Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.867537

53 (2015) 2604–2612
March

Taylor & Francis
Taylor & Francis Group

Polypropylene–zeolite polymer composites for water purification: synthesis, characterisation and application

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Received 14 March 2013; Accepted 12 November 2013

ABSTRACT

This paper reports on the preparation of polypropylene–zeolite polymer composites using the melt-mixing compounding technique. These polymer composites have shown unique and enhanced properties as compared to their monolithic constituents. All polymer hybrids were formed by solvent-less melt-intercalation and extrusion. The changes in conventional properties of the two mixed constituents were probed using techniques, such as scanning electron microscopy, X-ray diffraction (XRD), Fourier transform infrared spectroscopy and thermogravimetric analysis. XRD analyses showed a co-existence of intercalated and exfoliated zeolite phases. The influence of operational conditions such as exposure time, zeolite loading rate and solution pH were determined. An optimum zeolite loading of 15 wt.% was observed. Solution pH had the greatest influence on the removal of both heavy metals and substituted phenols. The polymer composites exhibited both adsorption and ion-exchange properties in the removal of heavy metals in aqueous media.

Keywords: Adsorption; Characterisation; Composites; Polypropylene; Zeolite

1. Introduction

The re-use of wastewater/impaired water sources to replenish the diminishing supplies of fresh potable water brought about by various treatment techniques, amongst which are ion-exchange and adsorption [1–5]. Ion-exchange and adsorption has been widely applied in water treatment using commercial adsorbents, such as activated carbon and carbon nanotubes, low-cost adsorbents such as chitosan, clay and zeolites and also industrial waste products, such as fly-ash, coal and oxides [6–9]. However, despite their prolific performance over the past decades these adsorbents have some undesirable drawbacks; when used in their powder form these adsorbents tend to agglomerate reducing the effective surface area [10,11]. The powder form presents difficulty in separating the adsorbent from the aqueous media after treatment requiring more tedious filtration steps. This then makes regeneration and re-use of the adsorbents inefficient. Researchers have therefore been interested in immobilising the adsorbents in polymer matrices that will

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provide mechanical support and minimise agglomeration [12]. This results in a new branch of materials, polymer composite; where the adsorbent/filler is embedded and disperse within a polymer matrix, thus increasing the effective surface area and improving regeneration as well as the operation of the technique.

Polymer composites involve dispersing macro-sized particles (filler) into a thermoplastic polymer (matrix) that is perceived to modify the properties of the polymer. Polymer composites and nanocomposites have been among the range of composite materials that have been developed and widely evaluated in various fields. They have received a considerable amount of interest from researchers due to the superior properties they have over conventional materials. These include improved mechanical strength, thermal stability, chemical and solvent resistance and also, most importantly, they are economical.

The wide ranges of polymers that have been used in preparation of polymer composites include vinyl polymers condensation polymers, polyolefin like polypropylene (PP) and polyethylene oligomers [13–16]. PP have found extensive application in various fields due to its valuable properties, such as low density (0.910–0.930 g/cm^3), excellent solvent resistance, high softening point, environmental inertness, simplicity of recycling and low cost [17–19].

PP and other thermoplastics have been modified/reinforced with a variety of filler systems ranging from particulates to plant fibres. The main aim for the synthesis of these materials was to produce superior materials, such as flame retardants, automobile parts and construction materials [20–22]. However, when modified with hydrophilic materials like zeolites and clay; the PP attains a water sorption property due to the porous structure of the composite films as well as the hydrophilic nature of the filler material.

As a result of their excellent ion-exchange capacity, selectivity and compatibility with the natural environment, natural zeolites have been used to modify hydrophobic polymers like PP. These are naturally occurring hydrated crystalline aluminosilicates containing exchangeable alkaline and alkaline earth metal cations, such as K^+, Na^+, Ca^{2+}, and Mg^{2+} that maintain charge neutrality within the crystal lattice. These cations are exchangeable with particular cations in solutions such as lead, cadmium, zinc and manganese [23]. The microporous crystalline structure of zeolites is able to exchange ionic species with diameters that fit through the entry ports of the internal zeolite framework, while larger species are excluded, giving rise to ion-sieving properties that are exploited in a wide range of commercial applications and scientific research [24]. Clinoptilolite is the most abundant naturally occurring member of the spectrum of zeolitic minerals.

Numerous works have been done in treating water with powdered zeolites; Erdem and co-workers investigated the removal of heavy metal ions by natural zeolites [5]. They found that the adsorption phenomena depend on charge density and hydrated ion diameter. The ion-exchange capacity was also evaluated in a range of metal cation concentrations [5]. On a similar study, Petrus and Warchol [25] reported that ternary and quaternary ion-exchange equilibra between heavy metal ions (Pb^{2+}, Cd^{2+}, and Ca^{2+}) and Na-form clinoptilolite was responsible for the observed adsorption processes. There are many other studies that involve the remediation of water with powdered modified zeolites [19,26–30] and they also showed prolific adsorption/removal efficiencies.

However, to the best of our knowledge particulate-reinforced polymer composites have not yet been widely applied to water purification. However, in our recent work [31] the performance of PP-clinoptilolite polymer composites in the removal of heavy metal ion (Pb^{2+}) from water was evaluated. The influence of clinoptilolite pre-treatment on the composite adsorption capacity was investigated. The selectivity of the composite was probed in a range of heavy metal ions (Pb^{2+}, Cu^{2+}, Fe^{3+}, Co^{2+}, and Ni^{2+}). The aim of the present work is to demonstrate the versatility of the PP-clinoptilolite composites in the removal of both heavy metal ions and phenolic compounds. Furthermore, the synthesis and characterisation of the polymer composites are described in a more detailed account than in our previous work [31]. Influential factors such as contact time, zeolite loading and pH were optimised.

2. Experimental

2.1. Materials and methods

The clinoptilolite sample materials (6–9 mm) used in this study was supplied by Pratley South Africa and was sourced from the Vulture Creek, KwaZulu-Natal Province, South Africa. PP, a commercial synthetic polymer, was obtained from Sasol. Lead (II) nitrate ($Pb(NO_3)_2$) and other chemicals used in this study were supplied by Sigma Aldrich (St. Louis, MO, USA) and Merck (Darmstadt, Germany) and were all of analytical grade (AR).

2.2. Zeolite preparation and conditioning

The zeolite (clinoptilolite) of size 6–9 mm was ground and sieved to size fractions of 53 μm and then washed with distilled water to remove soluble mineral salts and other impurities before being oven-dried at 110˚C.

2.3. Preparation of PP–zeolite composites

All PP–clinoptilolite composites were prepared using the melt-mixing compounding technique in a rheomixer (Haake Rheomex OS) at 170˚C and at a speed of 60 rpm for 30 min. The masses required for the different polymer: filler ratios (100: 0–70: 30) were calculated using Eq. (1):

$$m = \rho \times V_c \times W_t \tag{1}$$

where m is the mass (g), ρ is the density of polymer (or clinoptilolite), V_c and f are constants for the chamber volume and filler rate of the rheomixer, respectively. W_t (%) represents the required weight percentage of polymer or filler.

The mixed intermediates were then extruded through a single-screw extruder at 170˚C, to obtain polymer strips of 50 mm average width and 0.5 mm thickness. The polymers were then characterised with scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) and X-ray diffraction (XRD) spectroscopy.

3. Results and discussion

3.1. Morphological and physical properties

The determination of the composite surface morphology was to assess the dispersion of the zeolite particles within the polymer matrix. This was achieved by studying composite films using a SEM. Fig. 1 show typical SEM micrographs of melt intercalated PP–zeolite polymer composites. The micrograph in Fig. 1(a) shows a fair distribution of clinoptilolite particles within the matrix with the presence of agglomerated particles. The presence of semi and fully connecting micro-voids/cracks that are a result of mixing and extrusion are displayed in the cross-sectional view Fig. 1(b). These secondary spaces have a great influence on the composite density, tensile strength and the accessibility of embedded zeolite particles by water.

The introduction of particles into the ordered polymer chain has an impact on the crystallographic structure and arrangement of resultant composites, which turn to have a huge influence on the mechanical properties as well as the adsorption capacity. This could be ascertained through the use of XRD analysis. The XRD patterns in Fig. 2 belong to a PP composite reinforced with varying proportions of zeolites. There is the prevalence of characteristic PP peaks at 14.35˚, 17.11˚ and 21.8˚. The presence of an amorphous background in all peaks also indicates the semi-crystalline nature of PP. The presence of the clinoptilolite mineralogical phase is evidenced by the characteristic peaks at 9.83˚ and 22.37˚ with the latter being suppressed by the almost overlapping PP peak at 21.8˚. The analysis results reveal the presence and co-existence of intercalated, exfoliated and dealuminated/flocculated structures within the different composites. The limited intercalation is due to the rigid framework of zeolites, which can accommodate only a certain amount of polymer chains in their channels. The XRD patterns show a decline in peak intensity with the increase in clinoptilolite loading, a process that can be attributed to the disordered structures that result from agglomeration of zeolite particles with increased filler amount (dealumination) which is observed in the 30% clinoptilolite composite [29]. These observations confirm that the addition of the filler did alter the crystalline nature of the polymer to give new properties unique to the composite which is evidenced by the brittle nature of resultant composite material, an

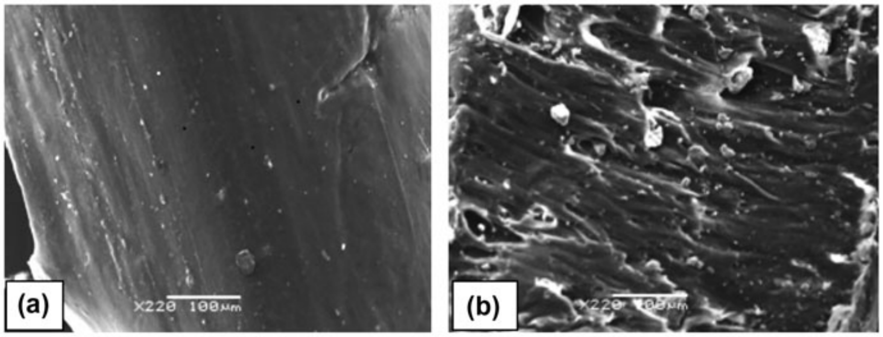

Fig. 1. SEM micrographs of PP-zeolite polymer composites: (a) surface and (b) cross-sectional view.

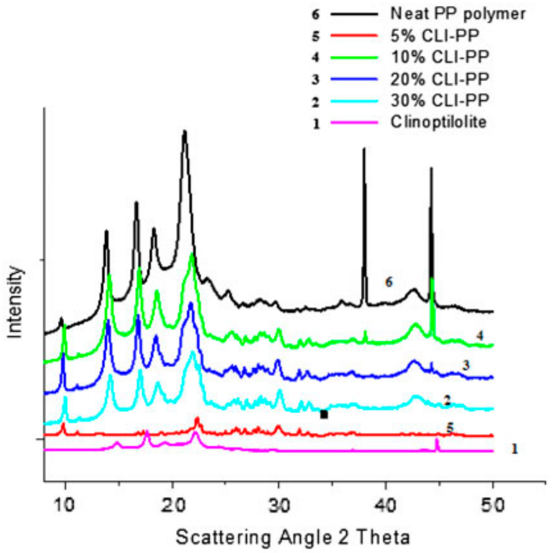

Fig. 2. XRD patterns of neat PP polymer and PP-zeolite composites with the varying zeolite loadings.

observation also made by Biswas et al. who worked on zeolite-reinforced PP [30]. This change was further complemented by observations obtained during Differential scanning calorimetry (DSC) analysis.

3.2. *FT-IR characterisation*

Since polymer composites are hybrid materials, it is important to determine their functionality (presence of certain functional groups). The sets of infrared spectra shown in Fig. 3 show the presence of strong stretching and vibrations of –C–C–H bonds, methyl (–C–H) bending in the 1 375.92 cm^{-1} region, R–CH=CH_2 medium bending in the 900 cm^{-1} region and these are characteristic of PP. Weak –C–O bending is also observed at 1,200 cm^{-1}. The presence of weak vibrations at the 1,600 cm^{-1} region, which are characteristic of clinoptilolite, indicates an interface interaction between the polymer matrix and the filler material. Although these spectra have very low transmittances due to restricted electron transmission during analysis, the 30% zeolite composite had the lowest absorbance since it has the most intense colour (much darker) allowing only a limited amount of light to pass through the sample. The prevalence of peaks characteristic of PP in the composite spectra reinforces the observations made on the SEM micrographs that the polymer acts as a coating layer over the zeolite particles.

3.3. *Thermal properties*

3.3.1. *Thermogravimetric analysis (TGA) analysis*

Among the many aforementioned advantages, thermal stability of polymer composites was improved and this was assessed through TGA. The TGA plots for the different composite samples are presented in Fig. 4. The curves are very similar with preliminary loss of weight beginning at around 150°C until the main (carbon chain depletion) degradation at about 410°C. The onset degradation temperature values reveal that there is a shift in the degradation temperatures towards lower temperatures with the increase in filler loading for the unmodified clinoptilolite-PP

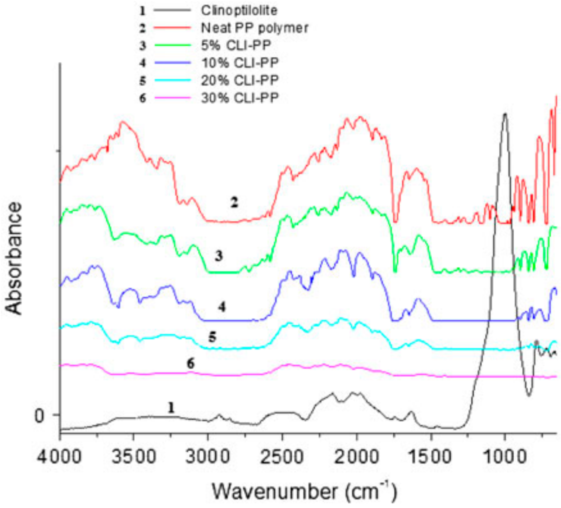

Fig. 3. FT-IR spectra of PP neat polymer and PP-zeolite polymer composites at varying zeolite loading.

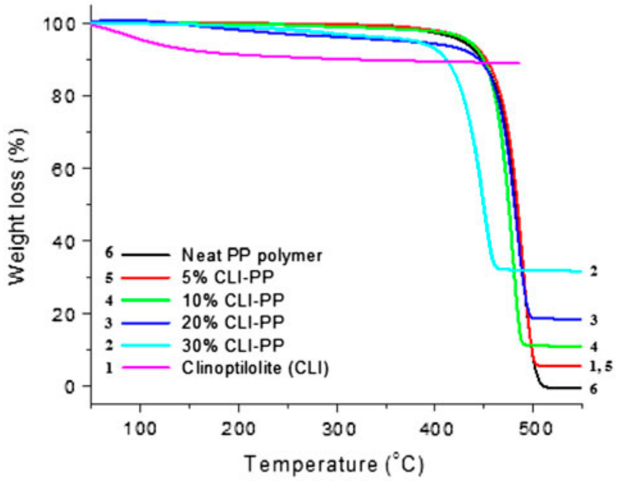

Fig. 4. TGA thermographs of as received clinoptilolite, neat PP polymer and PP-zeolite composites.

Table 1
Degradation onset temperatures for the neat polymer and all composite samples

AR CLI-PP samples	Onset temperature (℃)
Neat PP polymer	439.27
5%	438.43
10%	436.58
20%	422.09
30%	415.55

composites (see Table 1). In addition, the zeolite-filled composites had degraded at lower temperatures compared to the neat PP polymer with only the 5% loading overlapping with its curve. This is further complemented by the derivative temperature curves shown in Fig. 5 which clearly indicate the shift on the main degradation temperatures. Therefore, the addition of clinoptilolite into the polymer matrix did interfere with the polymer chain arrangement as also revealed by XRD analysis, an observation similar to that made by Espert et al. and Mengeloglu and Karakus who both observed a decline in composite thermal stability after reinforcing PP with cellulose and wheat straw flour, respectively [31,32].

3.3.2. DSC analyses

Thermal stability can further be probed with DSC analysis. The DSC plots showing the melting peaks are presented in Fig. 6. It can therefore be concluded that the melting temperatures do not vary significantly from each other as they ranged between 159.86 and 162.45℃. This suggests that clinoptilolite did not significantly affect the melting temperature of the PP (161.75℃) regardless of filler loading. The melting and crystallisation temperature values are presented in Table 2. The crystallisation temperatures were greater than 105℃ and were very close to each other (Fig. 6); an average temperature of 108.44℃ was observed for the different zeolite loading.

The enthalpy of melting (ΔH_m) for the unmodified clinoptilolite-PP samples show a decline with the increase in clinoptilolite loading, an indication that the filler absorbed more heat energy [33]. The crystallisation enthalpy (ΔH_c) showed an increase with increasing filler loading, an indication that the filler acts as a nucleating agent within the polymer matrix. The nucleation process is promoted by intercalation

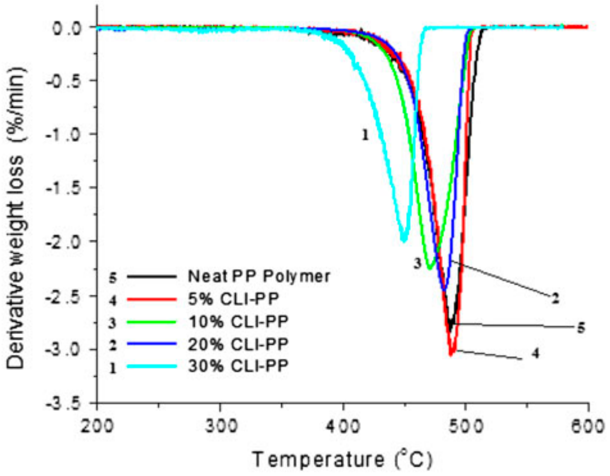

Fig. 5. DTG thermographs of the neat PP polymer and PP-zeolite composites showing the complete degradation of the polymer carbon backbone.

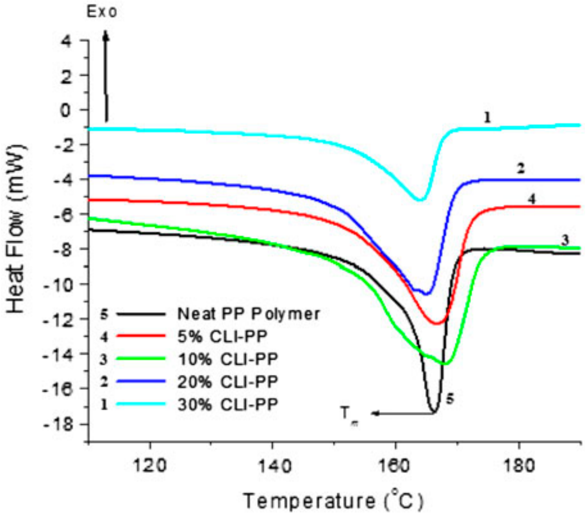

Fig. 6. DSC thermographs showing melting peaks for the neat PP polymer and PP-zeolite composites, T_m denotes the actual melting temperature of the polymer composite.

Table 2
DSC determination of some thermal characteristics of neat PP polymer and PP-zeolite composites

Composite type	Temperature (℃)		Enthalpy (J/g)		Crystallinity
	T_m	T_c	ΔH_m	ΔH_c	% X_c
Neat PP polymer	161.75	107.37	75.40	69.13	36.14
5% CLI-PP	161.99	108.18	71.53	76.32	39.90
10% CLI-PP	161.47	108.18	65.41	77.24	40.38
20% CLI-PP	159.86	109.24	68.54	81.20	42.24
30% CLI-PP	162.45	109.23	64.53	81.32	42.50

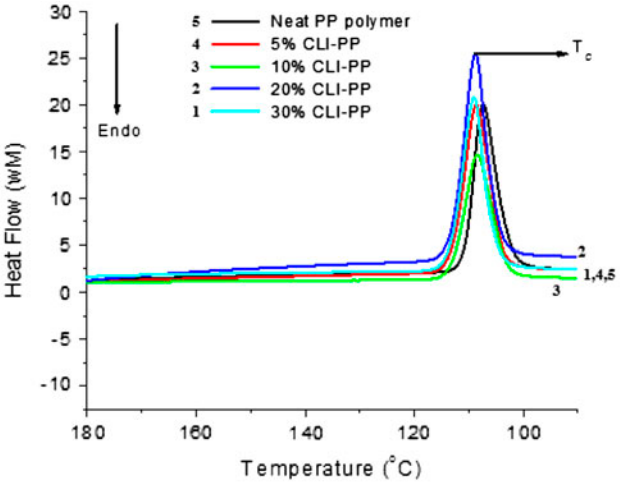

Fig. 7. DSC thermographs showing the crystallisation peaks for the neat PP polymer and PP-zeolite composites, T_c denotes the temperature of crystallisation of the composite blend.

and high crystallisation temperature that allows the polymer chains to fit within the channels of the clinoptilolite [34,35].

The percentage crystallinity (X_c) of the composite films was calculated using Eq. (2):

$$\% X_c = \frac{H_f}{H_o} \times 100 \tag{2}$$

where H_f is the sample's heat of fusion, H_o is the heat of fusion for the 100% crystalline isotactic PP.

The reported heat of fusion for 100% crystalline isotactic PP is 191.3 J/g [36] and this value was used to determine the percentage crystallinity for the composites. The neat PP polymer was 36.14% crystalline which is typical of isotactic PP [37]. The degree of crystallisation increased with increasing filler loading for the natural zeolite–PP composites. There was no significant difference between the crystallinity of the 20% and 30% composites. (Fig. 7)

4. Application of thermoplastic/particulate composites

The application of polymer composites in water purification has been scarcely documented in literature, however their major application has been reported in construction, packaging and automobile industries [38]. In this work, the adsorption efficiency of the PP–zeolite composites was determined in water spiked with heavy metals and phenolic compounds. During the extraction of these substances influential conditional parameters such as exposure time, zeolite loading and pH were optimised.

The extraction of lead and phenolic compounds by the polymer blends is in two phases; the fast initial phase and the later slower phase as depicted in Fig. 8. The significant removal of pollutants at the initial stages is due to the vast availability of exchange sites within the polymer blends; about 88% of the total absorbed amount was removed at this stage. Beyond the fifth hour the uptake rate dropped significantly and complete equilibrium was attained after 24 h. The longer equilibration time can be attributed to the hydrophobic nature of the polymer matrix which delays the composite wetting.

The amount of pollutant adsorbed increased with the increasing rate of zeolite/filler loading. The optimum zeolite loading was found to be 15% (w/w), increasing the filler beyond this loading improved filler aggregation and reduced its dispersion within the polymer matrix. This increased the composite compactness and brittleness, conditions that are not very ideal for adsorption particularly in aqueous media. The graph in Fig. 9 shows that for Pb^{2+} and *o*-Nitrophenol the adsorption capacity of 20% and 30% loadings is similar which reinforce what has been explained earlier. While it shows an increase in the amount of trichlorophenol removed which can be attributed to hydrophobic separation as a result of the PP polymer as well as the ionic exchange initiated by the hydrophilic zeolites.

The removal of heavy metals and the phenolic compounds critically depend on the solution pH. Fig. 10 displays a typical graph for the removal of Pb^{2+} from aqueous solution across the pH range. The

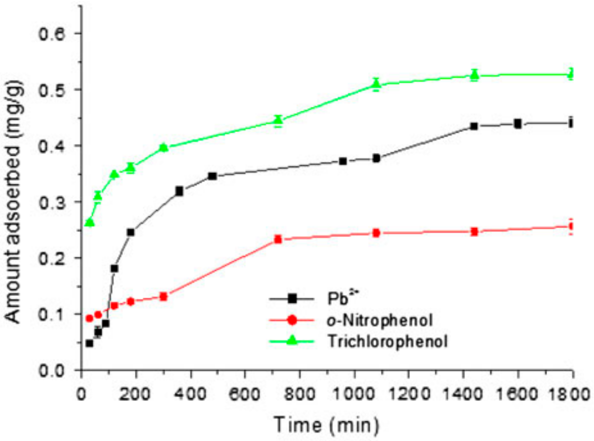

Fig. 8. The removal of Pb^{2+} and phenolic compounds as a function of time by PP-zeolite polymer composites from aqueous solutions.

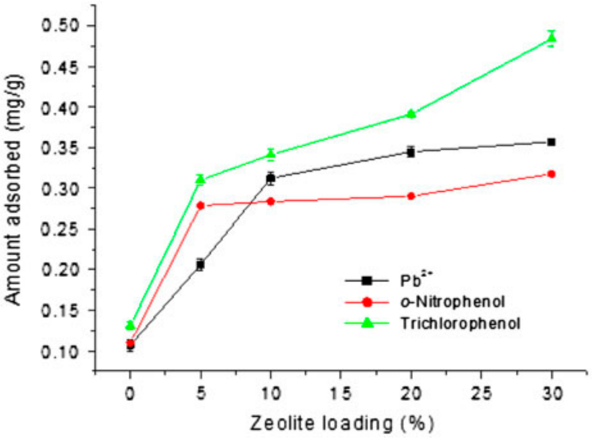

Fig. 9. Effect of filler loading on the uptake of Pb^{2+} and phenolic by PP-zeolite polymer composites from aqueous solutions.

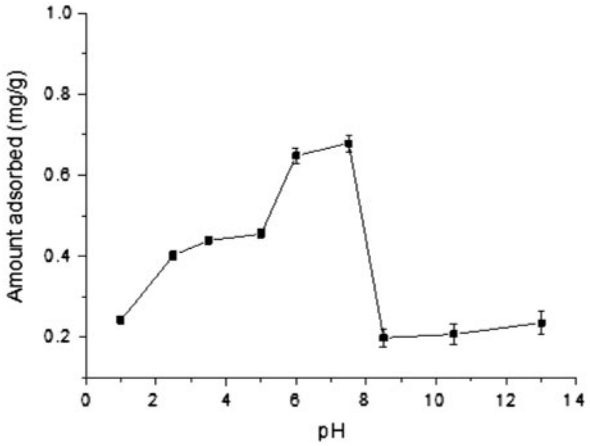

Fig. 10. The removal of Pb^{2+} as a function of solution pH by PP-zeolite composites from aqueous solutions.

optimum pH range for the removal of Pb^{2+} was found to be between 6.5 and 7.5. At lower pH there is a high abundance of H^+ ions that compete with the Pb^{2+} for the exchange sites resulting in lowered removal. While the balance in charge caused by the exchangeable alkaline cations improved adsorption within the 6.5–7.5 region. Increasing the pH beyond 8 leads to the formation of the insoluble $Pb(OH)_2$ due to the vast presence of OH^{-1} ions that hugely reduced the detectable Pb^{2+} ions.

There was no observable trend in the extraction of the phenolic compounds as a function of pH. The determined optimum pH range for the sorption of *o*-Nitrophenol was 2–6 and 4–6 for trichlorophenol. This was down to their predominance in pH values that are lower the pKa values (7.09 and 7.17).

Table 3
The performance of PP-zeolite composites in removing multiple pollutants in aqueous media

Pollutant	Amount adsorbed, Q_m (mg/g)
Pb^{2+}	1.6
Cu^{2+}	0.1
Fe^{3+}	0.08
Co^{2+}	0.08
Ni^{2+}	0.06
Ortho-Nitrophenol	1.0
Tri-chlorophenol	6.5

Table 3 gives a summary of the metals and organic compounds removed at optimised conditions by the zeolite–PP composites. It can be observed that the composites had superior adsorption capacity for the organic pollutants compared to the heavy metals. This observation can be attributed to their removal through the combined processes of hydrophobic separation aided by the hydrophobic polymer matrix as well as ion exchange between the zeolites and the phenolate ions. Amongst the metals, Pb^{2+} was the highest removed due to its low hydration radius which is specific to the zeolite channels.

4.1. Potential advantages of polymer composites

The results discussed in sections above reveal that PP–zeolite composites have a potential in purification of secondary waste water effluent. An added advantage is that the PP polymer used in this study is hydrophobic, enhancing the removal of organic contaminants through hydrophobic partitioning. Besides, zeolites are readily available and cheap; they are also environmentally benign, therefore alleviating problems of soil re-pollution during disposal. The possibility of reuse renders this technique both economical and effective. However, there are few challenges that will keep the technique at laboratory scale for an elongated period. The dispersion of zeolite on the polymer matrix is limited to 15% loading to allow complete particle distribution. This loading range however limits the uptake capacity of the composite films.

5. Conclusions

An adsorbent material bearing improved mechanical and water sorption properties was fabricated successfully using PP polymer with zeolites. The ability of the fabricated composites to bind/extract heavy metals and substituted phenols from aqueous solutions was investigated. The extraction of these substances largely depended on contact time, zeolite loading and solution pH. These operational parameters were optimised with the equilibration time found at 24 h. The optimum filler loading was observed at 15%. Solution pH had the greatest influence on the adsorption process; Pb^{2+} had the highest removal at 6.5–7.5. Trichlorophenol and ortho-nitrophenol were each maximally adsorbed between 4–6 and 2–6, respectively. The composites had better removal efficiency for the organics due to the polymer matrix that enhances hydrophobic separation. Despite this promising performance, the usage of hydrophilic polymers such as grafted polymers as well as acetate/cellulosic polymers can greatly enhance the performance of these polymer composites in removing heavy metals.

Acknowledgements

Funding for this project was obtained from the DST/Mintek Nanotechnology Innovation Centre (NIC) and the University of Johannesburg (UJ).

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