



Polymer–clay nanocomposites for the removal of trichlorophenol and trinitrophenol from water

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ABSTRACT

Phenolic compounds pose health and environmental hazards. This study focused on two priority pollutants, trinitrophenol (picric acid–PA) and trichlorophenol (TCP), which were detected in rivers, lakes and water reservoirs. Polycation–clay mineral nanocomposites were characterized and designed for the removal of these pollutants from water. The adsorption kinetics of polydiallyl dimethylammonium chloride (PDADMAC) and poly-4-vinylpyridine-co-styrene (PVPcoS) on montmorillonite (MMT) was significantly faster (2–4 h) than on sepiolite (3–4 days), which was explained by the latter's porous structure. Consequently, polycation–MMT composites were chosen to test pollutant adsorption. Both PA (anionic) and TCP (non-ionic) showed higher affinity to the less charged polycation PVPcoS (40% of the monomers charged) than to the highly charged polycation PDADMAC. However, PA removal by the PVPcoS–MMT composite was nearly complete whereas TCP removal reached 40 to 60% of the added amounts. The adsorption isotherms of the pollutants suggested that the binding to PVPcoS–MMT was driven mainly by hydrophobic interactions, but also by electrostatic interactions in the case of PA. Differences were also seen in the binding kinetics of PA and TCP to dried and wet composites. The hydration properties of PA enhanced its binding to wet composites whereas the hydrophobic properties of TCP enhanced its binding to dehydrated composites. The results of this study emphasize the importance of better understanding pollutant–adsorbent interactions to enable more efficient tailoring of polymer–clay mineral composites for water treatment.

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1. Introduction

Water contamination by priority pollutants such as phenolic compounds is of major concern due to their high toxicity and persistence in the environment (Liao et al., 2006; Suliman et al., 2006). For example, trichlorophenol (TCP) was listed by the Environmental Protection Agency (EPA) as one of 31 high-priority pollutants, appearing on the EPA's "persistent, bio-accumulative and toxic" (PBT) chemicals list (EPA, 1980b; EPA, 2002). Picric acid (PA) is an anionic phenol derivative used mainly in the explosives industry which was found to be toxic to both humans and the environment (EPA, 1980a).

Phenolic compounds are common by-products of the coal, tar, plastics, leather, paint, pharmaceutical and steel industries and are therefore frequently found in water reservoirs, rivers and lakes (Davì and Gnudi, 1999; Sekela et al., 1999; Suliman et al., 2006).

There are two major treatment technologies for phenolic compounds: the first consists of chemical oxygenation processes with reagents such as hydrogen peroxide (Britto and Rangel, 2008; Husain et al., 2009), and the second of adsorption and extraction processes (Dabrowski et al., 2005; Liao et al., 2006; Floody et al., 2009; Smith et al., 2009). Chemical adsorbents such as clays and clay minerals, polymers and activated carbon play an important role in the removal of these organic compounds (Faust and Aly, 1998; Zhao and Vance, 1998; Beall, 2003; Jiang and Zeng, 2003; Dabrowski et al., 2005; Gonen and Rytwo, 2006). Clay minerals, in particular, received a great deal of attention due to their large specific surface area and cation exchange capacity on the one hand, and low cost and toxicity on the other (Delle Site, 2001; Beall, 2003; Gonen and Rytwo, 2006). The adsorption of organic molecules to these minerals is affected by various parameters, such as the exchangeable cations, the distance between the clay mineral layers, and the existence of water molecules between the layers (Lee et al., 1990; Johnston, 1996; Rytwo et al., 1996; Delle Site, 2001; Bergaya et al.,

Abbreviations: TCP, 2,4,5-trichlorophenol; PA, 2,4,6-trinitrophenol; PVPcoS, poly-4-vinylpyridine-co-styrene; PDADMAC, polydiallyl dimethylammonium chloride; MMT, montmorillonite; SEP, sepiolite.

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2006). Hydration of exchangeable cations and the presence of Si–OH clay mineral groups contribute to the hydrophilic nature of clay mineral surfaces, suppressing the adsorption of hydrophobic molecules: non-polar organic chemicals cannot effectively compete with the water molecules for adsorption sites on the clay mineral surface (Lee et al., 1990; Johnston, 1996; Rytwo et al., 1996; Delle Site, 2001). In the absence of water, clay minerals have a higher affinity for hydrophobic compounds (Lee et al., 1990; Johnston, 1996; Delle Site, 2001; Bartelt-Hunt et al., 2003). The adsorption of benzene, toluene, and xylene to “wet” organo-clay minerals was significantly reduced relative to that of organic vapors on dry organo-clay minerals of the same type (Lee et al., 1990). On the other hand, thermal dehydration of montmorillonite (MMT) can reduce the basal spacing and thus reduce in the number of sites available for adsorption (Bray et al., 1988). A recent study suggested that hydration of the clay mineral surface apparently reduces the accessibility of the interlayer space to aromatic molecules (Borisover et al., 2008).

A well-developed approach to improving the affinity of organic pollutants to clay minerals is the design of organo-clay minerals (McBride et al., 1975; Mortland et al., 1986; Lee et al., 1990; Johnston, 1996; Churchman, 2002; Beall, 2003; El-Nahhal et al., 2005; Bergaya et al., 2006). In the last two decades, interest in the adsorption of polyelectrolytes on clay mineral surfaces for enhanced removal of pollutants has grown significantly (Seckin et al., 1997; Churchman, 2002; Zhang et al., 2006; Zadaka et al., 2009). For example, Churchman (2002) demonstrated the removal of toluene by polystyrene–MMT composites. Radian and Mishael (2008) showed that at high loadings with polydiallyl dimethylammonium chloride (PDADMAC) on MMT, the composite is positively charged, promoting the binding of anionic herbicides. In a recent study, the advantages of composites of poly-4-vinylpyridine-co-styrene (PVPcoS) and MMT over PDADMAC–MMT composites and activated carbon in the removal of atrazine from water, even in the presence of dissolved organic matter (DOM), were shown (Zadaka et al., 2009).

In this study, the two polycations PDADMAC and PVPcoS were adsorbed on two clay minerals, MMT and sepiolite (SEP), to form polymer–clay mineral composites. PDADMAC–MMT and PVPcoS–MMT, were chosen as optimal adsorbents for the removal of phenol derivatives from water. The first phenol derivative, 2,4,6-trinitrophenol (PA) is an anionic nitrophenol derivative (pKa 0.8) which, due to its negative charge, has very high mobility in soils (Fig. 1). The second, TCP, is a synthetic organic compound used mainly in the paper and pulp mill industry and as a precursor in the herbicide industry (Fig. 1). A better understanding of adsorption of phenolic compounds to polycation–clay mineral composites may enable more efficient tailoring of these composites for optimized pollutant removal.

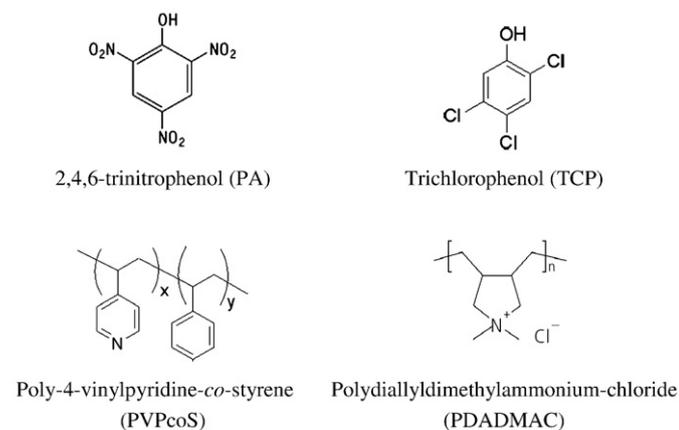


Fig. 1. Molecular structure of the pollutants and polymers.

2. Materials and methods

2.1. Materials

Wyoming Na-MMT (SWy-2) was obtained from the Source Clays Repository of the Clay Mineral Society (Columbia, MO). SEP Yuncillos (99%) was obtained from TOLSA S.A. (Madrid, Spain). Cation exchange capacities and specific surface areas were, 76.4 meq/100 g and 756 m²/g for MMT, and 15 meq/100 g, and 340 m²/g for SEP (van Olphen and Fripiat, 1979; Ruiz-Hitzky and Casal, 1985). PVPcoS (molar mass–1,200,000–1,500,000; PVP-to-S ratio 9:1), PDADMAC (molar mass 400,000–500,000) and TCP (99%) were purchased from Sigma Aldrich (Stenheim, Germany). PA (1.2%) was obtained from Ridley (Reidel-de Haan, Germany) and sulfuric acid was purchased from Tedia, (Fairfield, Ohio). PVPcoS was dissolved in a 6.5 mM sulfuric acid solution which resulted in a total of 40% charged monomers (Zadaka et al., 2009).

2.2. PVPcoS and PDADMAC adsorption on MMT and SEP

The PVPcoS and PDADMAC adsorption isotherms on MMT and SEP were prepared by adding the polymer solutions to dispersions of MMT or SEP (at a volumetric ratio of 2:1), reaching final concentrations of 0 to 0.2 g/L polymer and a clay mineral content of 0.5 g/L or 1.5 g/L. The PDADMAC–MMT composites were agitated for 4–24 h in centrifuge tubes on a reciprocating shaker while the PVPcoS composites were stirred by magnetic stirrer to avoid foaming, for 1–4 days.

The composites were then centrifuged at 2000 rpm for 25 min, and washed twice to remove free polymer by replacing the supernatant with distilled water. The amount of PVPcoS (adjusted to pH 2) and PDADMAC adsorbed on the clay mineral was measured by UV-Vis spectroscopy using a diode-array HP 5482A spectrophotometer at 254 nm ($\epsilon = 19.55 \text{ l g}^{-1} \text{ cm}^{-1}$) and a CHNSO analyzer (Thermo-Scientific, Fisons, EA1108), respectively.

Composites of the polycations with MMT were chosen for the pollutant-removal experiments: 1.4 mmol charged monomers of each polymer per g clay mineral corresponding to a PDADMAC–MMT composite of 0.15 g/g and PVPcoS–MMT loadings of 0.3 g/g in order to achieve an equal amount of charged monomers per mass unit of clay mineral (the content of charged monomers on the polycations were 100% and 40% respectively).

Desorption experiments were conducted for the MMT composites. After removing the supernatant, the same volume of distilled water was added and the tubes were agitated for 1 and 24 h. The procedure was carried out twice to ensure that no significant free polymer remained. Polymer loading after desorption was measured as described above.

2.3. Electrophoretic mobility

The electrophoretic mobilities of PDADMAC, PVPcoS, MMT and the two composites (0.3 g/g PVPcoS–MMT and 0.15 g/g PDADMAC–MMT) were measured using a Zetasizer Nanosystem (Malvern Instruments, Southborough, MA). The samples were measured as a diluted aqueous dispersion ($\sim 0.05\% \text{ m/v}$ clay mineral).

2.4. Pollutant adsorption: equilibrium experiments

Adsorption isotherms were determined with composite (PVPcoS– and PDADMAC–MMT) concentrations of 0.5 g/L or 1.75 g/L and pollutant concentrations ranging from 0.1 to 0.8 mM (TCP or PA). Batch adsorption experiments were conducted at room temperature in 10-mL glass tubes that were agitated for 3 days, the composites were separated by centrifugation and the supernatant was filtered through 0.45 μm nylon filters (Teknokroma, Olimpeak). The concentrations of PA and TCP were determined by UV-Vis spectroscopy at the

354 nm ($\epsilon = 13,320 \text{ M}^{-1} \text{ cm}^{-1}$) and 310 nm ($2440 \text{ M}^{-1} \text{ cm}^{-1}$) peak, respectively. The TCP supernatant samples were buffered to pH 11 (after filtering) to achieve a linear calibration curve since preliminary experiments showed that changes in the UV spectrum of TCP occur in a pH range of 2–9.

2.5. Pollutant adsorption: kinetic experiments (wet and dry conditions)

Adsorption kinetics of PA and TCP on PVPcoS–MMT were performed by adding a 0.1 mM solution of pollutant (20 ppm TCP or 23 ppm PA) to 200 mL of PVPcoS–MMT dispersion (0.5 g/L or 1 g/L). Samples of 10 mL were taken at equal time intervals from 0.3 min to 15 min, immediately filtered using 0.45- μm syringe filters (Teknokroma, Olimpeak Nylon, Spain) and measured by UV-Vis spectrophotometry. TCP samples were buffered to pH 11 before filtering and measuring in order to minimize analytical interference. Adsorbed amounts were evaluated by mass balance.

To examine the influence of composite hydration and dehydration on pollutant adsorption, the adsorbents were prepared as described above. “Wet conditions” indicated adsorption of the pollutant from solution to untreated composites. “Dry conditions” indicated that following composite preparation the samples were dried at 60 °C for 12 h. The dried composites were ground using a mortar and pestle and then dispersed for 5 min in distilled water. Then the pollutant solution was added.

3. Results and discussion

PDADMAC is a highly charged tertiary amine polycation and PVPcoS is composed of benzene and pyridine rings at a ratio of 1:9 in which only 40% of the monomers were charged. The hypothesis was that the anionic PA would show high affinity to the PDADMAC composites due to strong electrostatic attraction and that TCP would show higher affinity to the PVPcoS composites as a result of hydrophobic interactions. Indeed, as previously described by the authors of this study the binding of an anionic herbicide to PDADMAC–MMT composites for the design of controlled-release formulations (Radian and Mishael, 2008) and PVPcoS–MMT was employed for removal of the hydrophobic herbicide atrazine (Zadaka et al., 2009). However, in the latter study, PVPcoS was highly charged (90% of the monomers) whereas in the current study, PVPcoS was partially charged (40% of the monomers) in order to increase the hydrophobic regions available for pollutant binding.

The assumption made was that decreasing the charge density of the polycation would increase hydrophobic pollutant binding. In addition, polymer charge density plays a significant role in polymer configuration in the adsorbed state: at a high charge density, the polycation adsorbs mostly as “trains”, parallel to the adsorbent surface. As the charge density decreases, the polymer adsorbs more as “loops” and “tails” (Bauer et al., 1999; Breen, 1999; Claesson and Kjellin, 1999; Shin et al., 2002; Samoshina et al., 2005). The increase in loops in the adsorbed state may also enhance pollutant binding.

3.1. Polycation–clay mineral composites

Adsorption of PDADMAC (0–0.2 g/L) on MMT (1.5 g/L) was significantly higher (fivefold) than on SEP (0.5 g/L) and much faster, adsorption reached equilibrium within 4 h on MMT whereas on SEP, equilibrium took 1 to 3 days (Fig. 2). PDADMAC adsorption on MMT and SEP, when normalized to their specific surface areas (756 and 340 m^2/g , respectively), was 0.14 and 0.05 mg/m^2 , respectively, i.e., the adsorption on MMT remained threefold higher.

PDADMAC adsorption to clay minerals is due mainly to electrostatic interactions and therefore, its adsorption at equilibrium is nearly complete up to surface neutralization (Magdassi and Rodel,

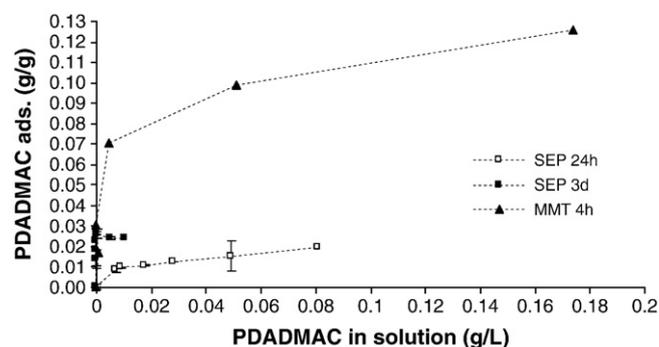


Fig. 2. Adsorption of PDADMAC (0–0.12 g/g clay mineral) on MMT and PDADMAC (0–0.04 g/g clay mineral) on SEP.

1996; Petzold and Buchhammer, 2000; Churchman, 2002), but a plateau is not reached and adsorption continues to increase (Radian and Mishael, 2008). PDADMAC adsorption is rapid, as previously reported for polycation adsorption on MMT (Theng, 1979; Durand-Piana et al., 1987; Tekin et al., 2006).

The trends observed for the adsorption of PDADMAC on SEP at equilibrium were similar to those found for MMT (despite the lower adsorption) due to a similar electrostatic mechanism. However, the reaction rates were substantially slower. The porous morphology of SEP may account for the slow kinetics since penetration of the polymer into the pores (mean pore size 1 nm) is slower than adsorption on a flat surface. Such a phenomenon was demonstrated with PDADMAC adsorption on controlled pore glass with a range of pore sizes (mean pore diameter of $7.5 \text{ nm} \pm 20\%$) (Mishael et al., 2007). The lower adsorption capacity of SEP may also be attributed to its porous structure, which includes surface areas that are not accessible to the polymer, unlike MMT where intercalation of PDADMAC was observed (Churchman, 2002; Radian and Mishael, 2008).

The adsorption kinetics of PVPcoS on MMT and SEP were similar to those of PDADMAC, i.e., much slower on SEP (Fig. 3). However, unlike PDADMAC adsorption, PVPcoS did not exhibit higher affinity to MMT. The two adsorption isotherms were similar. The decrease in PVPcoS adsorption on MMT at high polymer concentrations is explained by aggregation of the clay mineral particles, which decreases the available surface sites, and steric repulsion of the adsorbed polymer which hinders adsorption of additional polymer chains (Misra, 1996; Deng et al., 2006). The high adsorption of PVPcoS to SEP may be attributed to a dual adsorption mechanism. The charged pyridine groups adsorb via electrostatic interactions to the SEP's negative charges, and the styrene and uncharged pyridine groups can adsorb to the hydrophobic regions (siloxane groups) of the clay mineral (Johnston, 1996).

MMT composites were chosen to test pollutant adsorption, due to the kinetic advantage of polycation adsorption to MMT and to the enhanced affinity of PDADMAC to this clay mineral. The loading on the

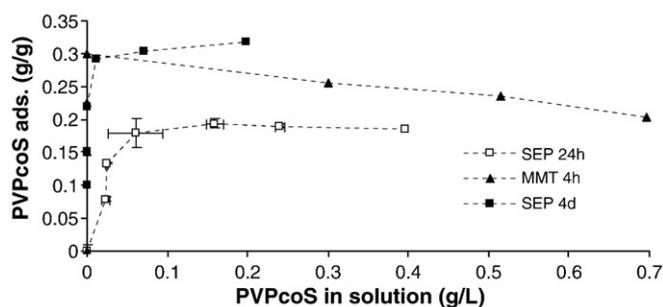


Fig. 3. Adsorption of PVPcoS (0–0.6 g/g clay mineral) on MMT and on SEP.

two composites selected for pollutant-removal experiments was the same: 1.4 mmol/g, which is equivalent to a PVPcoS composite of 0.3 g/g and a PDADMAC composite of 0.15 g/g. Although the loading of the charged monomers on the clay minerals was the same for both composites, the electrophoretic mobility of the PDADMAC composite was much higher than that of the PVPcoS, $+3.17 \pm 0.62$ and $+0.951 \pm 0.55 \cdot 10^{-8} \text{ m}^2/\text{Vs}$ respectively.

These PDADMAC- and PVPcoS-MMT composites have been characterized by FTIR and XRD measurements in previous (Sen et al., 2006; Radian and Mishael, 2008; Zadaka et al., 2009). The XRD results showed PDADMAC intercalation between the silicate layers at a 0.125 g/g loading of the clay mineral. At PDADMAC loading of 0.15 g/g (concentration used in this study) the basal spacing reached 1.46 nm which can be attributed to the intercalation of one polymer layer (Radian and Mishael, 2008). At polymer loadings of 0.3 g/g the basal spacing increased to 1.82 nm suggesting intercalation of two polymer layers. At even higher polymer loadings (0.8 g/g), the basal spacing increased to 6.25 nm which was attributed to a loop and tail conformation (Radian and Mishael, 2008). In contrast, the basal spacing of MMT after adsorption of PVPcoS (0–0.3 g/g) increased to 1.48 nm indicating intercalation of one polymer layer (as shown Zadaka et al., 2009) for the adsorption of PVPcoS 90% charged. Similar results were obtained for PVPcoS 40% charged (not shown).

FTIR measurements confirmed the electrostatic nature of the PDADMAC and PVPcoS interactions with MMT (Sen et al., 2006; Radian and Mishael, 2008). The FTIR spectrum of the polycations showed a distinctive band attributed to the quaternary ammonium (2084 cm^{-1} for PDADMAC and 1600 cm^{-1} for PVPcoS). These bands were not detected for the adsorbed polycations supporting the importance of electrostatic interactions between the quaternary ammonium group and the negatively charged clay mineral surfaces (Sen et al., 2006; Radian and Mishael, 2008). At extremely high loadings of PDADMAC (not applied in this study), in which a loop and tails configuration was suggested by the XRD measurements, the appearance of the quaternary ammonium group band supported this suggestion.

Polymer desorption from the composites was measured at a clay mineral content of 1.5 g/L. PVPcoS desorption from PVPcoS-MMT (0.3 g/g) was negligible. On the other hand, 25% of the adsorbed PDADMAC desorbed after 1 h of agitation and another 6% was released after 24 h of agitation from the PDADMAC-MMT composite (0.15 g/g), in contrast to previous studies where little to no desorption was observed (Breen, 1999).

3.2. PA binding to the composites: equilibrium studies

Although PA is anionic and showed high affinity to the highly positively charged composite PDADMAC-MMT, as expected, PA showed much higher binding affinity to the low charged composite PVPcoS-MMT at both high and low composite contents (1.75 g/L and 0.5 g/L) (Fig. 4). PA removal by PVPcoS-MMT (1.75 g/L) was complete at low concentrations of added PA (up to 34 ppm) and decreased slightly (90% removal) at higher concentrations (up to 180 ppm). As

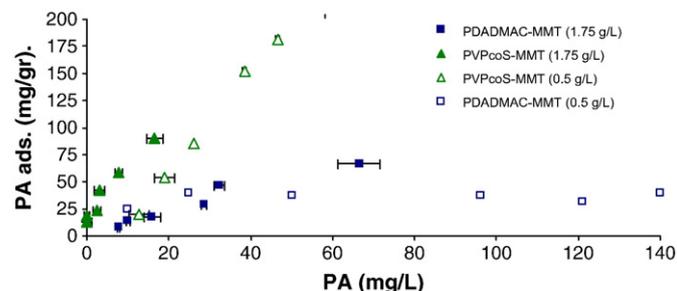


Fig. 4. PA binding to PVPcoS-MMT (0.3 g/g) and PDADMAC-MMT (0.15 g/g).

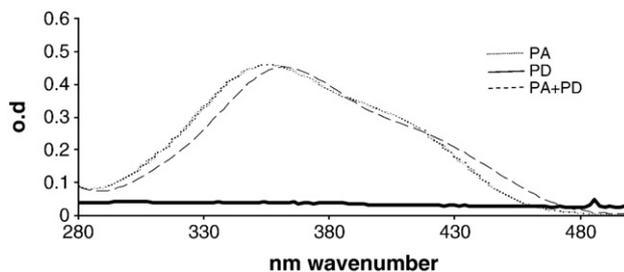


Fig. 5. UV-Vis measurements of PDADMAC (PD), PA, and PDADMAC-PA (PD-PA) complexes.

expected, PA adsorption increased with PVPcoS-MMT composite content (0.5–1.75 g/L).

The high affinity of PA to the PVPcoS-MMT may be attributed to van der Waals interactions, due to structural compatibility between PVPcoS and PA. Furthermore, PVPcoS-MMT provided a more suitable hydrophobic medium for binding as a result of its lower positive charge and consequently, a conformation consisting of more loops and tails (Breen, 1999; Claesson and Kjellin, 1999). Such molecular compatibility does not exist between PA and PDADMAC since PDADMAC is not aromatic. Strengthening these suggestions are the linear adsorption isotherms of PA on PVPcoS-MMT composites, which are typical of a partitioning mechanism and not of an electrostatic one as originally hypothesized.

Unlike the linear adsorption isotherm of PA on PVPcoS-MMT, the adsorption isotherm of PA on PDADMAC-MMT resembled L-type isotherms for the high and low composite content. PA adsorbed to PDADMAC-MMT via electrostatic interactions which typically result in an L-shape isotherm. The electrostatic interactions can also account for the significantly higher (twofold) adsorption of PA to the PDADMAC-MMT in comparison to that of the non-ionic pollutant TCP (Fig. 6).

At low PA concentrations, inhibited binding to PDADMAC-MMT (1.5 g/L) may be explained by complexation of the desorbed PDADMAC (see Section 3.1) with PA, which is enhanced at high composite content. The desorbed PDADMAC competes with the composite for pollutant binding. At higher PA concentrations, excess PA, which did not form complexes, adsorbed on the composite, and indeed an increase in binding was observed. UV-Vis spectroscopy measurements (Fig. 5) confirmed the formation of a soluble PDADMAC-PA complex in solution. The spectrum of PA with PDADMAC exhibited a red (bathochromic) shift from 354 nm to 362 nm at maximum absorbance, indicating lower excitation energy.

3.3. TCP binding to the composites: equilibrium studies

As expected, the non-ionic TCP adsorbed with higher affinity to PVPcoS-MMT than to PDADMAC-MMT (Fig. 6). TCP binding to PVPcoS-MMT reached approximately 45% of the added TCP, which was higher than reported for the adsorption of different phenols by various organo-clay minerals (Mortland et al., 1986). The adsorption isotherm of TCP on PVPcoS-MMT was linear, suggesting a partitioning mechanism. The

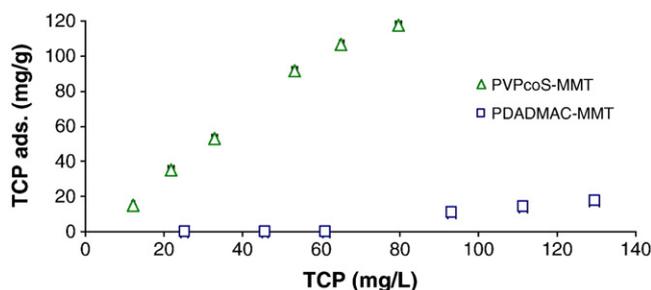


Fig. 6. TCP binding to PVPcoS-MMT (0.3 g/g) and PDADMAC-MMT (0.15 g/g).

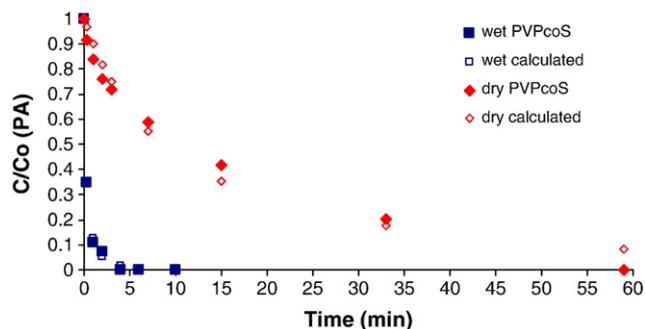


Fig. 7. Kinetics measurements of PA (23 mg/L) binding to wet and dry PVPcoS–MMT composites (0.5 g/L).

obtained partitioning adsorption coefficient ($K_d = 1.56$ L/g) was about half that found for PA on PVPcoS ($K_d = 3.76$ L/g), expressing the lower affinity of TCP to the composite.

The adsorption isotherm on PDADMAC resembled the behaviour of PA on this composite and may be explained by complexation of the pollutant with desorbed PDADMAC.

3.4. Reaction rates of PA and TCP adsorption (under wet and dry conditions)

Reduction in PA and TCP concentrations (C/C_0) due to adsorption on wet or dried PVPcoS–MMT composites (0.5 g/L) as a function of time are shown in Figs. 7 and 8, respectively. The adsorption behaviour was adapted to a pseudo second-order kinetics, using (Ho, 2001):

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \rightarrow q_t = \frac{t}{\frac{1}{kq_e^2} + \frac{t}{q_e}}$$

where t is the time (min), q_e is the equilibrium amount adsorbed (mg/g), and k the rate of adsorption (mg pollutant/mg adsorbent per minute). The model calculations for all kinetic experiments are given in Table 1.

For both the dry and wet PVPcoS–MMT composites, PA removal was complete within 60 min (Fig. 7). The similar maximum PA-adsorption capacities (q_e) at equilibrium of the dry and wet composites fitted the identical value of q_e (45.82 mg/g) calculated for both composites and indicated that the adsorption capacity was not influenced by dehydration of the adsorbent.

While maximum loading was the same for both dry and wet composites, complete PA removal by the composite was reached within less than 4 min for the wet composite, whereas complete removal by the dry composite was reached within approximately 60 min. This difference is reflected in the calculated rate of adsorption (k) which, for the wet composite, was 60 times larger than for the dry

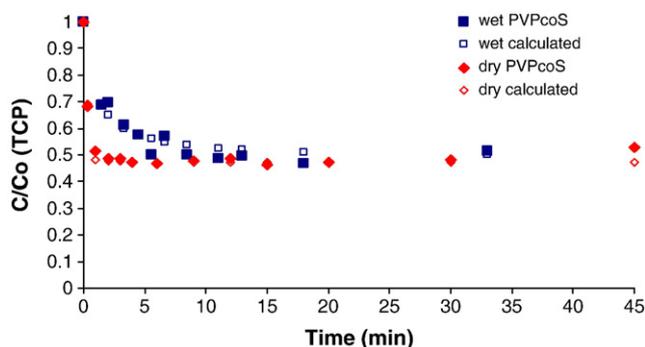


Fig. 8. Kinetics measurements of TCP (20 mg/g) binding to wet and dry PVPcoS–MMT composites (0.5 g/L).

Table 1

Calculated adsorption rates of PA (0.1 mM) and TCP (0.1 mM) on PVPcoS–MMT (0.5 g/L) applying pseudo second-order kinetics.

Pollutant	Adsorbent		q_e (mg/g)	k (mg/mg min)	R^2
PA	PVPcoS–MMT	Dry	45.82	2.11	0.979
		Wet	45.82	125	0.999
TCP	PVPcoS–MMT	Dry	20.8	2.3	0.963
		Wet	20.4	2.4	0.935

composite (Table 1). We suggest that enhanced adsorption by the wet composite is due to the hydration shell of the ionic PA which enables its high mobility in the aquatic medium. The lack of water in the dry composites may have inhibited the mobility of the hydrated PA molecules. The delay in PA adsorption by the dry composite may reflect the time required for the dry composite to rehydrate.

Contrary to the behaviour of PA on the composites, TCP binding to the dry composite was more rapid. Maximum removal of TCP (~46%) was reached by the wet composite after 8 min and by the dry composite after only 2 min. Since TCP does not have a hydration shell (Johnston, 1996), its binding may be enhanced by the more hydrophobic interlamellar regions which are free of water molecules. Similar results of vapor adsorption on “dry” and “wet” composites were shown (Lee et al., 1990). However, in that study the adsorption was from the gas phase and therefore the “dry” conditions did not include re-hydration. These results support the suggestion that TCP adsorption is dominated by van der Waals interactions.

4. Conclusion

The adsorption of PDADMAC and PVPcoS to MMT was significantly faster for both polyelectrolytes than their adsorption to the porous SEP (2–4 h on MMT as opposed to 3–4 days on SEP). The binding of PA and TCP to PVPcoS- and PDADMAC–MMT was studied both in equilibrium and as a function of time. Both pollutants showed higher affinity towards PVPcoS–MMT and binding was driven mainly by van der Waals interactions, corresponding to the linear adsorption curves obtained. However, PA exhibited a higher affinity to the composite relative to TCP, suggesting that electrostatic interactions may also play a role. The difference in binding characteristics of PA and TCP was also seen in their binding kinetics to dry and wet composites. The results of this study emphasize the importance of better understanding pollutant–adsorbent interactions to enable smarter and more efficient tailoring of polymer–clay mineral composites for water purification.

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