



Responsive materials based on magnetic polyelectrolytes and graphene oxide for water clean-up

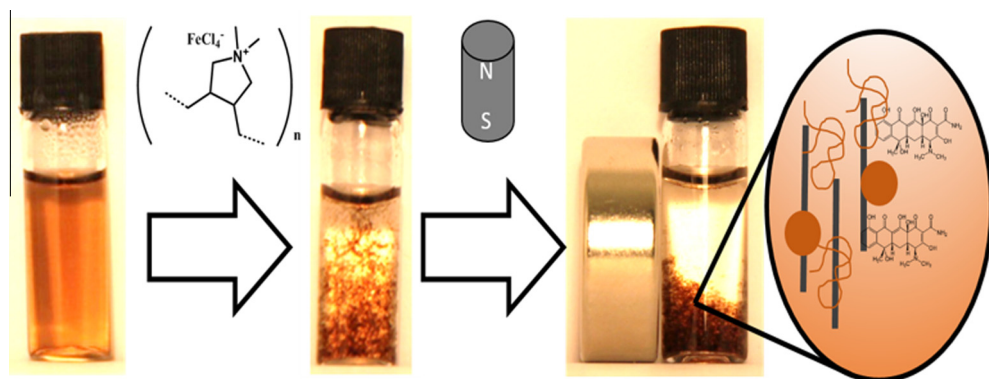


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GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Owing to attractive interactions between negatively charged graphene oxide (GO) and a paramagnetic cationic polyelectrolyte (polyallyldimethylammonium chloride with a FeCl_4^- counterion (Fe-polyDADMAC) it should be possible to generate 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 to make such responsive materials. 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 systems for 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.

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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 to yield carboxylate anions [11]. This means that these 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 and disinfection. However, the use of an adsorbent such as GO in water purification does pose one problem. How can the stable colloidal suspensions (with adsorbed toxic pollutants) be 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 suspension [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.

Polyelectrolytes of poly(diallyldimethylammonium chloride) (pDADMAC) with paramagnetic anions based on $FeCl_4^-$ (here denoted as Fe-polyDADMAC) can be synthesized 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 magnetic polyelectrolytes 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 other 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 findings made by previous studies that “virgin” GO, with electrostatically adsorbed magneto-responsive compounds is a potentially useful agent for water clean-up [21]. The polyelectrolyte 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 is associated with 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 Fig. 1. Graphene oxide is dispersed into a medium which requires purification and toxic/pollutant species adsorb onto its surface (e.g. antibiotics 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 counterions associated with quaternary ammonium groups on the polymer chains [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 $50^\circ C$ 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 h. 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 $50^\circ C$.

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 min or until it became deep red in colour. The solution was then cooled to room temperature.

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