Using Deep Eutectic Solvent for Conjugation of Fe$_3$O$_4$ Nanoparticles onto Graphene Oxide for Water Pollutant Removal

by

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Abstract

Deep eutectic solvents (DESs) have emerged as a substitute for ionic liquids with lower cost and enhanced biodegradability. The most common class of DES refers to a mixture of a quaternary ammonium or phosphonium salt and a hydrogen bond donor (e.g., carboxylic acid) with a melting point lower than that of individual components. DESs have recently shown promise for surface modification of graphene oxide (GO) nanosheets with different functional groups. We hypothesize that such surface functionalization of GO (and other carbon nanomaterials) with DESs can provide a new route to conjugate metallic nanoparticles onto GO surfaces (and similar). Here, we used a typical DES, based on choline chloride and urea, for the conjugation of presynthesized Fe3O4 nanoparticles onto GO nanosheets at different GO:Fe3O4 ratios. Physicochemical characterization not only confirmed the ability of DES to prepare DES/GO-Fe3O4 nanohybrids successfully, but also evidenced the influence of DES on the homogeneity and size distribution of Fe3O4 nanoparticles in these nanohybrids. DES/GO-Fe3O4 nanohybrids can perform better than both GO and Fe3O4 as adsorbents for organic dyes (methylene blue, MB) and heavy metals (Lead (II)). However, depending on the contaminant type, the contaminant removal performance varied differently for DES/GO-Fe3O4 nanohybrids with different ratios.

Keywords: ionic liquid, 2D nanomaterials, carbon nanomaterial, water treatment, green synthesis
1. Introduction

Iron-based nanoparticles, including magnetite (Fe₃O₄) nanoparticles, have emerged as one of the most promising technologies for organic and inorganic contaminant removal from water and wastewater (Xu et al., 2012). This can be attributed to their high specific surface area, adsorption and reduction capacity, and ease of recovery and reuse through magnetic separation (Sharififard and Soleimani, 2017). However, in aqueous media, these nanoparticles suffer from loss of surface area and reactivity due to aggregation because of inherently high van der Waals and magnetic attraction forces (Fu et al., 2015; Mehrabi et al., 2019). One way to resolve this issue is to immobilize iron-based nanoparticles onto carbon-based supports including activated carbon, carbon nanotubes, or graphene (Aich et al., 2018; Chen et al., 2016; Masud et al., 2018; Mehrabi et al., 2019). Among the carbon supports, graphene derivatives such as graphene oxide (GO) have emerged as the most promising with its two-dimensional planar surface and high contaminant adsorption capacity for both organic and inorganic pollutants (better than activated carbon and carbon nanotubes) as well as its superior electron transfer capacities for allowing fast redox chemistry (Masud et al., 2018; Mehrabi et al., 2019).

The synthesis of graphene-Fe₃O₄ nanohybrids happens in two major pathways: (i) co-reduction of GO and iron salts (Areerob et al., 2018; Barai et al., 2019) and (ii) attachment of pre-synthesized Fe₃O₄ nanoparticles onto GO nanosheets using chemical bonds (Han et al., 2012; He et al., 2010). The first approach requires either the addition of reducing agents which are mostly harmful chemicals like hydrazine (Chong et al., 2016; Dai et al., 2019; Oh et al., 2015; Thu and Sandhu, 2014) or the use of energy-intensive processes including ultrasonic pyrolysis (Nie et al., 2016). However, these methods allow the attachment of Fe₃O₄ nanoparticles onto GO sheets via weak physical or electrostatic forces, making them susceptible to detachment during the washing or
adsorption process in aqueous media (He et al., 2010). Thus, efforts towards conjugation of GO and Fe₃O₄ using strong bonds have been pursued, but they have mostly required functionalization of Fe₃O₄ nanoparticles with amine-group containing compounds and subsequent usage of coupling agents (Bagherzadeh et al., 2015; Gonzalez-Rodriguez et al., 2019). Large scale synthesis and manufacturing of these graphene-iron nanohybrids calls for faster, low-temperature, and environment-friendly functionalization strategies. The methods should also have the ability to control the size of the iron oxide nanoparticles and prevent their aggregation.

A new class of solvents named deep eutectic solvents (DESs) has emerged as a superior substitute of ionic liquids with similar properties but with much lower cost and toxicity (AlOmar et al., 2016a). DESs are formed when an organic compound – typically a quaternary ammonium or phosphonium salt (hydrogen bond acceptor) – is added to an uncharged hydrogen bond donor (e.g., amines, carboxylic acids, and alcohol) at a ratio to prepare a mixture that has significantly lower melting point (typically less than 100 °C) than the individual components (Li et al., 2018). For example, the most commonly used DES is a mixture of Choline chloride (ChCl, a quaternary ammonium salt) and urea (hydrogen bond donor), prepared at a molar ratio of ChCl:Urea=1:2. Both components are easily available, cheap, and environmentally benign (Khandelwal et al., 2016). DESs present unique properties such as low melting point (Tomé et al., 2018), non-flammability (Smith et al., 2014), low volatility (Smith et al., 2014), chemical and thermal stability (Smith et al., 2014), high solubility (Smith et al., 2014), and biodegradability (Smith et al., 2014) making it a suitable and environmentally green media for materials development with advanced properties for various applications (AlOmar et al., 2017b; Atilhan et al., 2017; Hayyan et al., 2015a; Tomé et al., 2018). The use of DESs has more recently extended to nanomaterial synthesis, processing, and functionalization. The opportunity to have a wide array of possible DES
combination along with tunable composition and functionality allows for effective exfoliation of 2D nanosheets (Abdelkader and Kinloch, 2016; Abdelkader et al., 2015), functionalization of both carbon and metallic nanomaterials (Atilhan et al., 2017; Hayyan et al., 2015a; Tomé et al., 2018), size- and shape-controlled synthesis of metal nanomaterials (Tomé et al., 2018), and as reaction media (Bozzini et al., 2016; Hammons and Ilavsky, 2017; Tomé et al., 2018). As a functionalization agent, DESs have shown to successfully introduce new functional groups to the surfaces of GO and CNTs surfaces at temperatures as low as 65 °C (Hayyan et al., 2015a). Furthermore, DES functionalized GO and CNT provided higher heavy metal removal due to the introduction of new functional groups and increasing the effective surface area of the adsorbents (AlOmar et al., 2016a; AlOmar et al., 2017a; AlOmar et al., 2016b; AlOmar et al., 2017b). Although few recent literatures showed the surface functionalization of pre-synthesized graphene-iron nanohybrids (synthesized by conventional methods) using DESs for applications in analytical chemistry (Huang et al., 2015), no studies thus far showed the applicability of DESs as a coupling agent for conjugating GO and Fe₃O₄ nanoparticles or any other carbon-metal nanohybrids.

Therefore, in this study, we aimed to test the hypothesis that through appropriate amine-functionalization of GO surface using ChCl:Urea DES, we can conjugate the pre-synthesized Fe₃O₄ nanoparticles onto GO surface without the need for any prior-functionalization of Fe₃O₄. The scientific premise of our hypothesis is that Fe₃O₄ nanoparticles have an inherent affinity for amine functional groups, and our DES-functionalized GO surfaces will contain a large amount of amine functional groups (both from ChCl and urea) for sufficient attachment of Fe₃O₄ nanoparticles (Mehrabi et al., 2019; Singh and Misra, 2015; Yan et al., 2013). Besides, DES-functionalized GO would obtain more suitable chemistry for hydrogen bond formation between GO and Fe₃O₄. We aim to demonstrate, for the first time, the applicability of DES-derived
graphene-iron nanohybrids for both organic and inorganic pollutants removal from water. To achieve these aims, we first functionalized GO with a DES of ChCl:Urea (2:1) and then subjected to conjugation with Fe₃O₄ to synthesize the DES/GO-Fe₃O₄ nanohybrids with different GO:Fe₃O₄ ratios of 1:1, 1:2, and 1:5. Physical and chemical properties of the synthesized nanohybrids were characterized by transmission electron microscopy (TEM), scanning transmission electron microscopy coupled with energy-dispersive x-ray spectroscopy (STEM/EDS), X-ray diffraction (XRD), and Raman and Fourier transform infrared (FTIR) spectroscopy. The ability of the prepared DES/GO-Fe₃O₄ nanohybrids to remove contaminants from aqueous media was evaluated by performing removal of methylene blue (MB) dye and lead (II), and was compared to the pollutant removal ability of parent materials, i.e., Fe₃O₄ and GO.

2. Material and methods

2.1. Preparation of Fe₃O₄ Nanoparticles

Magnetite (Fe₃O₄) was synthesized based on a well-established method described elsewhere (Ardiyanti et al., 2016). First, Ferric chloride (FeCl₃, 97%) and ferrous sulfate heptahydrate (FeSO₄·7 H₂O, >99%) salts were purchased from Fisher Scientific (Hampton, NH). 4.86 g of FeCl₃ and 3.34 g of FeSO₄·7 H₂O were dissolved in 100 mL of deionized (DI) water. Then, the mixture of iron salts and DI water was stirred at 500 rpm using a hotplate magnetic stirrer (Isotemp Advanced Series, Fisher Scientific, Hampton, NH) for 1 h at 55 °C under N₂ gas purge in a 250 mL three-neck flask to achieve a solution containing Fe²⁺ and Fe³⁺ ions. While the solution was being purged by N₂ and mixed by the stirrer, ammonium hydroxide (NH₄OH, 25%, Sigma Aldrich, St. Louis, MO) was added dropwise using a micropipette, until the pH of the solution reached 9.4. This addition of NH₄OH to the iron (Fe²⁺, Fe³⁺) solution helped the precipitation of black magnetite (Fe₃O₄) nanoparticles. Then, the solution was left stirring using a mechanical mixer at 500 rpm
for 3 hr. Finally, the Fe₃O₄ nanoparticles were attached to one side of the beaker using a magnet and washed with ethanol and water three times. The obtained Fe₃O₄ nanoparticles were dried at 45 °C under vacuum for 24 h and stored in a glass vial for further use.

2.2. Preparation of the DES solvent

Choline chloride (ChCl, >99%) and Urea (U, ACS Reagent) were purchased from Sigma Aldrich (St. Louis, MO). ChCl was dried overnight at 60 °C in a vacuum oven as it is highly hygroscopic and absorbs humidity quickly. Urea was dried overnight at 90 °C in an air-oven. A solid dry mixture of ChCl:Urea at a molar ratio of 1:2 was placed in a 10 mL vial, and mixed at 60 °C for 3 hrs at 400 rpm using a hotplate magnetic stirrer (Isotemp Advanced Series, Fisher Scientific, Hampton, NH) to prepare the DES solvent (Fig. S1). The solvent was prepared inside a glove box fume hood to avoid any possible change or destruction of the DES properties (Al-Mursheedi, 2018). It should be noted that the solid mixture starts liquefying after about 15 min and becomes completely liquid in approximately 3 hrs.

2.3. Preparation of DES/GO-Fe₃O₄ Nanohybrids

Single-layer graphene oxide (GO, > 99.3 wt.%, thickness 0.43-1.23 nm) nanosheets powder was purchased from US Research Nanomaterials, Inc. (Houston, TX). GO powders were placed in an oven overnight at 90 °C to remove its moisture content. Three DES/GO-Fe₃O₄ nanohybrids were prepared with different GO to Fe₃O₄ mass ratios of 1:1, 1:2, and 1:5. For the synthesis of DES/GO-Fe₃O₄ (1:1), 0.1 g of the GO was sonicated for 2 h in 7 mL of DES using a tip sonicator (Q700, Qsonica, Newtown, CT) on a pulse mode (power=50%, on=30 sec, off=5 sec), then 0.1 g of Fe₃O₄ (dried in the vacuum oven at 45 °C for 3 h) was added to the suspension and again sonicated for 1 hr. In the whole process, the suspension temperature was kept at 65 °C using a water bath with a temperature of 25 °C. Finally, the suspension was stirred at 400 rpm for 2 h at
65 °C. The synthesized DES/GO-Fe$_3$O$_4$ nanohybrids (1:1) were filtered through a 0.2 μm Polyethersulfone membrane (Sterlitech, Kent, WA) and washed three times with ethanol and water. The synthesis steps of DES/GO-Fe$_3$O$_4$ nanohybrids are presented briefly as a flowchart in Fig. S2. The obtained nanohybrids were dried overnight in the vacuum oven at 45 °C. In order to synthesize the DES/GO-Fe$_3$O$_4$ nanohybrids with the other two ratios of GO and Fe$_3$O$_4$ (1:2 and 1:5), the same procedure as above was followed where the total 0.2 g of GO and Fe$_3$O$_4$ were dispersed in 7ml DES, but the amounts of GO and Fe$_3$O$_4$ were changed to achieve the intended ratios.

2.4. Physicochemical property characterization of DES/GO-Fe$_3$O$_4$ nanohybrids

JEOL TEM 2010 transmission electron microscope (TEM, JEOL, Peabody, MA) operating at 200 kV was used to image GO, DES/GO, Fe$_3$O$_4$, and DES/GO-Fe$_3$O$_4$ nanohybrids to examine their physical morphology and Fe$_3$O$_4$ particle size distribution. For the TEM grid preparation, 1 mg of each sample was sonicated in 20 mL of pure ethanol for 30 min using a tip sonicator, followed by placing two drops of the prepared suspension on a carbon-coated copper grid (200 mesh, SPI Supplies, West Chester, PA). The prepared TEM grids were air-dried for at least 30 min at the room temperature before the TEM imaging. The surface morphologies and elemental composition of the samples were studied using a Hitachi SU70 Field Emission Scanning Electron Microscope (FESEM, Hitachi, Japan) at 20 kV coupled with an energy dispersive x-ray spectrometer (EDS, Oxford Instruments, Concord, MA).

Crystal structures of the samples in a powder form were studied using ULTIMA IV X-ray diffractometer (XRD, Rigaku, Wilmington, MA) equipped with Cu laser source at a scanning rate of 2°/min within a range from 5° to 90°. Vibrational frequencies and structural changes of the samples were obtained using a Raman microscope (InVia Qontor, Renishaw, West Dundee,
Illinois) with an incident laser wavelength of 514 nm. Functional groups of the parent nanomaterials and the nanohybrids were obtained using a Fourier-transform infrared (FTIR) spectroscopy instrument (1760 FTIR, Perkin-Elmer, Waltham, Massachusetts) in the wavenumber range of 400–3500 cm$^{-1}$.

2.5. Methylene blue (MB) and lead(II) adsorption

For MB removal experiments, a 25 mg/L stock solution of MB (Fisher Scientific, Waltham, MA) in DI water was prepared. Different amounts (3, 5, or 10 mg) of the synthesized DES GO-Fe$_3$O$_4$ nanohybrids (1:1, 1:2, 1:5) or their parent nanomaterials (i.e., GO and Fe$_3$O$_4$) were placed individually in different 20 mL vials. Then, 10 mL MB solution was poured into each of the vials. The mixture in each vial was bath sonicated for 5 min to provide a suitable contact between MB and the adsorbent (i.e., the nanohybrids or their parent nanomaterials) using a bath sonicator (Branson, 2800, Danbury, CT). Then, a simple ceramic block magnet with dimensions of 0.38x0.88x1.88 in$^3$ (Master Magnetics, Castle Rock, CO) was used to separate the adsorbents from the MB solution. MB concentration in each vial after the adsorption was determined by measuring the light absorbance of the solutions at 665 nm wavelength (indicative peak of MB in aqueous solution) using Cary 60 UV-vis spectrophotometer (Agilent, Santa Clara, CA) and comparing the obtained absorbance results with the absorbance of the prepared reference MB solutions. The reported MB removal percentage and standard deviation results were obtained from three identical experiments for each adsorbent dosage.

For lead(II) adsorption experiments, four different lead(II) stock solutions with different concentrations of 25, 50, 100, and 150 ppm were prepared. 10 mL lead(II) solution of a specific concentration (one from the above) was poured into a 20 mL vial, and 10 mg adsorbent (i.e., the nanohybrids or their parent materials) was added to it. After 5 min of bath sonication to uniformly
disperse the adsorbents in the suspension, the vials were shaken using a mechanical shaker for 48 h at 150 rpm to reach the adsorption equilibrium. Finally, Fe₃O₄ nanoparticles and DES/GO-Fe₃O₄ nanohybrids were separated using the ceramic magnet, while GO was separated by 15 min centrifuge at 10000 rpm using an Eppendorf 5424 centrifuge (Eppendorf, Hauppaue, NY). Lead(II) concentration in the supernatant was measured using Inductively Coupled Plasma Emission Spectrometer (ICP-ES, iCAP 6000, Thermo Scientific, Waltham, MA). A high purity Argon (Ar) gas was used as plasma, auxiliary (0.5 L/min), and nebulizing gas. Before the operation, the ICP-OES was purged with Ar gas for 1 hour. The radio frequency (R.F.) power was kept at 1150 W, and the sample pump rate was fixed at 50 rpm with 5 seconds of stabilization time. For lead(II) content determination, the measurements were observed at the most sensitive emission wavelength for lead(II) at 220.3 nm. A standard calibration curve (R² = 0.999) was prepared for known lead(II) concentrations (2, 5, 10, 15, and 20 ppm), which was used to determine the concentration of lead(II) solutions after adsorption by comparing with the light absorption spectrum of the lead(II) solution obtained after adsorbent separation. All the lead (II) adsorption experiments were carried out in triplicates, and the average adsorption capacities along with standard deviations were calculated.

3. Results and Discussion

3.1. Physical morphology and chemical composition of DES/GO-Fe₃O₄ nanohybrids

TEM images of the parent nanomaterials and the synthesized nanohybrids are presented in Fig. 1. For each of the samples, two images are presented, respectively, at low and high magnifications. Fig. 1(a, b) show TEM images of the GO nanosheets, indicating a quasi-transparent single to few layers GO nanosheets. Fig. 1(c, d) show the TEM images of DES functionalized GO nanosheets which we name DES/GO. Compared to GO, DES/GO shows an aggregated structure of GO
nanosheets with wrinkles that may be due to the hydrogen bonds between the amine functional 
groups after the functionalization of GO nanosheets (Caliman et al., 2018). Fig. 1(e, f) show the 
TEM images of Fe₃O₄ nanoparticles indicating a chain-like aggregated structure. Fig. 1(g, h), 1(i, 
j), and 1(k, l) show the TEM images of DES/GO-Fe₃O₄ nanohybrids in a sequence of low-to-high 
Fe₃O₄ content with GO:Fe₃O₄ ratios of 1:1, 1:2, and 1:5, respectively. It is evident from the figures 
that Fe₃O₄ nanoparticles are successfully conjugated on the GO substrate with homogenous 
distribution, and the higher Fe₃O₄ content, the higher Fe₃O₄ accumulation on the GO surface. 
Since the 30 min of high energy tip sonication for TEM sample preparation was not able to separate 
the Fe₃O₄ nanoparticles from the GO nanosheets, the conjugation probably happened because of 
the chemical bonds rendered by DES rather than a simple physical attraction (e.g., van der Waals 
attraction forces). Further confirmations of the conjugation mechanism for the DES/GO-Fe₃O₄ 
are provided in the following sections. In order to determine the effects of DES/GO support on 
controlling the aggregation of Fe₃O₄ nanoparticles, the particle size distribution of individual 
Fe₃O₄ particles was analyzed for all nanohybrids and bare Fe₃O₄, and the results are presented as 
histograms in Fig. S3. The average diameters of Fe₃O₄ nanoparticles were 13.6±4.3 nm for the 
parent Fe₃O₄, 11.9±3.0 nm for DES/GO-Fe₃O₄ (1:1), 11.8±3.1 nm for DES/GO-Fe₃O₄ (1:2), and 
12.3±3.5 nm for DES/GO-Fe₃O₄ (1:5). More importantly, the particle size distributions are much 
narrower for Fe₃O₄ nanoparticles in DES/GO-Fe₃O₄ nanohybrids than bare Fe₃O₄ nanoparticles. 
The Fe₃O₄ nanoparticles have size ranges of 6-30 nm for bare Fe₃O₄ with significantly right-
skewed distribution, 4-22 nm for DES/GO-Fe₃O₄ (1:1) with perfectly normal distribution, 6-22 
nm for DES/GO-Fe₃O₄ (1:2) with slightly right-skewed distribution, and 6-26 nm for DES/GO-
Fe₃O₄ (1:5) with moderately right-skewed distribution. Therefore, Fe₃O₄ particle sizes in the 
nanohybrids with low Fe₃O₄ contents (for GO:Fe₃O₄ of 1:1 and 1:2) are smaller and less
Fig. 1. TEM images of (a, b) GO (c, d) DES/GO (e, f) Fe$_3$O$_4$ nanoparticles (g, h) DES/GO-Fe$_3$O$_4$ (1:1) (i, j) DES/GO-Fe$_3$O$_4$ (1:2), and (k, l) DES/GO-Fe$_3$O$_4$ (1:5) nanohybrids.

Aggregated compared to the bare Fe$_3$O$_4$ particles mainly due to their attachment on the DES/GO as a substrate. By increasing the iron content (DES/GO-Fe$_3$O$_4$ (1:5)), Fe$_3$O$_4$ nanoparticle sizes on GO nanosheets get closer to the sizes of bare Fe$_3$O$_4$ nanoparticles as they start to aggregate (Fig. 1k). Thus, it is evident that using DES as a reaction medium, it is possible to conjugate homogeneously distributed Fe$_3$O$_4$ nanoparticles on the GO nanosheets, while the particle size distribution for the deposited Fe$_3$O$_4$ nanoparticles can be controlled by changing the GO:Fe$_3$O$_4$ ratio.
Fig. 2 shows the surface morphology of the DES/GO-Fe₃O₄ (1:1) nanohybrid along with the EDS elemental maps showing the presence of carbon, nitrogen, oxygen, and iron in the nanohybrid. This indicates the successful conjugation of GO nanosheets and Fe₃O₄ nanoparticles via GO surface modification using DES. Moreover, the elemental maps confirmed the homogeneous distribution of Fe₃O₄ nanoparticles on the GO nanosheets. Fig. S4 presents the surface morphologies of GO and all three nanohybrids along with their corresponding EDS spectra. The SEM image of GO (Fig. S4a) shows the presence of well-distributed nanosheets with defined edges, while SEM images of DES/GO-Fe₃O₄ nanohybrids show more aggregated graphene structures coated with Fe₃O₄ nanoparticles distributed throughout and covering the majority of the surface. EDS spectra show the presence of carbon and oxygen atoms for GO (Fig. S4a), and the presence of carbon, nitrogen, iron, and oxygen atoms for all the synthesized nanohybrids (Figs. S4b-4d) indicating the successful hybridization of GO nanosheets and Fe₃O₄ nanoparticles.

3.2. Crystalline structure of DES/GO-Fe₃O₄ nanohybrids

Fig. 3a presents the XRD spectra of GO, DES/GO, Fe₃O₄, and DES/GO-Fe₃O₄ nanohybrids. The peak around 10° in GO samples confirms the characteristic peak of GO, while this peak was suppressed by the presence of iron nanoparticles in the DES/GO-Fe₃O₄ nanohybrids (Stobinski et al., 2014). After the functionalization of GO with DES, the characteristic peak for carbon shifted to 26°, indicating the reduction of GO by DES without the need for additional reducing agents, which is consistent with previous literature reports (Hayyan et al., 2015a). Furthermore, this broadened peak at 26° indicates DES/GO sheet agglomeration that has been evidenced by TEM images (Fig. 1c and d). The characteristic peaks of magnetite were found at 30.4°, 35.7°, 43.5°,
Fig. 2. SEM image and EDS elemental mappings of carbon, nitrogen, oxygen, and iron of DES/GO-Fe$_3$O$_4$ (1:1).

53.8°, 57.2°, 63.0°, 71.4°, 74.4°, and 79.1° for the Fe$_3$O$_4$ nanoparticle sample (Silva et al., 2013). These characteristics peaks are also seen in the XRD spectra of DES/GO-Fe$_3$O$_4$ nanohybrids indicating the successful deposition and conjugation of Fe$_3$O$_4$ nanoparticles on the GO nanosheets through DES functionalization. While previous literature reports of XRD results have confirmed the DES functionalization of pre-synthesized GO-Fe$_3$O$_4$ nanocomposites for surface modification (Huang et al., 2015), our results for the first time, confirms the use of DES as a coupling agent between GO and Fe$_3$O$_4$ nanoparticles for synthesizing the magnetic graphene nanohybrids.
3.3. Molecular vibrations and functional groups of DES/GO-Fe$_3$O$_4$ nanohybrids

Fig. 3b shows the Raman spectra of GO, DES/GO, Fe$_3$O$_4$, and DES/GO-Fe$_3$O$_4$ nanohybrids. Raman shifts at 1605 and 1368 cm$^{-1}$ indicate the characteristic graphitic (G) and defect (D) bands observed in the samples containing GO. After the functionalization of GO with DES, $I_D/I_G$ ratio (an indicator of the defects and disorders in the graphitic matrix) increased from 0.87 to $\sim$1 showing a more disordered carbon structure in DES/GO. A similar increase of the $I_D/I_G$ ratio has been seen previously in the literature for Urea:ChCl modified graphene showing the displacement of oxygen functional groups with other groups (Hayyan et al., 2015a). The $I_D/I_G$ ratio for the DES/GO-Fe$_3$O$_4$ nanohybrids increased compared to GO, and DES/GO which corresponds to more defect sites on GO nanosheets created by the deposited Fe$_3$O$_4$ nanoparticles – an observation consistent with previous literature reports (Mehrabi et al., 2019; Zhang et al., 2019). However, a decreasing trend in the $I_D/I_G$ ratio is observed for increasing Fe$_3$O$_4$ loading in the nanohybrids, which indicates that the defects in structures have been repaired by more Fe$_3$O$_4$ nanoparticle coverage at higher Fe$_3$O$_4$ loading. Raman shifts at 220, 285, 398, 497, 694, and 1359 cm$^{-1}$ are due to Fe-O stretching vibration (Mehrabi et al., 2019). The presence of Fe-O characteristic shifts in the Raman spectra (although suppressed by GO peaks) of synthesized nanohybrids is another indicator of the successful conjugation of GO and Fe$_3$O$_4$ using DES as solvent (Mehrabi et al., 2019).
Fig. 3. (a) XRD spectra of GO, DES/GO, Fe$_3$O$_4$, DES/GO-Fe$_3$O$_4$ (1:1), DES/GO-Fe$_3$O$_4$ (1:2), and DES/GO-Fe$_3$O$_4$ (1:5) (b) Raman spectra of GO, DES/GO, Fe$_3$O$_4$, DES/GO-Fe$_3$O$_4$ (1:1), DES/GO-Fe$_3$O$_4$ (1:2), and DES/GO-Fe$_3$O$_4$ (1:5) nanohybrids

FTIR spectra of GO, DES, and DES/GO are presented in Fig. 4a, and FTIR spectra of Fe$_3$O$_4$ and DES/GO-Fe$_3$O$_4$ nanohybrids are presented in Fig. 4b. Also, fig. S5 shows all these spectra individually for providing clarity about each peak. The band at 3225 cm$^{-1}$ in all spectra can be assigned to O-H stretching vibrations due to the presence of hydroxyl groups (Caliman et al., 2018). The observed bands at 1724, 1619, 1217, and 1039 cm$^{-1}$ in the GO spectra indicate C=O stretching vibrations of carboxylic acid groups, C=C vibrations from unoxidized graphitic domains, and C-OH and C-O stretching vibrations, respectively (Alzate-Carvajal et al., 2018; Caliman et al., 2018). The spectrum of ChCl:Urea DES shows various characteristic bands including those at 787 cm$^{-1}$ (N-H bond out of plane bending from Urea) (Hayyan et al., 2015a), 867 cm$^{-1}$ (C-N$^+$ symmetric stretching from ChCl) (Du et al., 2016; Hayyan et al., 2015a), 1436 cm$^{-1}$ (C-N stretching from Urea) (Hayyan et al., 2015a), 1472 cm$^{-1}$ (CH$_2$ bending from ChCl) (Hayyan et al., 2015a), 1613 cm$^{-1}$ (N-H scissoring from Urea) (Hayyan et al., 2015a), 1661 cm$^{-1}$ (C=O
stretching vibration from Urea) (Hayyan et al., 2015a), 3192 cm\(^{-1}\) (N-H stretching vibration from ChCl) (Hayyan et al., 2015a) and 3323 cm\(^{-1}\) (-NH\(_2\) stretching vibrations from Urea) (Du et al., 2016; Hayyan et al., 2015a). After the functionalization of GO with DES, the carboxylic acid groups peak at 1724 cm\(^{-1}\) were weakened which might be due to the partial replacement of carboxylic acid groups by other functional groups (Hayyan et al., 2015a; Huang et al., 2015). Similarly, the O-H stretching vibration at 3225 cm\(^{-1}\) for the GO was replaced by N-H stretching vibration at 3192 cm\(^{-1}\) and -NH\(_2\) stretching vibration at 3323 cm\(^{-1}\). Besides, new characteristic bands specific to the nitrogen bonding in ChCl:Urea DES appear along with other GO characteristic peaks but overpowering them. The bands at 947, 1436, 1472, 1558, 1661, 3176, and 3349 cm\(^{-1}\) are attributed to C-N\(^+\), C-N stretching, CH\(_2\) bending, N-H bending vibration, 1° amide N-H scissoring band, N-H stretching vibration, and N-H vibrations, respectively (Alzate-Carvajal et al., 2018; Hayyan et al., 2015a).

In the FTIR spectra of Fe\(_3\)O\(_4\), the band at 558 cm\(^{-1}\) is corresponded to the Fe-O vibration, the bands at 1660, and 3225 cm\(^{-1}\) indicate the presence of the hydroxyl groups on the surface of the iron oxide (Yang et al., 2010). The characteristic iron band can also be seen in the FTIR spectra of the DES/GO-Fe\(_3\)O\(_4\) nanohybrids indicating the successful conjugation of GO and Fe\(_3\)O\(_4\) using DES as a reaction media (Huang et al., 2015; Mehrabi et al., 2019). Furthermore, the nanohybrids FTIR spectra also show predominant peaks at 1217 cm\(^{-1}\) (characteristic C-OH peak of GO), 947 cm\(^{-1}\) (C-N\(^+\) stretching from DES), 1472 cm\(^{-1}\) (CH\(_2\) bending from DES), 1696 cm\(^{-1}\) (shifted N-H scissoring band for DES), and 3192 and 3349 cm\(^{-1}\) (N-H stretching bands for DES) confirming the conjugation of Fe\(_3\)O\(_4\) by coupling through the ChCl:Urea DES.
Fig. 4. FTIR spectra of (a) GO, DES, and DES/GO (b) Fe₃O₄ nanoparticles, DES/GO-Fe₃O₄ (1:1), DES/GO-Fe₃O₄ (1:2), and DES/GO-Fe₃O₄ (1:5) nanohybrids.

3.4. Organic dye and heavy metal removal using DES/GO-Fe₃O₄

Fig. 5a presents the MB removal efficiencies of synthesized DES/GO-Fe₃O₄ nanohybrids and their parent nanomaterials as a function of three different dosages of 0.3, 0.5, and 1 mg/mL. Bare Fe₃O₄ nanoparticles could only remove 12.0-30.8% of MB, indicating its limited applicability for MB removal. Such low MB adsorption by bare Fe₃O₄ might be caused due to their aggregation tendencies as evidenced in TEM images. Although GO was able to remove 91.2-93.7% of MB at 0.3-1 mg/mL adsorbent dosages, its separation from water is difficult and needs to be done by centrifuge. At 0.3 mg/mL dosage, DES/GO-Fe₃O₄ nanohybrids with the lowest and highest iron content (GO:Fe₃O₄=1:1 and 1:5, respectively) showed much less MB removal than GO, i.e., only 75.6% and 47.4% MB removal, respectively. However, their MB removal efficiency increased to ~96-98% at 0.5 mg/mL dosage and reached 100% at 1 mg/mL, showing much better performance than GO at high dosages. Most interestingly, DES/GO-Fe₃O₄ (1:2) with the medium iron content showed 100% removal at all three dosages of 0.3, 0.5, and 1 mg/mL presenting this nanohybrid as
the most effective and optimum nano-adsorbent for MB removal in this study. The impressive optimization result for MB removal performance of the three nanohybrids indicates the importance of optimizing GO:Fe$_3$O$_4$ ratio during conjugation to provide sufficient and homogeneously distributed Fe$_3$O$_4$ nanoparticles on the GO sheet. Nevertheless, it is to be noted that all three synthesized DES/GO-Fe$_3$O$_4$ nanohybrids were separated from solutions within 5 min by magnetic separation while the GO separation needed 15 min centrifugation time. Furthermore, GO is much more expensive than Fe$_3$O$_4$; thus the higher MB removal performance of DES/GO-Fe$_3$O$_4$ (1:2) nanohybrid at low dosage, which contains only 33% GO, is indicative of cost minimization through novel nanosorbent generation via DES-coupling.

Due to the literature reported limited lead (II) adsorption capacity of Fe$_3$O$_4$, we used 1 mg/mL of each nanohybrid and parent nanomaterial for testing lead (II) adsorption. We determined lead (II) adsorption capacity of all the samples as a function of lead (II) concentration, as shown in Fig. 5b. Results indicated that DES/GO-Fe$_3$O$_4$ nanohybrids were able to remove lead(II) from aqueous solutions more effectively compared to the bare Fe$_3$O$_4$. This was probably due to the presence of the GO, functionalization effect of the DES, and the homogenous distribution of the Fe$_3$O$_4$ nanoparticles in the synthesized nanohybrids. However, at high lead concentrations, nanohybrids with higher iron contents (GO:Fe$_3$O$_4$=1:2 and 1:5) showed similar lead (II) adsorption capacity as Fe$_3$O$_4$. The maximum lead (II) adsorption capacity of the nanosorbents at the highest lead (II) concentration of 150 mg/L were 120.5±1.3 mg/g for DES/GO-Fe$_3$O$_4$ (1:1), 118.14±0.3 mg/g for GO, 73.2±1.7 mg/g for DES/GO-Fe$_3$O$_4$ (1:2), 71.1±5.4 mg/g for DES/GO-Fe$_3$O$_4$ (1:5), and 68.4±5.5 mg/g for Fe$_3$O$_4$. Results indicate that the lower the Fe$_3$O$_4$ content in the nanohybrids, the higher the lead (II) adsorption capacity. Both GO and DES/GO-Fe$_3$O$_4$ (1:1) nanohybrid showed the highest lead (II) adsorption capacity, indicating that the deposition of Fe$_3$O$_4$ onto GO at a 1:1
ratio via DES functionalization can improve the adsorption significantly. Similar to MB removal, this provides multiple advantages: i) provides a synergistically enhanced lead (II) adsorption for both GO and Fe₃O₄, (ii) provides magnetic separation capability in the new nanosorbents, and (iii) 50% of the GO can be replaced with much cheaper material Fe₃O₄ to achieve the same level of lead (II) adsorption capacity.

The performance of the newly synthesized DES/GO-Fe₃O₄ nanocomposites was compared with the literature that used nanocomposites based on graphene oxide and iron oxide for adsorption of MB and Lead(II) from water. Tables S1 and S2 show the MB and lead(II) removal presented in the literature with similarly used nanocomposites and operating conditions. Compared to the study results presented in Table S1, our synthesized DES/GO-Fe₃O₄ (1:2) nanohybrid was able to provide the highest MB removal efficiency within a much shorter time (5 min) and at a lower adsorbent dosage (0.3 g/L). For instance, 0.3 g/L of DES/GO-Fe₃O₄ (1:2) was able to remove about 100% of the MB from 25 ppm MB solution while 1 mg/mL of magnetic cellulose/graphene oxide composite was able to remove 96.7% MB from 30 ppm MB solution in 840 min. The same behavior is seen for lead(II) removal by DES/GO-Fe₃O₄ (1:1) nanohybrid. This may be considered as a piece of evidence for the potential of the DES as a solvent for improving the adsorption property of the nanohybrids through physical and chemical modifications.
Fig. 5. (a) MB removal from aqueous solution using GO, Fe$_3$O$_4$, DES/GO-Fe$_3$O$_4$ (1:1), DES/GO-Fe$_3$O$_4$ (1:2), and DES/GO-Fe$_3$O$_4$ (1:5) (b) Lead(II) removal by GO, Fe$_3$O$_4$, DES/GO-Fe$_3$O$_4$ (1:1), DES/GO-Fe$_3$O$_4$ (1:2) and DES/GO-Fe$_3$O$_4$ (1:5).

4. Conclusions

In this study, we successfully utilized a ChCl:Urea based DES as a coupling agent for conjugation of GO nanosheets and Fe$_3$O$_4$ nanoparticles at different GO:Fe$_3$O$_4$ ratios, as evidenced by the physicochemical property characterization. We used the synthesized novel DES/GO-Fe$_3$O$_4$ nanohybrids for the removal of wastewater contaminants, i.e., organic dyes (MB) and heavy metal Lead (II). DES/GO-Fe$_3$O$_4$ nanohybrids provide a synergistically enhanced adsorption for both MB and lead (II); however, the adsorption behavior was dependent on the ratio of GO and Fe$_3$O$_4$ in the nanohybrid. Among the three nanohybrids with different GO:Fe$_3$O$_4$ ratios, DES/GO-Fe$_3$O$_4$ (1:2) at the lowest dosage of 0.3 mg/mL showed the best MB removal performance by removing ~100% of 25 mg/L MB within 5 min. Moreover, the maximum adsorption capacity of 120.5±1.3 mg/g Lead (II) at initial Lead (II) concentration of 150 mg/L was obtained by DES/GO-Fe$_3$O$_4$ (1:1) nanohybrids with decreasing trend in adsorption capacity with increasing Fe$_3$O$_4$ amount in the nanohybrid. We believe that this method of DES functionalization of GO and hybridization with
iron-based nanomaterials can be extended to conjugate other carbon and metallic nanomaterials. Though we used only one type of DES (ChCl:Urea), the availability and wide variety of other DESs are promising for coupling carbon nanomaterials (e.g., GO, CNT) with other metal or metal oxide nanoparticles (e.g., TiO$_2$, ZnO, Ag, Au) and can be used for various environmental applications via control of the physicochemical properties.

**Conflict of Interests**

The authors declare that they have no conflict of interests.

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