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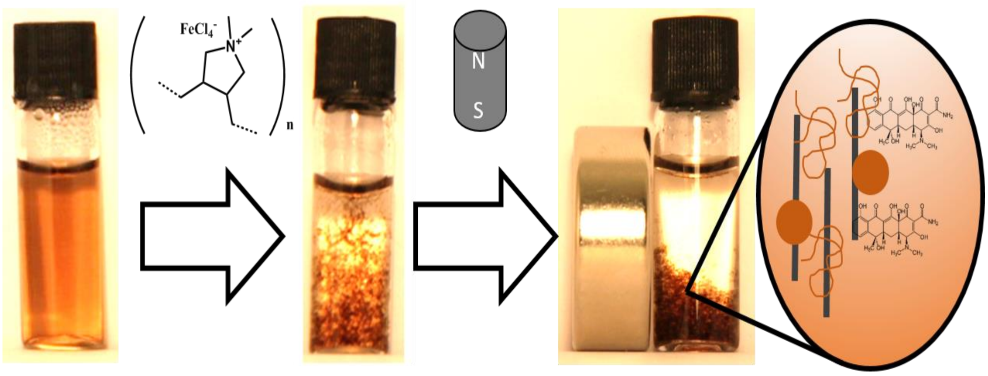

Magnetically Responsive Materials based on Polymeric Ionic Liquids and Graphene Oxide for Water Clean-up

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Abstract

Hypothesis

Owing to attractive colloidal interactions between graphene oxide and a paramagnetic polymeric ionic liquid (polyallydimethylammonium chloride with a $FeCl_4^-$ counterion (Fe-polyDADMAC) it should be possible to form magnetic materials. The benefit of using charge-based adsorption is that the need to form covalently linked magnetic materials is offset, which is expected to significantly reduce the time, energy and cost of these systems. These systems could have a wide use and application in water treatment.

Experiments

Non-covalent magnetic materials were formed through the mixing of Fe-pDADMAC and GO. A systematic study was conducted by varying polymer concentration at a fixed GO concentration. UV-Vis was used to confirm and quantify polymer adsorption onto GO sheets. The potential uses of the system in the field of water purification were demonstrated.

Findings

Fe-polyDADMAC adsorbs to the surface of GO and induces flocculation. Low concentrations of the polymer (< 9 mmol/L) favour flocculation, whereas higher concentrations (> 20 mmol/L) induce restabilization. Difficult-to-recover gold nanoparticles can be separated from suspensions as well as the pollutant antibiotic tetracycline. Both harmful materials can be magnetically recovered from the dispersions. This system therefore has economical and practical applications in decontamination and water treatment.

Keywords: graphene oxide, magnetic nanomaterials, adsorption, polymeric ionic liquid, water treatment.

1. Introduction

Graphene oxide (GO) is of interest for a vast array of laboratory (stabilization of interfaces[1, 2], optics[3], sensors[4]) and industrial applications (paper[5] and anti-corrosive[6]/medical coatings[7]). One recent application which has been demonstrated is its use in water treatment[8]. GO forms stable colloidal dispersions in aqueous environments[9] owing to the low acidity constant of carboxyl groups ($pK_a = 4.3$) at the periphery of its characteristic sheet like structures[10]. These outer groups readily dissociate into carboxylate anions[11]. This means that the colloidal dispersions benefit from charge stabilization effects down to very low, and across a wide range, of pH values[12]. As well as being capable of forming stable dispersions, GO also has an extremely high surface area to mass ratio (many hundreds of $m^2\ g^{-1}$)[13]. For these reasons GO is an attractive candidate for the efficient removal of toxic species from aquatic environments.

It has been demonstrated that GO is capable of removing toxic species such as heavy metals (arsenic[14], cadmium[15], selenium[16]), dyes[17] and antibiotics[18] from water with impressive adsorption capacities (ca. 100 mg g^{-1} for some heavy metal ions[19]) approaching that of the zeolites which are already commonly used. However, GO has the added advantage that it can be produced cheaply from natural graphite deposits.

The use of an adsorbent for water purification is also highly attractive from an economic perspective. Adsorbing pollutants onto the surface of another material negates the need to perform high energy and expensive steps such as centrifugation, filtration, disinfection etc. However, the use of an adsorbent such as GO in water purification does pose one problem. How the stable colloidal suspension (with adsorbed toxic pollutants) is recovered post-adsorption? One approach has been to covalently bind magnetic particles onto the GO matrix, forming magneto-responsive adsorbents that can be easily retrieved by the application of an external field[20]. However, such covalent attachment is expensive, requires a large energy/time input and potentially compromises the adsorption capacity of the GO. Recently it has been shown that GO can be removed from suspension through the adsorption of magneto-responsive materials. Iron oxide micro/nanoparticles as well as magnetic ionic liquid surfactants were electrostatically adsorbed to the surface of GO and were found to facilitate the magnetic recovery of the material from solution[21]. The use of Coulombic attraction between adsorbent and magneto-responsive compound, as opposed to covalent attachment, allows the use of “virgin” GO as an adsorbent for water decontamination. The magnetic recovery of adsorbents is a promising technique for water clean-up. Magnetic recovery of GO must be investigated further if these processes are to become applicable for use in large-scale water treatment.

Polymeric ionic liquids composed of poly(diallyldimethylammonium chloride) (pDADMAC) with paramagnetic anions based on $FeCl_4^-$ (now denoted as Fe-polyDADMAC) can be synthesised in one step from cheap starting materials[22]. The polymer maintains a high surface positive charge independent of pH[23] and is expected to show a strong Coulombic attraction with sheets of dispersed GO.

This study investigates the adsorption of such polymeric ionic liquids onto GO and allows for its removal from water by an applied magnetic field. More importantly, it is shown that adsorption of magnetically active species does not hinder the adsorption and recovery of pollutants and/or toxic compounds from water. This has been achieved by demonstrations with two model, but industrially relevant, examples. One which highlights the removal of gold nanoparticles, and the second which demonstrates the removal of the antibiotic tetracycline from solution. This reinforces the argument made by previous studies that “virgin” GO, with electrostatically adsorbed magneto-responsive compounds is a powerful tool for water clean-up[21]. The polymeric ionic liquid used here has the added advantages that it is capable of interacting with GO over a large pH window, induces strong flocculation and aids magnetic recovery simultaneously. The polymer benefits from multiple charged moieties per chain and is therefore expected to interact with GO to a greater extent than previously reported magnetic ionic liquid surfactants. Given that each charged group contains a paramagnetic counter-ion, it is expected that this will also strengthen magnetic recovery. The polymer is also highly soluble in aqueous environments and therefore does not require agitation, stirring or dispersion. The experimental concept is demonstrated schematically in figure 1. Graphene oxide is dispersed into a medium which requires purification and toxic/pollutant species adsorb onto its surface (e.g antiobiotics and nanoparticles). The polymer is then added to the system and strong flocculation is induced. A magnetic field is then applied to the system and the GO is recruited at the magnet due to the presence of the adsorbed magnetically active polymer. The toxic species adsorbed on the surface of the GO are also drawn towards the magnet and recovery is now possible.

2. Experimental

2.1 Materials

Polydiallyldimethylammonium chloride (polyDADMAC, 20 % w/w in water), iron (III) chloride, graphite flakes, sulphuric acid, phosphoric acid, potassium hydroxide, potassium permanganate, hydrogen peroxide (30 % w/w in water), gold (III) chloride trihydrate, sodium citrate and tetracycline hydrochloride (all 98 % purity or higher) were purchased from Sigma and used without further purification.

For the synthesis of the cationic polyelectrolyte, one equivalent (with respect to monomer units) of $FeCl_3$ was dissolved in the minimum amount of water/methanol at room temperature. Added drop-wise to this was polyDADMAC, previously dissolved in water. This was left to stir overnight. The polymer was then freeze dried to obtain the solid. Reacting polyDADMAC with $FeCl_3$ in this way facilitates its conversion to $FeCl_4^-$ utilizing the extant chloride counter ions associated with quaternary ammonium groups on the polymer chain[24].

Graphene oxide was synthesized from graphite flakes using a variation on the Hummers method described in Marcano et al[25]. Briefly, graphite powder (1 g) was added to a 9:1 mixture of concentrated sulphuric acid and phosphoric acid. The mixture was then stirred and added gradually to this was potassium permanganate (6 g). The temperature was set at 50 ^{0}C and the mixture stirred overnight. The resulting brown mixture was cooled to room temperature and poured over ice with around 1 mL of a hydrogen peroxide solution, 30 % (w/w) in water. Any large particles that had formed were filtered off and the filtrate was centrifuged at 6000 rpm for 1 hour. The supernatant liquid was removed and replaced with distilled water. This process was repeated three times and the GO obtained was dried in an oven at approximately 50 ^{0}C.

Gold nanoparticles were synthesized using the method of McFarland et al[26]. Briefly, a 1 mmol/L solution of gold (III) chloride was heated to boiling point whilst being vigorously stirred. To this a 38 mmol/L sodium citrate solution was added. The mixture was boiled for around 10 minutes or until it became deep red in colour. The solution was then cooled to room temperature.

2.2 Methods

All samples were made up to a standard volume of 1.5 mL. Any adjustment to the pH of solutions was done so with either concentrated hydrochloric acid or potassium hydroxide.

Before any analysis was performed on the prepared samples they were always equilibrated for 24 hours.

Magnetic response of the GO-Fe-polyDADMAC materials was assessed by placing a strong, permanent magnet next to the vials containing the samples. The magnets used were made of sintered NdFeB (N42) with a triple coat Ni casing (eMagnets, U.K). The magnets were discoidal in shape with diameter 25 mm and thickness 10 mm, and a magnetic field intensity at the surface of around 1 T.

UV-Visible spectrophotometry measurements were carried out using a Nicolet evolution 300 from Thermo Scientific. For samples in which the equilibrium aqueous polymer concentration was of interest, the GO was centrifuged down to ensure the spectra were representative of the free polymer only. For samples in which the equilibrium concentration of tetracycline was of interest, the GO-tetracycline composite was centrifuged down and the sample was injected through a polycarbonate syringe filter with 0.02 μm pore size. This ensured removal of the polymer. Equilibrium aqueous concentrations of both the polymer and tetracycline were calculated from prepared calibration curves (see supporting information).

3. Results and Discussion

3.1 Polymeric ionic liquid interaction with graphene oxide

The opposite electro kinetic charges of the GO particles and the poly(DADMAC) drive adsorption of the poly(DADMAC) on GO surfaces (Figure 1). This makes for an appealing and versatile water treatment system. It has been demonstrated that assembly via charge is an appropriate tool for water purification when using GO. This has been shown through layer-by-layer assembly techniques[27-29] and assembly at gold-water interfaces[30]. Figure 1 shows the apparent decreasing zeta potential of GO sheets as the pH changes from 2 through 10. This is surprising as the pKa of the peripheral carboxyl groups on the GO sheets is 4.3. If the negative electro kinetic charge on GO was driven solely by these outer carboxyl groups then the zeta potential should exhibit an inflection point at pH 4.3 (commensurate with the pKa of the carboxyl groups). The fact that the pH continues to drop past this point lies in the fact that the method of GO preparation (modified Hummers method) does more than simply make edge carboxyl groups, and in addition produces facial carboxyl groups and defects. Such groups have alpha-unsaturation, and this greatly lowers the effective pKa[12].

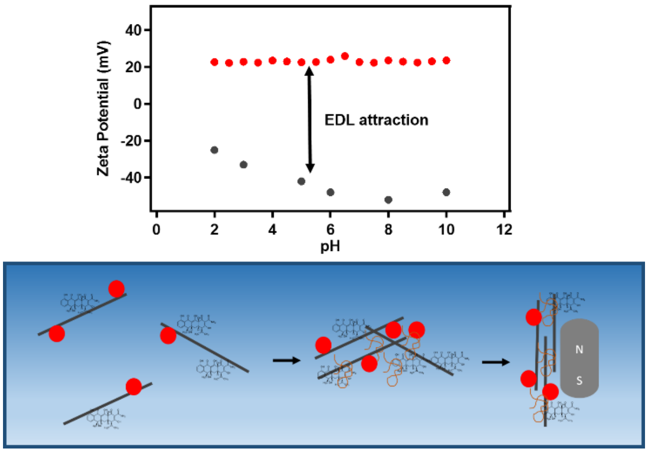

Figure 1. (above) Zeta potential as a function of pH for Fe-pDADMAC and GO. Data for GO is from Chen et al[12]. (below) Schematic representation of pollutant recovery from water using GO and Fe-polyDADMAC. GO sheets are dispersed in medium for purification (shown here is a mixture of antibiotic pollutants and nanoparticles). The polymer is added, adsorbs to GO and flocculation is induced. A magnetic field is applied and recovery of GO sheets with adsorbed toxins is now possible.

Figure 2a and b show that it is possible to flocculate and magnetically recover GO from solution using Fe-polyDADMAC. Figure 2a is an image of a stable dispersion of GO alone. Figure 2b highlights flocculation using conventional polyDADMAC with no paramagnetic counter-ion present. Also shown is the flocculation and magnetic recovery using the paramagnetic polymeric ionic liquid, Fe-polyDADMAC. Although flocculation is achieved using both polymers, magnetic recovery is only possible when the paramagnetic polymer is present. In order to show that interaction, flocculation and magnetic recovery is possible over a wide range of pH values, figure 2 c,d shows identical sets of vials at two different pH values (2c = pH 4 and 2d = pH 9). It is clear that pH exerts little effect on the polymer adsorption to the surface of GO and hence flocculation of the composites.

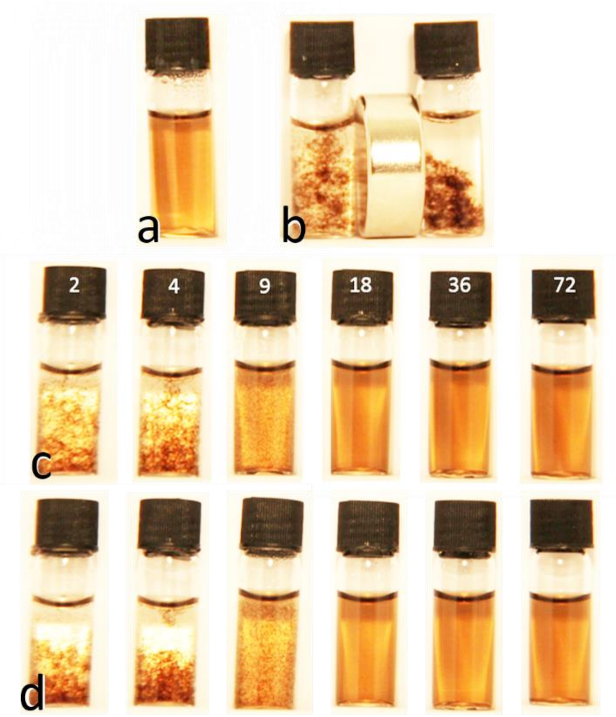

Figure 2. (a) GO dispersion in water without added polymer. (b) Flocculation of GO with polyDADMAC (left) and flocculation with magnetic recovery of GO using Fe-polyDADMAC (right). (c and d) Interaction of Fe-polyDADMAC at different concentrations of the polymer (concentration is mmol/L of polymer) at pH 4 and 9 respectively.

These effects have been investigated quantitatively by maintaining a fixed GO concentration and varying polymer concentration at pH 4. At low polymer concentrations (< 9 mmol/L) the polymer induces rapid flocculation and forms a magnetically responsive "network", leaving clear water as the supernatant (figure 3 c,d). At first sight it appears that all of the GO has been flocculated. It is likely that the co-flocculated network has a structure by where the cationic polymer links GO sheets and acts as a bridging flocculant. Similar systems have been reported for GO co-flocculated with Fe_2O_3 microparticles[21] and polyelectrolyte induced flocculation[31]. At higher concentrations of the polymer it is shown that GO can be re-dispersed. This is due to overcharging of the GO surface as the polymer acts to re-stabilize the colloidal suspension. At higher concentrations (> 20 mmol/L) the polymer adsorbs to the surface of GO and forms a dense layer of polyelectrolyte with a high positive surface potential. Here the cationic polymer acts as a dispersant for the GO and is no longer able to induce flocculation. This phenomenon has been reported previously for nanoparticles stabilizing large colloidal systems[32] as well as for magnetic Fe_2O_3 nanoparticles on GO[21].

The adsorption isotherm for the polymer on GO is shown in figure 3. Fe-polyDADMAC adsorbs with high affinity onto the surface of GO with adsorption as high as 50 mmol of polymer per g of GO at high polymer loading. This is significantly higher than the adsorption capacity for the magnetic ionic liquid surfactants previously reported[21], which have adsorptions of 20 mmol per g of GO at high surfactant loading. This is readily explained by the presence of multiple charged groups per polymer chain, which act to significantly enhance the interaction between polymer and GO sheets. Due to the experimental uncertainty in measuring small changes in absorbance at high polymer loading it was not possible to observe the saturation point of adsorption (this would have been observed by an asymptotic flattening of the isotherm). For magnetic ionic liquid surfactants it has been suggested that GO sheets become coated with a significant amount of surfactant which renders them hydrophobic causing them to attract one another. This is unlikely for the polymer system presented here given that it is very hydrophilic, and has multiple charged groups per polymer chain. It can therefore be suggested that the polymer adsorbs onto the GO sheets by interaction with the peripheral anionic carboxylate groups, neutralising the charge and inducing colloidal instability. Given the high loadings of polymer seen in the adsorption isotherm this is the most likely explanation for the mechanism of flocculation.

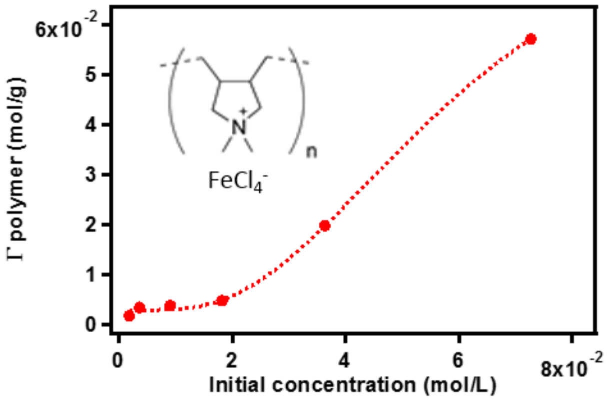

Figure 3. Adsorption isotherm for Fe-polyDADMAC on GO at pH 4. The dashed trendline has been added as a guide to the eye.

It is important to remember that the counterions are paramagnetic in these systems and not the polymer chain itself; the counterions are therefore prone to dissociation[33]. As reported for the magnetic ionic liquid surfactants the magnetic response of the co-flocculated network is dictated by two key processes. The main driving force for magnetic recovery is likely to be the adsorption of undissociated, bound polymer chains largely interacting with the GO sheets through polar interactions, which are capable of direct interaction with the magnetic field. The second is the interaction of dissociated, bound surfactant ions which form a diffuse layer in the proximity of the GO-surfactant interface. These dissociated species still retain their counterions and osmotically “drag” the co-flocculated network towards the magnet[21].

3.2 Removal of gold nanoparticles from aqueous environments

Figure 4 shows the first application of the GO/Fe-polyDADMAC complexes for water treatment by demonstrating that gold nanoparticles can be captured and magnetically recovered from an aqueous environment. At low values in pH the gold nanoparticles exhibit a small positive surface charge[34] and are attracted to the negatively charged GO surfaces. The nanoparticles will selectively adsorb to the GO as no interaction is expected between them and the high positive charge polymer. Figure 4, a shows pictures of the mixed GO-gold nanoparticle system before and after polymer addition: once the polymer is added, flocculation occurs and magnetic recovery of the GO-nanoparticle composite is possible. The supernatant phase after magnetic recovery appears to be clear water. To demonstrate the power of this technique UV-Vis spectroscopy was performed, and Figure 4, b shows UV-Vis spectra for gold nanoparticles only, the GO-gold nanoparticle composite (before the addition of the polymer) and the supernatant water phase left behind after magnetic recovery. The gold nanoparticles alone exhibit the characteristic localized surface plasmon resonance (LSPR) peak at ca. 500 nm[35]. This is somewhat diminished when GO is added to the system owing to adsorption of nanoparticles on the surface of GO and the signal from GO itself. However, after magnetic recovery and analysis of the supernatant phase it is clear that the gold nanoparticles have been almost entirely removed from solution as the LSPR peak completely disappears (at least within the detection limit of these experiments).

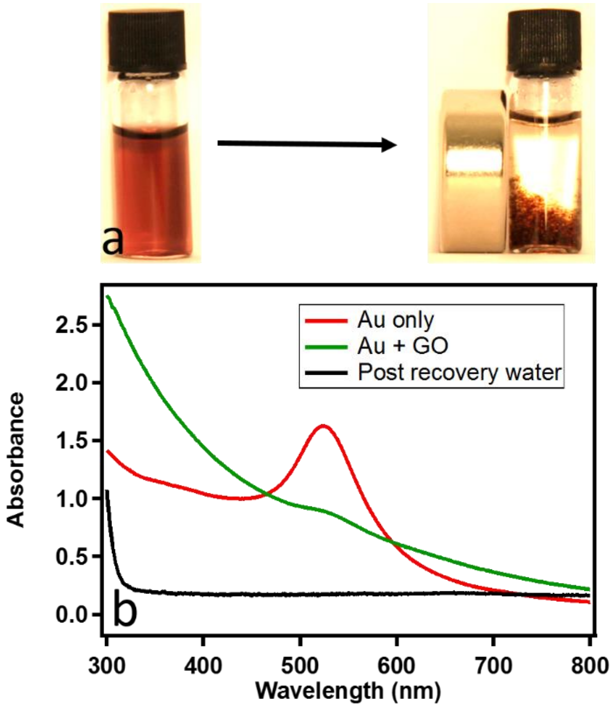

Figure 4. (a) Pictures showing the GO-gold nanoparticle composites before and after polymer addition, flocculation and magnetic recovery. (b) UV-Vis spectra for suspensions of gold nanoparticles only, GO-gold nanoparticle composite and the clear supernatant phase after magnetic recovery.

3.3 Removal of antibiotic pollutants from aqueous environments

Pharmaceutical antibiotics are poorly metabolized when absorbed by treated humans and animals, and therefore notable levels of these drugs are found in wastewater as unmodified parent compounds[36, 37]. Antibiotics are often detected in agricultural runoff, wastewater treatment plants and even drinking water[38, 39]. Potential dangerous effects include acute and chronic toxicity, harmful impact on aquatic life and contribution to growing concerns with regard to antibiotic resistant organisms[40]. This has provided the motivation for the second application of the GO/Fe-polyDADMAC water treatment system. Figure 5 shows UV-Vis absorption spectra for GO, the polyketide antibiotic tetracycline and GO with adsorbed tetracycline molecules. GO exhibits the characteristic flat absorption curve at higher wavelengths[41]. However, when it is mixed with tetracyline it demonstrates additional absorption peaks at around 300 and 350 nm. This is consistent with tetracycline being adsorbed onto the surface of the GO[18]. It is expected that tetracycline strongly interacts and adsorbs at the GO interface through π-π interactions and cation-π bonding[42].

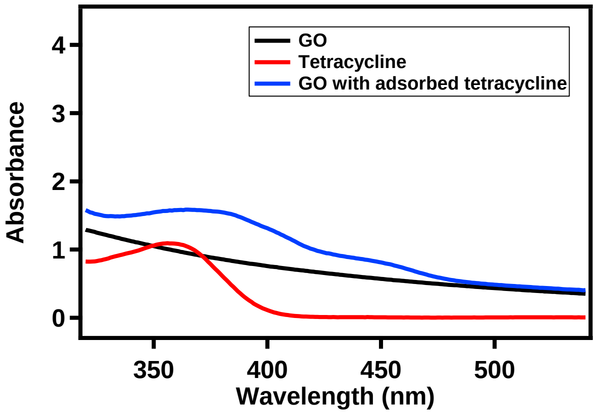

Figure 5. UV-Vis absorption spectra for GO alone, tetracycline and GO-tetracycline composite dispersions.

The inset in figure 6 shows it is possible to flocculate the GO-tetracycline composite with Fe-polyDADMAC and recover the dense phase magnetically. It is noticeable that the supernatant phase maintains a slight yellow colour. This is due to the presence of non-adsorbed tetracycline. Given that the antibiotic shows such prominent features under UV-Visible light it is possible to derive an adsorption isotherm for the molecule on GO. This is also shown in figure 6. As the initial concentration of tetracycline increases the adsorbed amount of the antibiotic on GO increases until the isotherm appears to plateau at around 2.5 mmol/g. This pattern of adsorption of antibiotics has been reported for adsorption onto silica[43, 44] and other carbon based adsorbents including graphite, activated carbon and carbon nanotubes[45, 46]. At a fixed concentration of adsorbate of 3.6 mmol/L the amount of tetracycline adsorbed on GO is 2.8 mmol/g. This is compared to the amount of polymer adsorbed at the same concentration which is 3.5 mmol/g. The fact that the polymer has a higher affinity for GO is not surprising. There are multiple positively charged groups per polymer chain which are free to interact with the negative surface charge of GO and the affinity of tetracycline for GO does not seem to be compromised by the presence of the cationic polymer. Again this is easily explained when the two modes of interaction by which tetracycline can adsorb are considered. 1) The antibiotic may adsorb onto the surface of GO through strong through π-π interactions owing to the presence of four aromatic rings within the molecule. 2) At low pH values tetracycline is in a cationic form[47] and will benefit from electrostatic interactions with GO which is negatively charged at low pH.

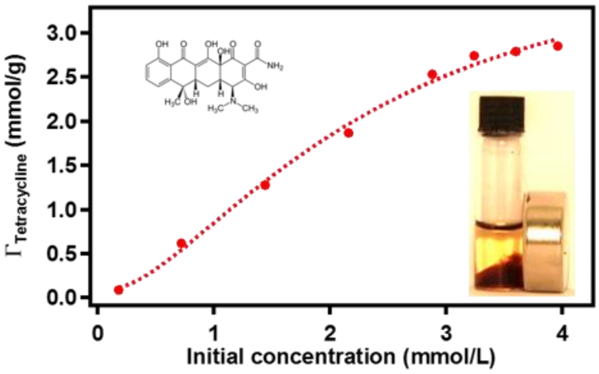

Figure 6. Adsorption isotherm for tetracycline on GO. (inset) Demonstration of flocculation and magnetic recovery of GO-tetracycline composite.

4. Conclusion

Magnetically responsive materials based on non-covalent interactions between graphene oxide (GO) and polymeric ionic liquids composed of polyDADMAC and $FeCl_4^-$ counterions have been formed. Fe-polyDADMAC adsorbed to the surface of GO caused the composite material to flocculate. The co-flocculated material could then be captured by applying an external magnetic field. Adsorption of the polymer onto GO has been explained by large attractive electrical double-layer forces between the two components. The polymer is capable of adsorbing across a wide pH range. Such non-covalent interactions which result in strong flocculation and magnetic recovery have economic benefits in terms of cost and energy input, compared to covalently linked magnetic materials[14, 48, 49]. Furthermore, the wide pH range of operation provides an attractive alternative compared to other systems which require specific pH values[12]. Interestingly, at higher polymer concentrations the system re-stabilized through overcharging of the GO surfaces. This has been reported previously for similar systems[21, 50], but may be used generally to provide colloidal dispersions with higher stability.

Perhaps most importantly, it was demonstrated that these materials were applicable to two industrially relevant model systems for water clean-up. GO-Fe-polyDADMAC has been applied to the removal of gold nanoparticles and pollutant antibiotics from aqueous environments. This demonstrates it is possible to remove and recover harmful compounds from water using cheap starting materials and low cost, energy efficient capture processes. The systems reported here have obvious advantages over covalent magnetic structures[16], centrifugation[51] and filtration[52]. These characteristics make the use of polymeric ionic liquids and GO for industrial scale water treatment an exciting and practical prospect.

Acknowledgements

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