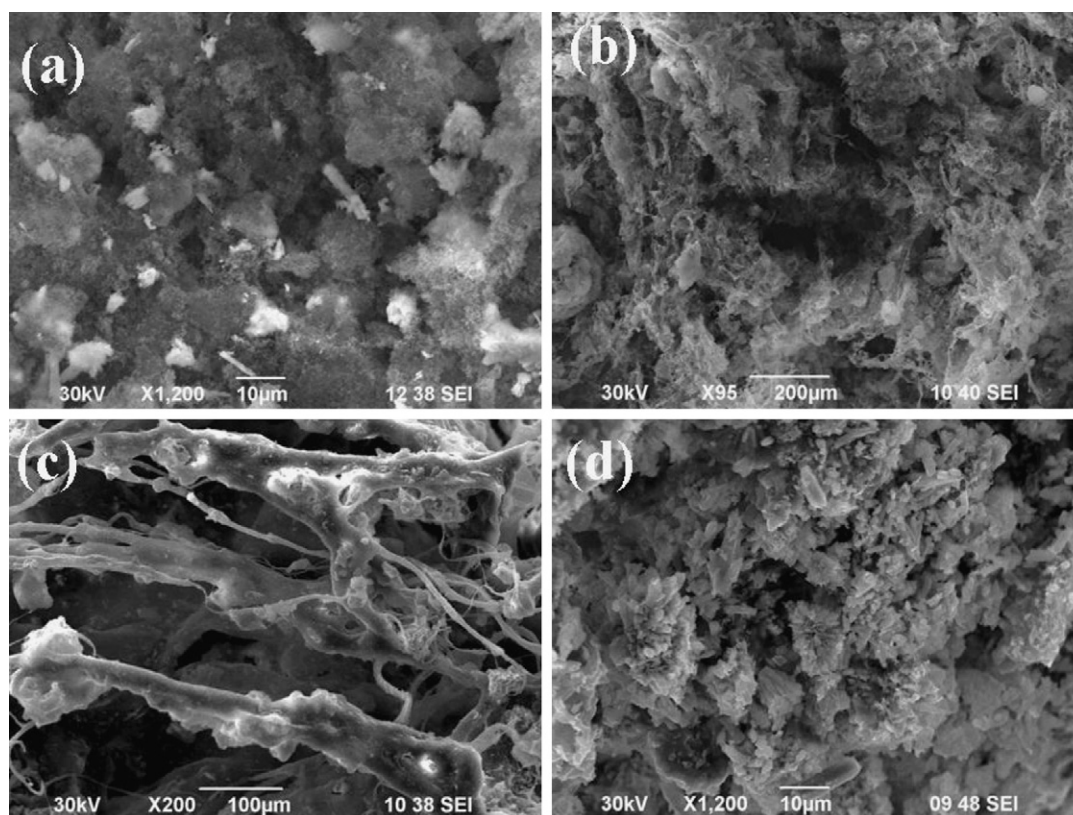

Fig. 1. SEM images of (a) BA-1, (b) BA-2, (c) BA-3 and (d) BA-4 PVC composites.
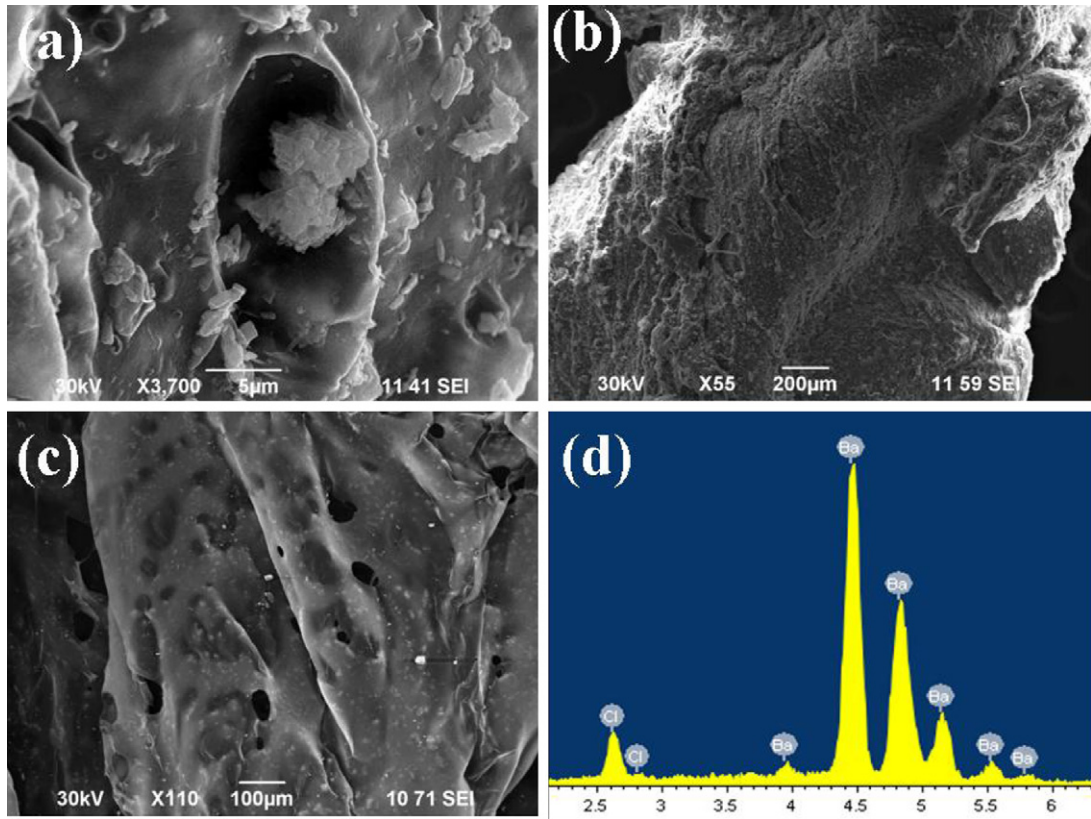
Fig. 2. SEM images of PVC composites (a and b) BA-5, (c) control PVC without BaCO$_3$ loading, and (d) EDS spectra of BA-5.
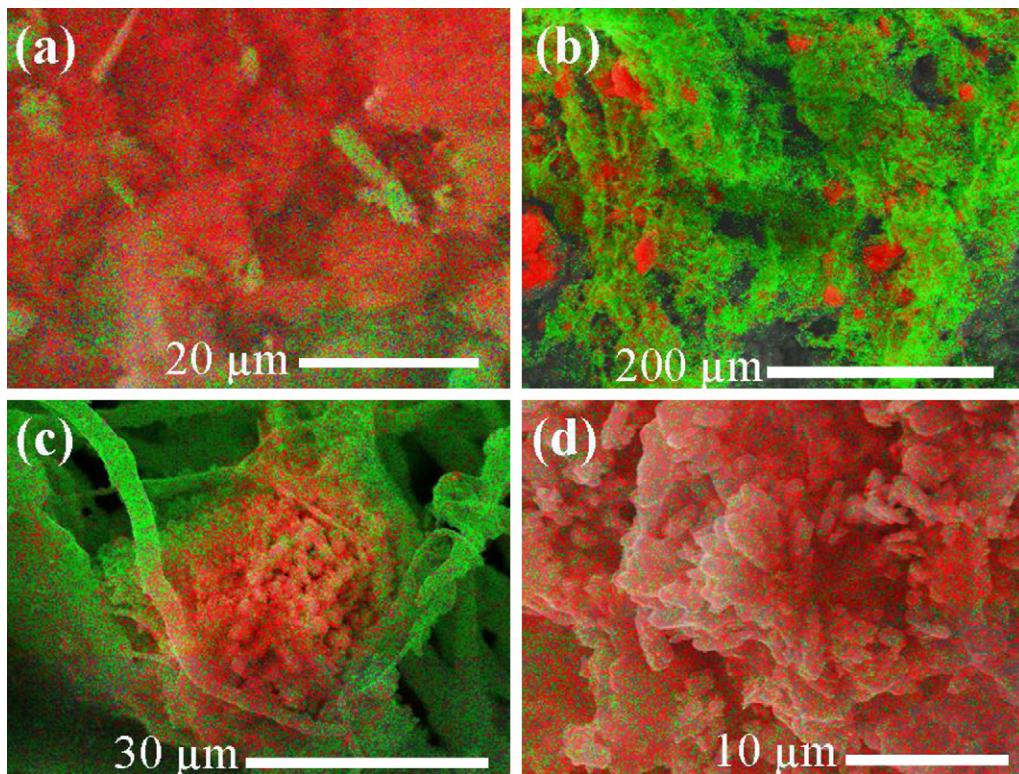

Fig. 3. X-ray mapping image of (a) BA-1 (red-silica and green-barium), (b) BA-2 (red-silica and green-chloride), (c) BA-3 (green-chloride and red-barium), and (d) BA-4 (red-barium and green-chloride) PVC composites (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

and (2) aero-gels can form a porous network with barium, which is necessary for the sulfate removal.

Depending on the concentration ratio of PVC to $BaCO_3$, or barium-loaded silica aero-gels, it is possible to control the barium concentration in the polymer matrix. Fig. 1 shows the SEM images of barium-embedded silica aero-gels and/or $BaCO_3$-loaded PVC composites. It is clear from the SEM images that an increase in $BaCO_3$/barium-loaded silica aero-gels decreased the polymer bonding. Different compositions were made and the sample composition and codes are given in Table 1.

Fig. 2 shows SEM images of PVC composite BA-5 (a and b), control PVC without $BaCO_3$ loading (c), and (d) EDS spectra of BA-5. The $BaCO_3$ was trapped inside and on the surface of the PVC matrix (Fig. 2a), and the control PVC had only a porous structure without $BaCO_3$ (Fig. 2c). The presence of $BaCO_3$ was confirmed using EDS, as indicated in the spectrum for BA-5 (Fig. 2d and supporting information Figures S1–S6 and Table S1–S5 for complete analysis).

X-ray mapping images of one such representative PVC composite image shows good dispersion of barium in the PVC matrix (Figs. 3 and 4).

In order to determine the thermal properties of PVC after composite formation, we conducted thermogravimetric analysis on representative barium loaded composites which are shown in Fig. 5. The silica aerogel loaded trace is shown in Fig. 6. PVC is one of the least stable thermoplastics, and will degrade during melt processing if no stabilizer or plasticizer is present [21]. One of the most important property enhancements exhibited by polymer/clay nanocomposites is their increased thermal stability at a low filling level. Because of the thermal insulation effect of montmorillonite clay (MMT), the formation of a polymer nanocomposite can retard the thermal degradation. The thermal stability can also be affected by other factors, such as the type of polymer and the experimental conditions of the material degradation. Wang et al. [21] reported that the addition of clay caused an initial drop in the onset of degradation in PVC/MMT nanocomposites. Apparently, the thermal stability of the nanocomposites could be slightly improved by the addition of MMT. Wan et al. [22] also reported that, when
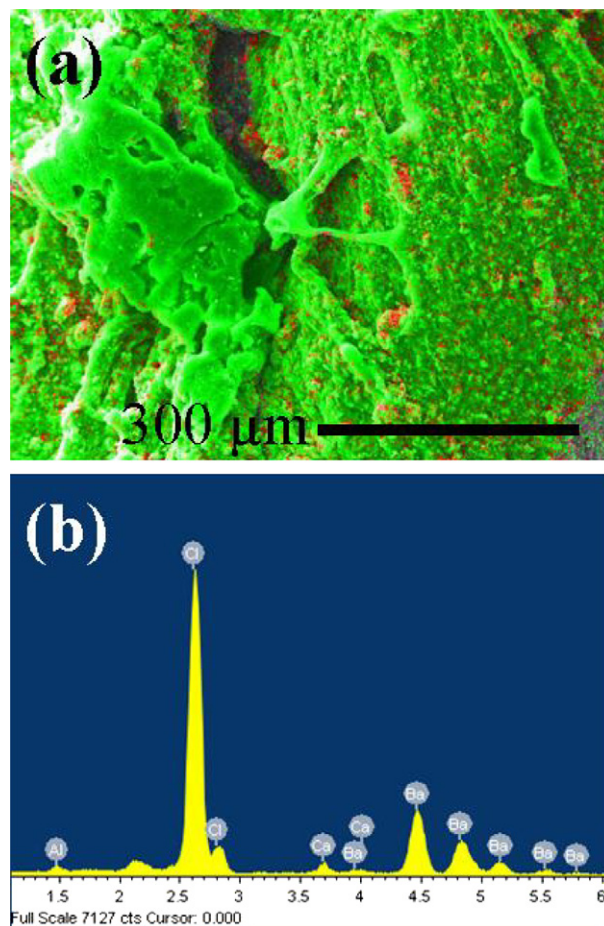

Fig. 4. X-ray mapping image of (a) BA-6 (green-chlorine and red-barium), and (b) its EDS spectrum (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).
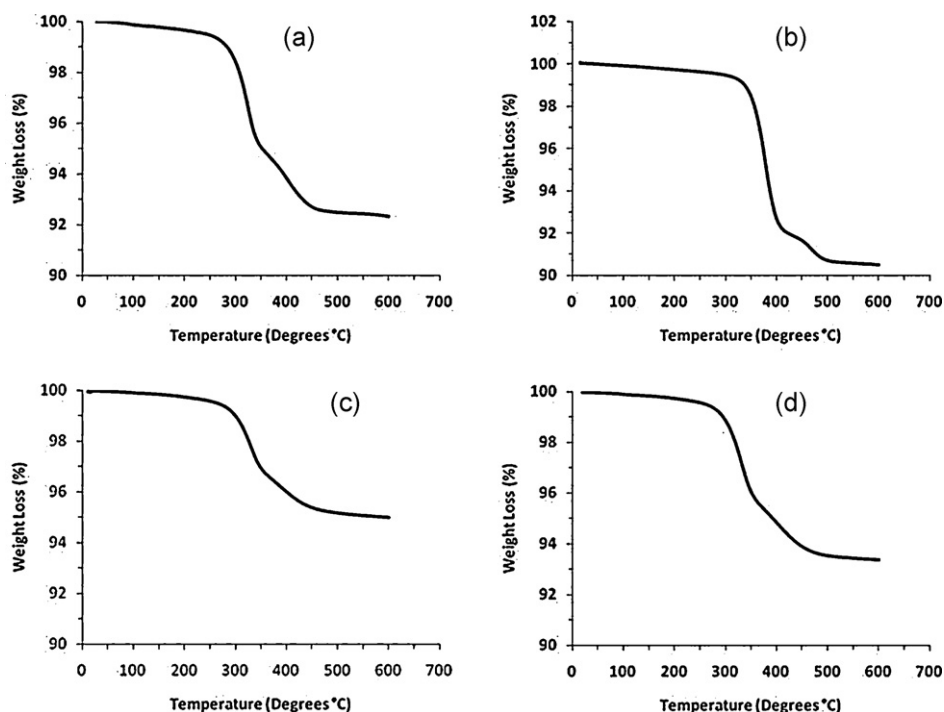

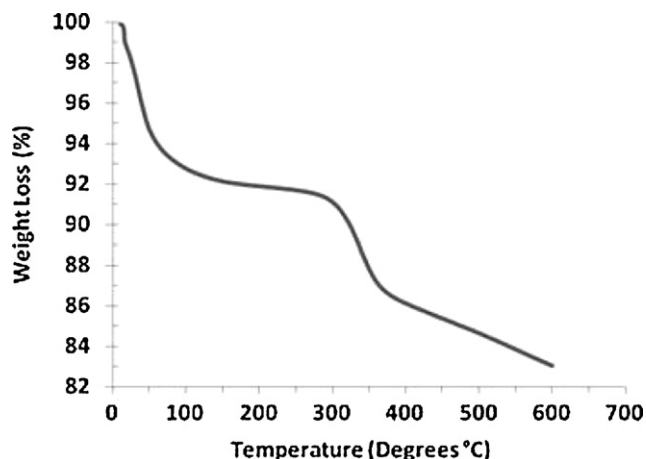**Fig. 5.** TGA thermogram of (a) control PVC, (b) BA-4, (c) BA-6, and (d) BA-7 PVC composites.

Fig. 6. TGA thermogram of BA-1 sample.

comparing PVC/Na-MMT with PVC/organic MMT nanocomposites, PVC/Na-MMT was more stable. Fig. 5 shows the TGA curves for barium carbonate and or barium carbonate-loaded silica aero-gels PVC composites. The maximum dehydrochlorination temperature and olefinic breakage temperature of pure PVC are 280 and 445 °C, respectively. The degradation temperature for the hydrochlorination of PVC in the composite are higher indicating the stabilization of PVC due to presence of barium carbonate and or silica-aerogel.

The addition of inorganic BaCO₃/BaCO₃-loaded silica gels could play a more effective role in stabilizing PVC. The degradation temperature value of the composites is at least 20–30 °C higher than that of PVC. It is surprising to observe that the values of BA-1 started decomposing in the early stage (see Fig. 6) compared with other compositions. This may be due to evaporation of the solvent which was trapped in the polymer composite. The degradation of composites proceeds by the loss of hydrogen chloride, leading to the formation of double bonds in the polymer, and it is an autocatalytic process. The production of nonvolatile residue arises from cyclization reactions of these double bonds [23,24]. The decrease in degradation temperature means that the degradation is accelerated, but the fact that the fraction of nonvolatile residue is decreased means that the formation of double bonds and the subsequent cyclization, or both, must be repressed. The tracer NaCl study was conducted to evaluate the bed time contact of chloride and is shown in Fig. 7. It is clear from Fig. 7 that the time needed for chloride to travel through the column is ~13.1 min. After 1 h of
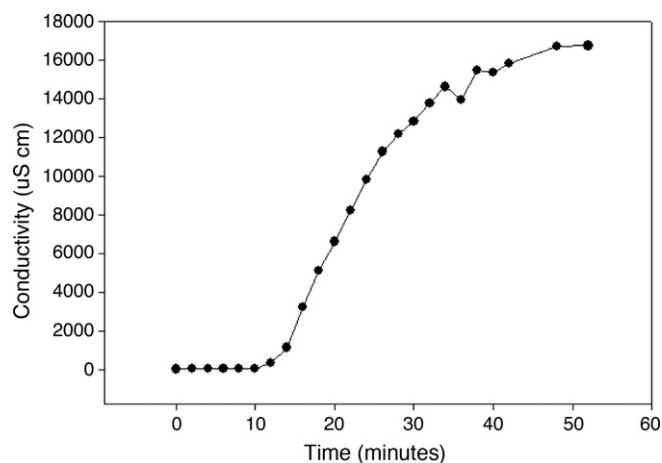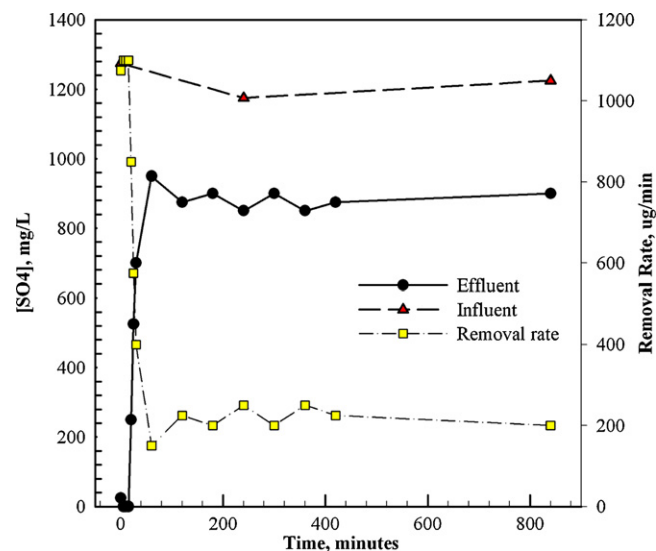

Fig. 8. Sulfate removal curve using BaCO₃ loaded PVC composites (BA-6). The flow rate was.1 mL/min.
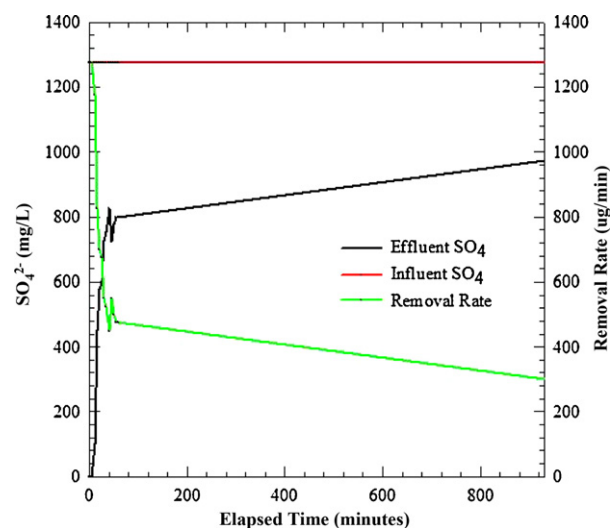
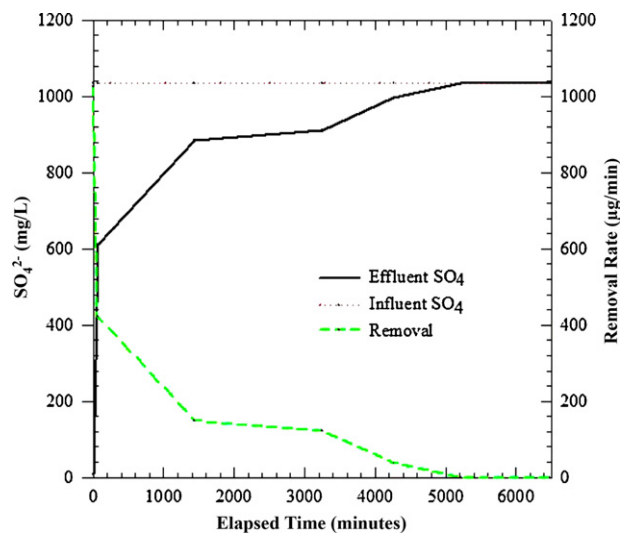**Fig. 9.** Sulfate removal curve (BA-6) after crushing to fine powder. The flow rate was 1 mL/min.

Fig. 7. Tracer study using NaCl on BaCO₃ loaded PVC composite. The flow rate was 1 mL/min.

Fig. 10. Sulfate removal curve until the break through curve. The flow rate was 1 mL/min.
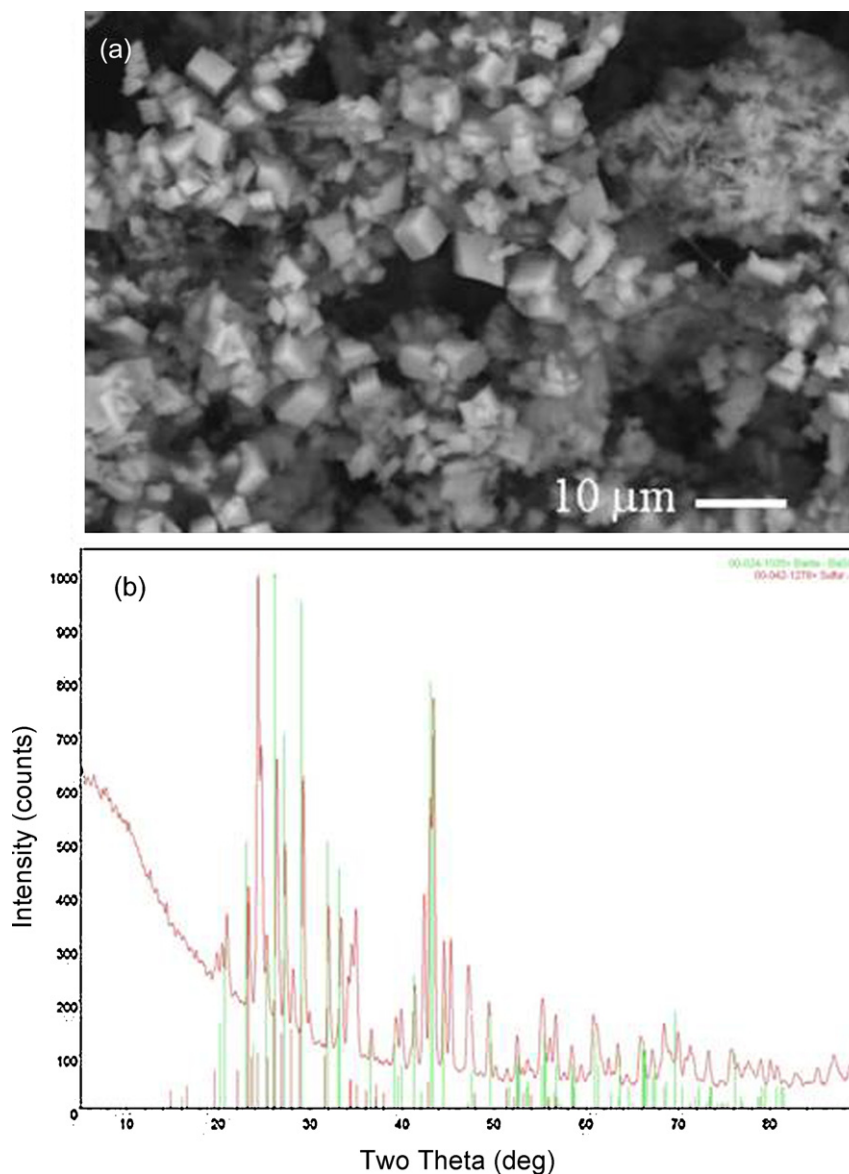
Fig. 11. SEM image of (a) BaSO$_4$ crystals adsorbed unto the polymer surface and (b) its XRD pattern indexable to BaSO$_4$.

bed time contact there was no significant increase in conductivity value indicating the saturation point of chloride ions. The BaCO$_3$ composite was studied for sulfate removal, and is shown in Fig. 8. The influent sulfate concentration was around 1075 mg/L. The flow rate was kept constant at 1 mL/min.

The calculated empty bed contact time of the column was calculated to be 5.2 min (Eq. (1)) and determined experimentally by way of a tracer study to be 13.1 min. Influent sulfate averaged 1075 mg/L over the course of the study. Effluent sulfate dropped to, and maintained, approximately 800 mg/L after 20 min (approximately 1 EBCT). The average removal rate from minute 20 to the end of the study was 213 mg/L/min which equates to 213 μg/min at a flow rate of 1 mL/min. Over the 800 min study, approximately 160 mg of sulfate was removed by the media.

$$EBCT(min) = \frac{Volume\ of\ filter\ media\ (mL)}{flow\ rate\ (mL/min)} \qquad (1)$$

Based on the EDX determination of Ba content in the tested composite (BA-6), the theoretical capacity was 4.2 g of sulfate molecules. In order to determine whether the diffusion of sulfate is internal or external, the composite powders were crushed into fine

powders and subjected to sulfate removal. Fig. 9 shows the sulfate removal curve for BA-6 after crushing to fine powder. There was not much difference in adsorption capacity when compared to before crushing. To examine the complete break through curve, we ran the experiment for several days until the break through occurred and is shown in Fig. 10. Initially sulfate adsorption was high and decreased with the time and finally becomes saturated. The effluent was tested for barium content through ICP-MS analysis at different intervals and found to significantly below EPA requirements.

After sulfate removal, the polymer composite was analyzed for its morphology and X-ray diffraction studies. The SEM image and XRD patterns are shown in Fig. 11(a and b) respectively. The SEM revealed that the formation of cubic crystals on the surface and inner pores of the polymer composite (see Fig. 11a). X-ray diffraction studies indicated that formation of barium sulfate on the surface of composite (see Fig. 11b).

4. Conclusions

In conclusion, BaCO$_3$ dispersed PVC composites were prepared through a polymer re-precipitation method. The composites were

tested for sulfate removal using rapid small scale column test (RSSCT) and found to significantly reduce sulfate when compared with control PVC. The method was extended to synthesize barium carbonate-loaded silica aero-gels-polyvinyl chloride (PVC) polymer composites. The method has advantages over conventional sulfate precipitation (sulfate removal process) using $BaCO_3$ wherein clogging of the filter can be avoided. The method is environmentally friendly and does not interfere with natural organic matter as the conventional resin does. The other advantages over those reported in available literature include simplicity, the method's robust nature, and the ability to be carried out at room temperature. Some of the composites were thermally stable as compared with the pure PVC discussed in the literature. The adsorption of sulfate on these composites was found to be significant, and may prove to be applicable in water remediation processes.

Disclosure

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.01.005.

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