Synthesis and Characterization of Ultrasound Assisted “Graphene Oxide – Magnetite” Hybrid, and Investigation of its Adsorption Properties for Sr (II) and Co (II) Ions

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Abstract. Magnetite nanoparticles with a size distribution of 15 to 21 nm were synthesized and decorated onto surface of graphene oxide by ultrasound assisted precipitation. Size and size distribution of the obtained M-GO hybrid were appreciably finer than the hybrids prepared by stirring method. M-GO is a superparamagnetic material with saturation magnetization of 31 emu.g⁻¹. The Langevin equation was successfully applied for estimation of size of Fe₃O₄ nanoparticles in M-GO hybrid, with maximum error of 17.5%. The study put forward a formation mechanism for M-GO, based on instrumental analyses. Adsorption isotherms of Sr²⁺ and Co²⁺ ions, which were fitted by Langmuir monolayer model, displayed two-fold higher capacity for Co²⁺ ions, presumably due to its similarity to Fe²⁺ (of Fe₃O₄ component). Uptake of both Co²⁺ and Sr²⁺ ions were endothermic, and spontaneous, however the former proceeded through inner-shell complex formation, while the latter took place via ion exchange mechanism. Rate of adsorption of Co²⁺ was faster, but for both ions, chemical reaction was the rate determining step. Sorption of Sr²⁺ and Co²⁺ ions greatly increased at pHs above 5, where 1: surface zeta potential changed its sign, and 2: deprotonating reactions at the surface became complete.

Keywords: Magnetite, Graphene oxide, Formation mechanism, Langevin equation, Inner- shell complex

Introduction. Nuclear power is a prominent alternative of fossil fuels that can effectively solve global warming, acid rains and other consequences of air pollutions, caused by combustion. Despite such obvious advantage, this highly compact form of energy suffers from two unsolved shortcomings as: 1-Painful outcomes of nuclear accidents (e.g. Chernobyl), and 2- Lack of a comprehensive scheme for handling of the reactor wastes[1]. Recent advances, however, have shed light on both of these problems by: (a) developing the inherently safe four-generation reactors, and (b) devising partitioning-transmutation (P-T) process[2]. In the P-T process, reactor spent fuels which are initially reprocessed for recovery of uranium and plutonium, undergo partitioning process, in which the most hazardous radioactive isotopes are removed from high level liquid waste (HLW), and the volume and radioactivity of the waste is reduced, substantially.

One of the most hazardous radioisotopes whose separation from HLW has been subject of a long study is ^{90}Sr [3, 4]. The examined methods for isolation of this isotope include: chemical precipitation[5, 6], solvent extraction, ion exchange[7, 8], and adsorption[9, 10]. So far, various adsorbents have been tested for sequestering of Sr^{2+} such as: zeolites[11, 12], kaolinite[13, 14], activated carbon[15, 16], carbon nanotube[17, 18], and magnetite.[19, 20]. Although some appreciable results were achieved, there is still a need for more efficient adsorbents in low cost, and an environmentally friendly fabrication process.

Another heavy metal ion that poses hazard on the health of human and animals is Co^{2+} [21]. This ion occurs in the effluents of the solvent extraction and electrolysis processes of the cobalt production lines, as well as other chemical industries. Separation of the Co^{2+} ion is carried out through several different methods, but similar to Sr^{2+} ions, a high capacity, and cost efficient adsorbent for its isolation is still demanded.

Graphene oxide (GO), a lamellar material with wide range of surface functional groups such as epoxy (C-O-C), hydroxyl, and carboxyl offers large surface area as well as high sorption capacity for the metallic cations [3, 22, 23]. Adsorption of a great deal of metal ions by GO were investigated and it was shown that GO has a notable affinity toward hard and semi-hard cations. Of worthy of consideration among these ions, are some of the most common radioactive ions such as U(VI)[24], Eu(III)[25], Sr (II)[3, 26], Th(IV)[27], and Tc (VII)[28]. Furthermore, several reports dealt with application of functionalized GO for simultaneous removal of multiple radionuclides. Song et al. stated that polyacrylamide (PAM) grafted GO is a promising material for simultaneous adsorption of radionuclides from waste waters[29]. Furthermore, Sun et al. demonstrated that sorption of radionuclides by graphene oxide-supported

polyaniline proceed through complex formation between radionuclides ions and nitrogen or oxygen containing functional groups of the graphene oxide-supported polyaniline surface [30].

Unfortunately, colloidal behavior of GO dispersion makes separation of its reaction products with metallic cations quite cumbersome. Integration of magnetite nanoparticles (NPs) with GO is a possible solution to this problem. In contrast to centrifugation and filtration, magnetic separation of the M-GO hybrid from solutions is rapid and efficient.

Magnetite, although not as selective as the other sorbents, is an inexpensive and readily available adsorbent. Nonetheless, the material suffers from some drawbacks such as agglomeration, and chemical instability in acidic media that makes its industrial applications troublesome.[31] Combining the magnetite nanoparticles with GO, not only brings about a hybrid with higher adsorption capacity, but also enhances the chemical resistance of Fe_3O_4 as a result of its coverage with the graphene nanosheets [32]. In spite of extensive researches on the synthesis and application of magnetite-GO (M-GO) or magnetite-graphene hybrids for removing of heavy metal ions [33-35], dyes [36, 37], and organic pollutants [38, 39], there is still a paucity of data on the synthesis of narrow sized M-GO, and its application on adsorption of Sr^{2+} and Co^{2+} ions.

The present study pursues: (1) Synthesis of the M-GO hybrid using ultrasound precipitation; (2) Exploring the formation mechanism of M-GO, and the nature of chemical bonds between Fe_3O_4 and GO sheets; (3) Comparison of its physical characteristics particularly the magnetic property with stirred type M-GO hybrid, (4) Investigating of its adsorption properties for Co^{2+} and Sr^{2+} ions. The eventual objective of this work is to develop a cost efficient, operationally convenient adsorbent for the environmental applications.

Material: Natural flake graphite, sulfuric acid 98%, hydrochloric acid 35%, hydrogen peroxide 30%, ammonia solution (20 wt. %), sodium nitrate, potassium permanganate, ferrous chloride tetra-hydrated ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferric chloride hexa-hydrated ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were purchased from Merck, Germany and used without purification.

Synthesis of Magnetite-Graphene Oxide hybrid (M-GO): The M-GO hybrid was prepared using co-precipitation of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, in the presence of GO. The used GO for this synthesis was prepared by the modified Hummer's method as described in Supplementary Information file. Synthesis of the M-GO hybrid was begun with preparation of 50 cm^3 of GO solution with $1\text{mg}/\text{cm}^3$ concentration in the ultrasonication bath (Elmasonic, S 30H, country). Next, a mixed solution of $\text{FeCl}_3:\text{FeCl}_2$ (2:1) was added slowly to the GO solution. Then, the bath temperature was raised to 85 °C, and a 30% ammonia solution was added to it to increase pH to 10. With constant ultrasonication for

30 min, the solution was cooled to room temperature. Afterward, the formed precipitate was separated from the solution by a magnet placed behind the glassware, and it was washed two folds with pure ethanol and water, and dried at ambient condition.

In addition to ultrasound synthesis, we utilized the conventional stirrer hot plate method for fabrication of M-GO to compare their sizes and magnetic properties. This form of M-GO was codenamed as “Stirred M-GO”.

Characterization: Morphological microscopic pictures of the GO nanosheets and M-GO hybrid were obtained using low and high-resolution transmission electron microscopy (TEM / HRTEM, JEOL, JEM-2100, Japan). The employed HRTEM mode also supported the selected area electron diffraction (SAED) and energy dispersive X-ray (EDX) analysis of the samples. Atomic force microscopy (AFM, Park Scientific CP-Research model, VEECO) was used to find thickness and morphology of the GO and M-GO hybrid. The employed AFM system worked in the tapping mode, with frequency of 320 kHz, and by using a 20 nm thick silicone tip. Samples for AFM imaging were prepared by drop casting of dilute GO and M-GO suspensions onto a cleaned mica substrate.

Raman spectroscopy (SENTERRA BRUKER, Germany) was performed on the samples at room temperature using a 785 nm Nd-YAG laser excitation source. Meanwhile, the X-ray photoelectron spectroscopy (XPS) revealed the chemical states of the GO and M-GO nanosheets. The XPS instrument was equipped with a hemispherical analyzer, a data acquisition system, and an Al K_{α} X-ray source ($h\nu=1486.6$ eV) operating at pressure lower than 10^{-7} Pa. The XPS peaks were deconvoluted by Gaussian components model after Shirley background subtraction. The X-ray diffractometry (Rigaku Miniflex XRD, Texas, U.S.A.) and Fourier transforms infrared spectroscopy (FTIR, Perkin-Elmer, SpectrumRX, USA) were respectively utilized for crystallographic and chemical bond analysis of the prepared materials. The magnetic hysteresis cycle of the powdered M-GO was obtained by a QMPS SQUID magnetometer at the field range of -1T to 1T at room temperature. Optical characteristics of the diluted GO and M-GO suspensions (0.01 mg/cm³) were studied by a UV-Visible spectrophotometer (PerkinElmer UV-Vis-NIR model Lambda 950, USA).

Adsorption tests: All of the adsorption tests were carried out batch wise. In every test, about 20 mg of adsorbent was transferred into a conical flask, which contained 10 cm³ of Co^{2+} or Sr^{2+} solutions. Then, the mixture was ultrasonicated for a certain period, after which, the M-GO particles were separated from the solution by a magnet that was placed behind the vessel wall. Concentration of the decanted supernatant was measured by atomic adsorption spectrometry (AAAnalyst, 800, PerkinElmer, USA).

In order to investigate the effect of pH, different amounts of HCl or NaOH were added to the Co^{2+} or Sr^{2+} solutions, to place their pHs in the range of 3 to 9. Kinetics of the uptake and capacity of the adsorbent were examined by conducting the above-mentioned batch experiments in different time intervals, and concentration of the solution. All of the experiments were conducted at pH 6.5 except for the experiments checking the effect of pH. Moreover, the initial concentrations of Sr^{2+} and Co^{2+} in all of the experiments were 50 ppm except the ones related to the adsorption isotherms.

In analysis of the adsorption data, adsorption capacity (Q), uptake percentage (R , %), fractional attainment to equilibrium (X), and distribution coefficient (K_d) are defined as: .

$$Q = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$R, \% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

$$X = \frac{C_0 - C_t}{C_0 - C_e} \quad (3)$$

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (4)$$

where C_0 , C_t , C_e (ppm), are the concentration of ions at the initial, time t , and equilibrium state, respectively; m (g) denotes the mass of the adsorbent, and $V(\text{cm}^3)$ stands for volume of the solution.

Results and discussions

Morphology: Figure 1a and b show AFM image of GO on the surface of mica and corresponding height profile of marked-line. Thickness of synthesized GO was measured about 1.2 nm indicating formation of monolayer graphene sheet [40]. Figure 1c represents low magnification TEM image of GO in which transparent regions especially the zones indicated with the arrows refers to monolayer graphene sheets. It can be seen that the wrinkled sheets of the graphene are folded back at the edges to form multilayer graphene with the dark gray color. The SAED pattern in inset Figure 1c shows diffraction spots and resolved rings that are corresponding to the crystalline structure of GO.

[Insert Figure 1 about here]

Magnetite nanoparticles are often synthesized by the Massart's method [41] through co-precipitation of Fe(III) and Fe(II) in an alkaline solution:

As was described in the experimental section, two kinds of M-GO hybrids were prepared in this study as ultrasound assisted M-GO and “Stirred M-GO”. The TEM image of “Stirred M-GO” hybrid is shown in Figure S1 according to which the magnetite NPs that were deposited on GO surface via stirring method had an average size of 30 nm, while the ultrasound assisted Fe₃O₄ NPs were appreciably smaller and in average were about 17 nm (Inset Figure 2c). This result evidently shows the superiority of ultrasound irradiation (at frequency 60 kHz) to mechanical agitation in reducing the size of Fe₃O₄ NPs.

Figure 2 shows the SEM, AFM, and TEM images of Fe₃O₄ NPs deposited on the surface of the GO by the ultrasound assistance. In Figure 2a, the Fe₃O₄ NPs are anchored on the surface of GO. The large surface area of wrinkled GO increases the rate of loading of Fe₃O₄ NPs. At the same time, it provides enough space for the Fe₃O₄ NPs to be deposited apart from each other's; and hence decreases their agglomeration tendency. Figure 2b exhibits AFM image of M-GO hybrids in which the bright dots denote Fe₃O₄ NPs. More detail about the structure of M-GO hybrid can be found in Figures 2c. It can be seen that even rigorous sonication, conducted for the preparation of TEM specimens, could not detach the firmly adhered magnetite NPs from the GO surface (Figure 2c). The figure also shows the average size of magnetite NPs which is around 17 nm. The upper inset of Figure 2c demonstrates HRTEM image of the Fe₃O₄ NPs whose 0.25 nm inter-planar spacing corresponds to distance between two (222) plans of the magnetite [42]. Figure 2d shows the same image with higher magnification. According to these figures, the Fe₃O₄ NPs grafted onto the GO surface were of high purity. This outcome is further evidenced by SAED pattern of M-GO in the inset Figure 2d that displays distinguishable resolved rings of both GO and Fe₃O₄ crystals.

[Insert Figure 2 about here]

Chemical structure: Figure S3 in supplementary information illustrates a schematic view of the M-GO synthesis, along with the subsequent adsorption process. The GO surface hosts different oxygen functionalities such as epoxy, hydroxyl, and carboxylic groups. These functional groups act as active sites for sequestering and growth of the magnetite nanoparticles (NPs). Presence of innumerable oxygen functionalities, as well as the huge surface area of the graphene bring about homogenous deposition of Fe₃O₄ NPs on the GO surface. Ultrasound waves assist such uniform deposition principally by preventing their agglomeration. The imbedded Fe₃O₄ nanoparticles grant appreciable magnetic property to the M-GO hybrid, and thus makes its quick (and simple) separation from the solutions possible.

Figures S4a and b in supplementary information represent the EDS spectra of the GO and M-GO hybrid. According to these Figures, only iron, carbon (and hence hydrogen) and oxygen comprise structure of the aforesaid hybrid.

The XRD pattern of as-prepared M-GO hybrid is presented in Figure 3a. It can be seen that owing to intercalation of oxygen functionalities and water molecules between the graphene layers, interlayer space increased from 3.36 Å ($2\theta = 26^\circ$) of graphite to 7.9 Å ($2\theta = 10.3^\circ$) in GO. The XRD pattern of M-GO hybrid depicts seven characteristic peaks at 30.1° , 35.4° , 37.1° , 43.1° , 53.4° , 56.9° and 62.5° , that are corresponding to (220), (311), (222), (400), (422), (511) and (440) planes of magnetite (Fe_3O_4). No peak of hematite (Fe_2O_3) or other impurities is detected in the XRD pattern.

The chemical structure of the GO and M-GO hybrid were investigated by FTIR spectra (Figure 3b). Graphene oxide (GO) showed the following characteristic peaks: the O-H stretching vibration at 3424 cm^{-1} , the C=O stretching vibration of carboxyl and carbonyl at 1724 and 1402 cm^{-1} ; the stretching vibration of aromatic C-C and C=C which is placed at 1634 cm^{-1} ; and eventually the peaks at 1165 and 1035 cm^{-1} which are corresponded to the C-O stretching vibration of epoxy and alkoxy groups. The IR spectrum of the M-GO indicates a stretching vibration peak of the Fe-O at 574 cm^{-1} which confirms deposition of magnetite NPs on the surface of the GO [34]. Another new peak appeared at 1550 cm^{-1} that can be attributed to the formation of covalent bond between the oxygen atoms of the GO and the Fe[43].

Raman spectroscopy is a commonly exploited tool for characterization of the carbon products. The intensity of G-band, D-band, and full width at half maximum (FWHM) are three indicators of the sample defects, which are formed by substitution of the functional groups on the surface of the graphene sheets. When oxygen functionalities are attached to the hexagonal rings of the graphene, some of the aromatic carbon atoms take a sp^3 hybridization [44]. Therefore, the sp^2/sp^3 carbon ratio expressed by the I_D/I_G ratio increases. Figure-3c represents Raman spectra of the as-prepared materials with a D-band at 1350 cm^{-1} and a G-band at 1580 cm^{-1} . It can be seen that the I_D/I_G ratio of GO increased compared to the graphite as a result of the aforementioned $\text{sp}^2 \rightarrow \text{sp}^3$ transformation. Nevertheless, after decorating of the surface of graphene with magnetite NPs, the I_D/I_G ratio decreased. This demonstrates that anchoring of the magnetite NPs to the surface of graphene, takes place through a kind of chemical interaction (e.g. bonding) between iron or oxygen atoms of Fe_3O_4 with sp^3 hybridized atoms of GO, which decreases the freedom of the sp^3 atoms of GO, and accordingly the relative intensity of the D-band[35, 45]. Besides reducing the I_D/I_G ratio, deposition of Fe_3O_4 NPs brings about three other effects on the Raman peaks as: 1- Both D-peak and G-peak are slightly shifted to the right hand, 2-

The area under the Raman curve between D and G band increases, 3-Three Raman characteristic peaks of Fe_3O_4 at 394, 578, and 756 cm^{-1} appear that confirm presence of some intact Fe_3O_4 on the graphene surface [46].

It can be noticed in Figure 3d that UV absorption peak of the GO suspension appears at 231 nm, while for M-GO it emerges at 267 nm, indicating a red-shift, arisen from formation of chemical bond between GO and Fe_3O_4 . In addition, inset Figure 3d represents a dark black color for the M-GO that is different from the light brown color of GO.

[Insert Figure 3 about here]

The XPS analysis was carried out to clarify the surface chemistry of the obtained adsorbents. The wide XPS spectra of GO and M-GO are shown in Figure 4, in which only two GO characteristic peaks at 285 eV (C1s) and 532 eV (O1s) are identified; while, the full scan XPS spectrum of M-GO exhibits additional fingerprint of Fe2p around 711 eV.

[Insert Figure 4 about here]

In order to achieve more information about the nature of oxygen functionalities on the surface of GO and M-GO, we deconvoluted the C1s and O1s peaks of the XPS spectra, and depicted them in Figure 5, and panels (b) and (c) of Figure (6), respectively.

Figure 5a displays the C1s deconvoluted peaks of GO prior to deposition of the magnetite, in which considerable presences of C=C, C=C, C-OH, C-O-C, and O=C-OH groups at 285, 286.2, 287.1, and 289.1 eV, is obvious [47]. The oxygen-containing functional groups on the surface of M-GO were attenuated compared to GO, as a result of first: connection of Fe_3O_4 NPs to GO, and second: the slight reducing action of ammonia solution on GO (Figure 5b). In order to have a better estimation about the amounts of oxygen functional groups, the peak areas were calculated and tabulated in Table 1. It can be seen that the concentration of the oxygen functional groups on the surface of M-GO was reduced about 55% compared to pristine GO, in which the concentration of C-O-C bond was reduced noticeably.

Discussion about deconvolution of the O1s peaks will be given in the next section, due to its close correspondence to the formation mechanism.

[Insert Figure 5 about here]

[Insert Table 1 about here]

Putting all of the pieces of evidence provided by UV, FTIR, XPS and Raman analyses together into a combined framework reveals that a small fraction of Fe_3O_4 is connected to GO through covalent bonding, and the next

stacking layers of Fe_3O_4 are deposited on this sub-layer by normal growth of Fe_3O_4 crystal. Considering such picture of the interaction between Fe_3O_4 and GO has two immediate consequences: 1- Firm adherence of the magnetite NPs to the GO surface through chemical bonding of Fe_3O_4 sub-layer and the GO, 2: Preservation of major part of the magnetite property of the Fe_3O_4 , by the upper layers of its nanocrystals.

Formation mechanism of M-GO hybrid. Pure magnetite NPs are often synthesized by the Massart's reaction (eq.5) whose formation mechanism has been studied extensively [48]. But, regarding the growth of Fe_3O_4 NPs on the GO surface, there is still a paucity of data. The current study intends to address this inquiry by suggesting a coherent mechanism as follows: At first, Fe (II) and Fe (III) ions are connected to oxygen-containing groups of GO to form C-O-Fe dative bond (step1 in Figure 6). Since the sequestered iron ions have positive charge, their coordination bonding with oxygen leaves the surface of GO positively charged. Moreover, the foregoing iron ions are only connected to one oxygen atom, and need more dative bonds to fill their coordination numbers. Thus, some water molecules, as well as OH^- ions will be connected to those Fe ions. Among the incoming H_2O , and OH^- ions, some play roles of the bridge between the initial (i.e. sequestered) Fe atoms and the iron atoms of the $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_2$ molecules via hydrogen bonding (step 2). Since at the temperature of reaction ($T=95^\circ\text{C}$) the Fe-OH-OH-Fe bridge is unstable [31], it breaks down to a more stable Fe-O-Fe bond with liberation of water molecules (dehydration step 3). Dehydration and connection of Fe atoms are frequently repeated until nearly all Fe ions of the solution are consumed, and the hydrated Fe_3O_4 NPs (i.e. $\text{Fe}_3\text{O}_4 \cdot n\text{H}_2\text{O}$) is formed on the GO surface. In the solution, reaction is terminated at this stage. But, our synthesis process involved separation of the M-GO hybrid from the solution, and its drying at the ambient temperature. The drying process, completes removing of the water molecules from $(\text{Fe}_3\text{O}_4 \cdot n\text{H}_2\text{O})$ structure, and converts it to a Fe_3O_4 NP, whose borderline Fe atoms are connected to the carbon atoms of GO via Fe-O-C bridge (step 4).

The suggested mechanism is supported by theoretical and experimental evidence. From theoretical standpoint, $\text{Fe}(\text{OH})_3$ and to a lesser extent $\text{Fe}(\text{OH})_2$ are unstable at high temperature (e.g. 95°C) [31], and tend to be converted to the more thermodynamically stable Fe_3O_4 by losing of water. The experimental evidence is provided by comparing the O1s XPS peaks of GO and M-GO, which demonstrates formation of Fe-O-C bonds in the latter. In Figure 6b, the O1s peak of GO is deconvoluted to two finer peaks at 532 and 530 eV that are attributed to C-O (epoxy and hydroxyl) and C=O (carbonyl and carboxyl) groups, respectively.[49] The O1s spectrum of M-GO can be deconvoluted to three peaks at 528, 529.5, 531.7 eV (Figure 6c). The peak at 531.7 eV should be referred to the remaining oxygen atoms of M-GO that are primarily in the form of C-O. The emerging peak at 528 eV is attributed to Fe_3O_4 [50]. The peak at 529.5 eV

corresponds to the bonding between Fe₃O₄ and the graphene. The positive shift of Fe-O-C bonds (529.5 eV) compared to Fe-O (528 eV) is previously reported for the other “metal-O-C” bonds such as Cu-O-C[51], Ag-O-C[52], and Zr-O-C[53].

[Insert Figure 6 about here]

Magnetic properties. Figure 7 depicts magnetization hysteresis loop of the magnetite NPs, and two forms of M-GO hybrids which were synthesized by using ultrasound or stirred method at the ambient temperature (inset the photograph of M-GO) dispersed in aqueous solution (left) and that in the presence of a magnet (right)).

[Insert Figure 7 about here]

As it can be seen, the magnetic intensities of both M-GO hybrids are lower than the pure magnetite NPs, due to the following reasons: 1-Presence of graphene, as a diamagnetic material [54], reduces (i.e. dilutes) the superparamagnetic property of the Fe₃O₄, 2- Nanometric size of the magnetite NPs cause further diminishing of the magnetic property. Between these factors, the effect of the latter can be elaborated through application of Langevin's equation [55], which correlates average size of the magnetic nanoparticles to the saturated magnetization and magnetic susceptibility as follows:

$$D_{Fe_3O_4} = \left(\frac{18k_B T}{\pi \mu_0 \rho_{Fe_3O_4} M_S^2} \left(\frac{dM}{dH} \right)_{H \rightarrow 0} \right)^{1/3} \quad (6)$$

$$D_{M-GO} = \left(\frac{18k_B T}{\pi \mu_0 \rho_{Fe_3O_4} M_S^{*2}} \left(\frac{dM}{dH} \right)_{H \rightarrow 0} \right)^{1/3} \quad (7)$$

where k_B denotes Boltzmann's constant (1.38×10^{-23} J/K), μ_0 shows the permeability of free space ($4\pi \times 10^{-7}$ N/A²), $\rho_{Fe_3O_4}$ (kg/m³) indicates mass density of the magnetite (5180 kg/m³), M_S stands for the saturated magnetization,

$\left(\frac{dM}{dH} \right)_{H \rightarrow 0}$ is susceptibility of the M-GO at zero field, which is obtained from magnetization curve (Figure 7), and

eventually $T = 298$ K is the measurement temperature. For the M-GO composites, effective saturated magnetization (M_S^* , eq (7)) was obtained from measurement of the Fe₃O₄ content of the samples by the following procedure. About 0.01 g of M-GO composite was dissolved in 20 cm³ of concentrated hydrochloric acid, and its iron content was

measured by atomic absorption spectrometry (AAS). Table 2 shows results of such analyses along with some other data. Evidently, the ratio of magnetization of M-GO to the magnetization of pure Fe_3O_4 , is smaller than the corresponding mass fraction ratio, presumably due to the smaller sizes of magnetite NPs, which were formed on the graphene surface. This argument is supported by the close agreement between the sizes of nanoparticles calculated from eqs. (6) - (7), with those obtained from the TEM images and diffraction light scattering (DLS) analysis (Figure S2 in the supplementary information). Detailed derivation of Langevin's equation, and its application on the data of Table 2 is given in Appendix (1).

[Insert Table 2 about here]

Adsorption properties

Adsorption capacity. In order to estimate the uptake capacity of the ultrasound synthesized M-GO hybrid, its adsorption isotherms for Sr^{2+} and Co^{2+} ions were obtained by the experiment. As shown in Figure 8, M-GO is saturated at the loading of 0.28 and 0.56 meq/g of Sr^{2+} and Co^{2+} ions, respectively.

The two-fold higher adsorption capacity of M-GO for the Co^{2+} ion, may be attributed to greater affinity of Fe_3O_4 toward the Fe (II)-like Co^{2+} cations. The iron triad in the periodic table, comprised of Fe, Co and Ni is familiar for every chemist, owing to the close similarity of its consisting elements. Table 3, presents some data regarding the resemblance between these elements. Among these data, electronegativity is of particular importance, because in transition metals, higher electronegativity corresponds to greater tendency for receiving electron pair through dative bonds (i.e. the Lewis acidity of Fe^{2+} and Co^{2+} ions). Similarity between cobalt and iron allows effective sequestering of Co^{2+} ions on Fe_3O_4 .

[Insert Figure 8 about here]

[Insert Table 3 about here]

Taking into account, the simplicity of magnetic separation of the M-GO from the solution (see inset Figure 7), the M-GO hybrid is turned out to be a promising adsorbent for the treatment of the Sr^{2+} or Co^{2+} bearings effluent. Table 4 represents a comparison between the uptake capacities of the M-GO hybrid (this work) with some similar adsorbents. Evidently, the M-GO hybrid is superior to all of its competitor, especially to the magnetite-graphene composites synthesized by stirring co-precipitation method.

[Insert Table 4 about here]

In order to acquire more information about the adsorption mechanisms, the Langmuir and Freundlich's models were applied on the experimental data (Figure 8). The Langmuir model is expressed by [56]:

$$Q_e = \frac{bQ_{\max}C_e}{1+bC_e} \quad (8)$$

The Freundlich model is represented by the following equation[57]:

$$Q_e = KC_e^n \quad (9)$$

where $Q_{\max}$ (meq/g) denotes maximum adsorption capacity, Q_e (meq/g) shows the equilibrium loading on the adsorbent, C_e (meq/g) stands for equilibrium concentration of ions in solution, and b ($\text{dm}^3 \text{ mg}^{-1}$), K and n are the empirical constants that depend on the nature of ions and the adsorbent. The experimental data for adsorption of Sr^{2+} and Co^{2+} ions on the M-GO were regressively simulated with Langmuir and Freundlich's models (Figure 8), and the corresponding fitting parameters were listed in Tables 5 and 6.

It can be inferred from the correlation coefficients R^2 and fitting curves (Figure 8) that the Langmuir model provides a better fitting than the Freundlich, and hence, monolayer coverage of the adsorbent surface according to the Langmuir model, appears to be the main adsorption mechanism. Here, “monolayer” and “multilayer” respectively correspond to adsorption on “outer surface” and “within the internal pores” of the nanoparticles.

According to Tables 5 and 6, the higher is the temperature, the greater is the adsorption capacity of the adsorbent. For Co^{2+} and Sr^{2+} ions, the maximum achieved values of the $Q_{\max}$ were equal to 0.91 and 0.48 meq/g, respectively.

[Insert Table 5 about here]

[Insert Table 6 about here]

Thermodynamic parameters such as ΔG^0 , ΔH^0 , ΔS^0 provide valuable information about the endothermic or exothermic nature of the reaction and its degree of spontaneity. These parameters can be estimated from temperature-dependent uptake data by the following equations:

$$\Delta G^0 = -RTL\ln K^0 \quad (10)$$

$$\frac{\partial \left(\frac{\Delta G^0}{T} \right)}{\partial T} = -\frac{\Delta H^0}{T^2} \quad (11)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (12)$$

where K^0 is the uptake equilibrium constant. Having plotted $\text{Ln}K_d$ curves versus C_e (Figure S5 in supplementary information) and extrapolating C_e to zero, $\text{Ln} K^0$ values can be obtained for every temperature. The $\text{Ln} K^0$ values then are used for calculation of ΔG^0 using eq. (10). Thereafter, the $\frac{\Delta G^0}{T}$ values, which are obtained from $\text{Ln} K^0$, can be re-plotted against $\frac{1}{T}$ to result in the ΔH^0 by application of eq. (11) on their line slopes. (Figure S6 in supplementary information). Also, the entropy difference ΔS^0 is obtained from eq. (12).

The results of calculation of the above thermodynamic parameters are presented in Table 7. The positivity of the ΔH^0 values reveals endothermic nature of the sorption process. This result is in a good agreement with the previous observation about improving of the maximum uptake rate (i.e. $Q_{\max}$) with increasing of the temperature.

[Insert Table 7 about here]

Adsorption kinetics. The rate of adsorption of Co^{2+} and Sr^{2+} ions by M-GO was studied at initial concentration of 50 ppm and pH=6.5, and the results were depicted in Figure 9 a. According to this figure, the uptake attained equilibrium within 3 h for Co^{2+} and 5 h for Sr^{2+} ions, indicating a faster rate of adsorption for the former.

A worth noting fact is that by plotting the kinetics data in the normalized “X” coordinate, Co^{2+} always shows a faster kinetics than Sr^{2+} (Inset Figure 9a). This phenomenon is probably arisen from similarity in the size and nature of the cobalt ions with the iron atoms that initially exist in the magnetite structure. Similar behavior has been reported for some other metal oxides by Dyer et. al. [58].

The kinetics data were fitted with pseudo second order reaction model, represented by:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (13)$$

where K_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) is the ion-specific rate constant, Q_t ($\text{mg} \cdot \text{g}^{-1}$) is the amount of Co^{2+} and Sr^{2+} ions adsorbed into M-GO at time t (min), and Q_e ($\text{mg} \cdot \text{g}^{-1}$) is the adsorption capacity at equilibrium. Inset Figure 9b shows the table of fitting parameters for pseudo-second-order reaction model. The correlation coefficient R^2 is very close to 1, indicating remarkable fitting of the data for both Co^{2+} and Sr^{2+} ions.

There are three pieces of evidence that show the rate determining step of adsorption is more likely chemical reaction of the ions with M-GO hybrid. 1: Nanometric magnetite or graphene particles cannot present intraparticle resistance, due to their small sizes, 2: Uptake kinetics greatly depends on the nature of ions so that for Co^{2+} ion, it is nearly two times faster; Indeed in a series of experiments that were conducted on adsorption of Th^{4+} ions by graphene oxide and graphene, the present authors observed an instantaneous rate of adsorption of thorium. 3: The Diffusion coefficient of Sr^{2+} ion in water which is about $7.9 \times 10^{-6} \text{ cm}^2/\text{s}$ is higher than $6.5 \times 10^{-6} \text{ cm}^2/\text{s}$ of Co^{2+} , thus if liquid film resistance had been the rate controlling factor, adsorption of Sr^{2+} ions should take place faster than the Co^{2+} .

[Insert Figure 9 about here]

Effect of the pH and ionic strength. Figures 10 (a) and (b) demonstrate the uptake rates of Co^{2+} and Sr^{2+} ions as the functions of pH in 0.001, 0.01, and 0.1 M NaNO_3 solution by M-GO adsorbent. For both of the studied ions, the uptake percentage remains quite small up to $\text{pH} \approx 5$, but then, it rapidly increases from 20% to 80%, at pH range of 5-8.5. Above $\text{pH} \approx 8.5$, the uptake curve of Co^{2+} again takes a slight ascending trend, and reaches to 100% adsorption level at $\text{pH} \approx 10$; whereas for Sr^{2+} ion, increase in the uptake after $\text{pH} \approx 8.5$ is insignificant.

There are two mechanisms that stand for the aforementioned pH-dependency of the uptake curves. These are in the order of their importance: 1- Change of the surface charge of the M-GO adsorbent, and 2- Altering of the speciation of cations at higher pHs.

The abrupt increase of the uptake rate of both Co^{2+} and Sr^{2+} ions at $\text{pH} \approx 5$ can be attributed to change of the surface charge of the M-GO adsorbent. In acidic media ($\text{pH} < 4$), surfaces of both GO and magnetite NPs acquire positive charge, as a result of the following protonation reactions:

Electrostatic repulsion between positive surface of the adsorbent and cations appreciably reduce the extent of adsorption. In addition, at lower pHs, H^+ successfully competes with the hard Co^{2+} and Sr^{2+} ions for the adsorption.

When pH increases, both of these effects attenuate, and the succeeding deprotonating reactions cause the surface charge to become gradually negative.

To affirm the effect of the above-mentioned electrostatic mechanisms on the adsorption of Co^{2+} and Sr^{2+} ions, the Zeta potential of M-GO surface was determined as a function of pH (Figure S7). It can be observed that zero charge point (ZCP) of M-GO emerges at pH=3.7. At $pH < pH_{ZCP}$, surface of the M-GO possesses positive charge and consequently acts as an anion adsorber; but at $pH > pH_{ZCP}$, the surface charge becomes negative and thus favors accommodation of positive ions. Here, there is a fine phenomenon that deserves especial attention: The break point of the adsorption curves in Figures 10 (a) and (b) arise at $pH \approx 5$ while zero charge point occurs at $pH_{ZCP} \approx 3.7$. The reason for discrepancy between these two values may be found by a closer look at Figure S7, in which the slope of the surface charge curve changes not at $pH_{ZCP} \approx 3.7$ but indeed at $pH \approx 5$. Probably at $pH \approx 5$ the above-mentioned deprotonating reactions become complete, and thus tendency of the surface for adsorption of positive ions is abruptly and greatly elevated.

Above $pH \approx 8.5$, the second mechanism (i.e. change of the speciation of cations) becomes operative, but this mechanism is principally only valid for the Co^{2+} ion. According to the relative species distribution of Co^{2+} assessed from the hydrolysis constants ($\log K_1 = 9.6$, $\log K_2 = 9.2$, and $\log K_3 = 12.7$)[33], at pHs above 8, Co^{2+} ion are greatly replaced by first $Co(OH)^+$ ion and then $Co(OH)_2$ at $pH > 10$. Since the positive charge of these species is lower than Co^{2+} ions, tendency for their adsorption is lesser than the Co^{2+} ions.

In order to study the effect of ionic strength on the uptake of Co^{2+} and Sr^{2+} ions, a series of experiments were carried out in presence of 0.001, 0.01, 0.1 M of $NaNO_3$ solutions. As it can be seen in Figure 10 a and b, variation of the ionic strength affects differently on the adsorption of Co^{2+} and Sr^{2+} ions, presumably as a result of differing between the reaction of those ions with the surface.

A metal cation can connect to the surface of an adsorbent as an inner-sphere or outer-sphere complex. In the former case, a covalent dative bond is formed between the metal ion and the electron-donating oxygen atom of the surface, while in the latter case (outer complex) a cation approaches toward the surface groups of adsorbent till a critical distances. To recognize which mechanism are dominant on adsorption of Co^{2+} and Sr^{2+} ions on M-GO hybrid the effect

of ionic strength was investigated. Since in the outer-sphere complexes, the ions of the electrolyte medium are present nearly at the same plane with the adsorbing ions, the outer-sphere complexes are more susceptible to variation of the ionic-strength. As shown in Figure 10a, adsorption of Co^{2+} is independent of the ionic strength, while the Sr^{2+} sorption trails an opposite fashion (Figure 10b). Thus, based on the aforementioned argument, one may conclude that adsorption of Co^{2+} ion is controlled by inner-sphere complex formation, whereas the Sr^{2+} uptake is governed by outer-sphere complex mechanism. Other reasons for formation of inner-sphere complex in the case of Co^{2+} ions are: 1- Lower electronegativity of cobalt compared to strontium (see Table 3), and consequently its higher affinity for receiving dative electron pair, and 2- Close similarity of cobalt and iron that helps substitution of Fe by Co in the magnetite structure.

The effect of coexisting cations on adsorption of Co^{2+} and Sr^{2+} ions was examined by accomplishing the uptake experiments in aqueous media of 0.01 M NaNO_3 , KNO_3 , and LiNO_3 solutions (Figure 10 c and d). According to these figures, uptake rates of both Co^{2+} and Sr^{2+} ions are affected by the presence of aforementioned cations at $\text{pH} < 8$. Such adverse effect is more likely arisen from the effective competition of K^+ , Na^+ , and Li^+ ions for sequestering on the surface of M-GO. The order of interference of the coexisting ion was $\text{K}^+ < \text{Na}^+ < \text{Li}^+$. The similar trend was reported by reference [33] for adsorption of Co^{2+} ions by the stirred type magnetite-graphene composite.

The ionic radii of alkali metal ions have the following orders:

In crystals (un-hydrated): $\text{Li}^+ (94) < \text{Na}^+ (117) < \text{K}^+ (149) < \text{Rb}^+ (163) < \text{Cs}^+ (186)$

In solution (hydrated): $\text{Li}^+ (382) > \text{Na}^+ (358) > \text{K}^+ (331) > \text{Rb}^+ (329) \approx \text{Cs}^+ (329)$

where the values in the parenthesis denote radii in pm. Since according to the last paragraph, potassium and lithium ions have the least and the most adverse effect on the adsorption of Co^{2+} and Sr^{2+} ions; competition between the target ions (i.e. Co^{2+} and Sr^{2+}) and the alkali metal ions for adsorption must take place on the active sites of the M-GO surface, where the sequestered ions have an un-hydrated form. In other word: since the radius of Li^+ is smaller than those of Na^+ and K^+ ions; it has a greater chance to be sequestered on the surface of the M-GO, and hence it decrease the number of fresh active sites for adsorption of Co^{2+} and Sr^{2+} ions, more remarkably.

[Insert Figure 10 about here]

Conclusion: Ultrasound assisted precipitation is an effective method for decoration of magnetite NPs on the surface of graphene oxide, which is able to reduce size of the NPs from 30 nm of conventional stirring method to about 17 nm, and is capable of producing NPs with narrow size distribution.

Based on the collected evidence, the study put forward a poly condensation mechanism for formation of magnetite NPs on the GO surface as follows: the first layer of iron atoms are connected to GO through C-O-Fe covalent (dative) bonds, while the next Fe layers are linked to the preceding ones by repeated formation of Fe-OH-OH-Fe bridge, followed by immediate dehydration to Fe-O-Fe structure. This assembling procedure produce a standard Fe₃O₄ crystal on the aforementioned C-O-Fe sub-layer and maintain its magnetic properties substantially preserved.

One of the examined issues in the current study was checking of the applicability of Langevin's equation for estimation of the size of a superparamagnetic nano crystal when it is deposited on the graphene surface (i.e. a diamagnetic material). The formula had been successfully used for calculation of size of pure Fe₃O₄ NPs in previous studies. Our results demonstrated that the equation works equally well in the case of nano composite materials.

The adsorption properties of M-GO was examined for Sr²⁺ and Co²⁺ ions. The uptake capacity for Co²⁺ ion was about two folds higher than Sr²⁺ ion, likely because for the former ion, Fe₃O₄ showed higher affinity due to the similarity of Co²⁺ and Fe²⁺ ions. For both of the Sr²⁺ and Co²⁺ ions, uptake was closely simulated by the Langmuir's monolayer adsorption model, with the maximum capacity of 0.28 and 0.56 meq/g Sr²⁺ and Co²⁺, respectively.

The adsorption kinetics obeyed pseudo-second-order reaction model for both of the studied ions, indicating that the chemical reaction of ions with unoccupied fraction of the adsorption sites is the rate controlling factor of adsorption. This argument is supported by three piece of evidence that are presented in the kinetics section.

Thermodynamic data indicated that adsorption of both of the Sr²⁺ and Co²⁺ ions was endothermic, and the absolute value of the term TΔS⁰ was about two times larger than the term ΔH⁰.

Investigation of the pH-dependent sorption of the Sr²⁺ and Co²⁺ ions, along with examining Zeta potential of the M-GO, revealed that by increasing of the pH, surface charge of the M-GO changes from positive to negative at pH=3.7. This change of charge is followed by deprotonating reactions (16) and (17) at pH≈5, that when is completed, cause an abrupt increase of Sr²⁺ and Co²⁺ adsorption at pHs>5.

It was demonstrated that adsorption of the Co²⁺ ions takes place through inner-sphere complex formation, more likely because of the similarity of cobalt and iron ions that makes substitution of Fe with Co on the surface of magnetite

quite plausible. On the other hand, adsorption of strontium seems to proceed through an ion exchange mechanism, which is quite sensitive to the variation of ionic strength of the solution.

Acknowledgment

The authors would like to thank the Research Deputy of Sharif University of Technology, and its Dept. of Energy Engineering for financial support of the project.

- **Appendix: Derivation of Langevin's equation and its application on magnetite and M-GO NPs**

Langevin demonstrated that magnetization of a superparamagnetic particle can be expressed as multiplication of the saturated magnetization M_s and the so called Langevin function, which shows the extent of alignment of the magnetic dipoles in direction of the external field.

$$M = M_s L(x) \quad (A-1)$$

In which Langevin function is defined as:

$$L(x) = \text{Coth}(x) - \frac{1}{x} \quad (A-2)$$

For small values of x , Langevin function can be approximated by truncation of its Taylor series:

$$L(x) = \frac{1}{3}x - \frac{1}{45}x^3 + \frac{2}{945}x^5 - \frac{1}{4725}x^7 + \dots \quad (A-3)$$

With

$$x = \frac{\mu_0 m_p H}{k_B T}$$

where k_B (1.38×10^{-23} J/K) denotes Boltzmann's constant, μ_0 ($4\pi \times 10^{-7}$ N/A²) shows the permeability of free space, M_s is the saturated magnetization, m_p stands for magnetic moment of the nanoparticle, H displays the applied magnetic field, and eventually, $T = 298$ K is the measurement temperature.

By substituting of the constant values, and order of magnitude of applied magnetic field in definition of “ x ” parameter, it is readily seen that further truncation of the Langevin function to a one-term formula is possible:

$$x \approx \frac{10^{-7} \times 10^{-21}}{10^{-23}} \approx 10^{-5} \Rightarrow L(x) \approx \frac{1}{3}x \quad (A-4)$$

This approximation will reduce eq. (A-1) to a simpler form:

$$M = M_s L(x) \Rightarrow M = \frac{M_s x}{3} = \frac{M_s \mu_0 m_p H}{3k_B T} \quad (A-5)$$

On the other hand, magnetization can be written in terms of magnetic susceptibility and magnetic field as follows:

$$\left. \begin{aligned} M &= \chi H \\ \chi &= \left(\frac{dM}{dH} \right)_{H \rightarrow 0} \end{aligned} \right\} \Rightarrow M = H \left(\frac{dM}{dH} \right)_{H \rightarrow 0} \quad (A-6)$$

Combining eqs. (A-5) and (A-6) will result in:

$$\frac{M_s \mu_0 m_p H}{3k_B T} = H \left(\frac{dM}{dH} \right)_{H \rightarrow 0} \Rightarrow m_p = \frac{3k_B T}{M_s \mu_0} \left(\frac{dM}{dH} \right)_{H \rightarrow 0} \quad (A-7)$$

For a nanoparticle, the maximum value of magnetization depends on the volume of the particle so magnetic moment could be derived as below:

$$\left. \begin{aligned} m_p &= \rho_{Fe_3O_4} M_s V \\ V &= \frac{\pi}{6} D^3 \end{aligned} \right\} \Rightarrow m_p = \frac{\pi \rho_{Fe_3O_4} M_s D^3}{6} \quad (A-8)$$

Using eqs. (A-7) and (A-8), the diameter of the aimed nanoparticle is obtained:

$$\frac{\pi \rho_{Fe_3O_4} M_s D^3}{6} = \frac{3k_B T}{M_s \mu_0} \left(\frac{dM}{dH} \right)_{H \rightarrow 0} \Rightarrow D = \left(\frac{18k_B T}{\pi \mu_0 \rho_{Fe_3O_4} M_s^2} \left(\frac{dM}{dH} \right)_{H \rightarrow 0} \right)^{1/3} \quad (A-9)$$

The value of magnetic susceptibility $\left(\frac{dM}{dH} \right)_{H \rightarrow 0}$, is obtained from magnetization curve of Figure (7), at the limit of

zero field. The diameter of pure iron oxide nanoparticles could be calculated as follow:

$$D^3 = \left[3.62 \times 10^{-18} \times \frac{\left(\frac{dM}{dH} \right)_{Fe_3O_4, H \rightarrow 0}}{M_s^2} \right]_{Fe_3O_4} \Rightarrow D = 30nm \quad (A-10)$$

For M-GO composite, we should take into consideration the mass fraction of iron oxide. For this reason, the effective saturated magnetization is defined as:

$$M_s^* = \frac{M_s}{Fe_3O_4 \text{ mass fraction}} \quad (A-11)$$

Which for stirred and ultrasound assisted M-GO was calculated as below:

$$M_{S,Stirred}^* = \frac{41}{0.7} = 59$$

$$M_{S,Ultrasound}^* = \frac{30}{0.58} = 52$$
(A-12)

Using these values, the diameter of magnetite nanoparticles in M-GO can be calculated as:

$$D^3 = 3.62 \times 10^{-18} \times \frac{\left(\frac{dM}{dH} \right)_{M-GO \quad H \rightarrow 0}}{M_S^{*2}} \quad \Rightarrow D = 35nm$$

(A-13)

$\downarrow M-GO(Stirred)$

$$D^3 = 3.62 \times 10^{-18} \times \frac{\left(\frac{dM}{dH} \right)_{M-GO \quad H \rightarrow 0}}{M_S^{*2}} \quad \Rightarrow D = 20nm$$

$\downarrow M-GO(Ultrasound)$

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Figures Caption

Figure 1: (a) Typical AFM image of GO sheet on mica (b) Corresponding height profile analysis of marked-line, and (c) Low magnification TEM image of GO sheet and inset corresponding SAED of GO.

Figure 2: (a) FE-SEM, and (b) AFM images of Fe_3O_4 NPs on the surface of M-GO, (c) Low magnification TEM image; and (d) HRTEM images of M-GO. Inset Figure 3d is SAED pattern of M-GO.

Figure 3: (a) XRD patterns of as-prepared materials, (b) FTIR spectra of the synthesized products, (c) Raman spectra of graphite, GO, and M-GO, and (d) UV-visible absorbance of GO and M-GO.

Figure 4: The full scale XPS survey of GO, and M-GO hybrid.

Figure 5: XPS C1s high resolution spectra of (a) GO; and (b) M-RGO

Figure 6: (a) Formation mechanism of M-GO, XPS O1s high resolution spectra of (b) GO; and (c) M-GO.

Figure 7: Magnetization behavior of M-GO hybrid at room temperature indicating superparamagnetic properties of prepared materials, inset shows M-GO composite dispersed water solution and magnetic separation.

Figure 8: Sorption isotherms of (a) Co^{2+} and (b) Sr^{2+} (II) onto the M-GO composite at three different temperatures.

Figure 9: (a) Kinetics of adsorption of Co^{2+} and Sr^{2+} ions by M-Go hybrid, inset chart compares the uptake rates in a normalized coordination (X), (b) Fitting of the kinetics data with pseudo-second order reaction model.

Figure 10: Variation of adsorption of (a) Co^{2+} , and (b) Sr^{2+} onto M-GO hybrids as a function pH and ionic strengths; and the effect of coexisting ions on adsorption of (c) Co^{2+} , and (d) Sr^{2+} .

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Figure 7: Comparison of the magnetization behaviors of magnetite, with two types of M-GO hybrids, at room temperature, inset figure shows separation of the M-GO hybrid from its dispersion in water by a simple magnet.

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Table 1: The peak area of oxygen-containing bonds and the CC bonds for as-prepared GO and M-GO hybrids.

Peak	GO	M-GO
C=C and C-C	56	75.5
C-OH	15.2	12.8
C-O-C	22.9	9.4
HO-C=O	5.8	2.3

Table 2: Magnetite nanoparticles size estimation using Langevien equation.

Sample	M_s	Ratio of $M_s/M_{s, \text{Magnetite}}$	Mass fraction of Fe_3O_4	$D_{\text{Theoretical}} \text{ (nm)}$ from eq. (5)	$D_{\text{Experimental}} \text{ (nm)}$
M-GO (Stirred Method)	41	0.56	0.7	35	30 (Figure S1)
M-GO (Ultrasound Method)	30	0.42	0.58	20	17 (Figure 2c)
Magnetite (Fe_3O_4)	72	1	1	30	29 (Figure S2)

Table 3: Comparison between different atoms indicating the higher affinity of iron atoms toward cobalt.

Elements	Iron	Cobalt	Nickel	Strontium
Electron Configuration	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^1$	$5s^2$
Atomic radius (empirical), pm	124	125	125	215
First Ionization Energy, kJ mol^{-1}	759	758	737	549
Second Ionization Energy, kJ mol^{-1}	1561	1646	1753	1064
Third Ionization Energy, kJ mol^{-1}	2957	3232	3393	4138
Ionic Radius of 2+ ions, pm	75	79	83	132
Ionic Radius of 3+ ions, pm	69	68.5	70	-
Electronegativity (Pauling's scale)	1.83	1.88	1.91	0.95

Table 4: Previous reported adsorption capacities of various adsorbent for Co^{2+} and Sr^{2+} .

Adsorbent	pH	Concentration Range (mg.dm^{-3})	Adsorption Capacity (mg.g^{-1})		References
			Sr	Co	
Activated Carbon	8	10-200	6	-	[15]
Magnetite NPs	9	5-50	0.7	0.46	[59]
Multiwall CNTs	7	5-75	1.3	2.5	[60] [18]
Oxidized-MWCNTs	7	5-75	6	-	[60]
Magnetite-MWCNTs			9		[17]
$\text{TiO}_2\text{-SiO}_2$	10.6	1-5	1.2	-	[61]
Dolomite powder	7	10-50	1.1	-	[62]
Functionalized silica	6	5-90	-	9	[63]
Magnetite/Graphene Oxide (Prepared by co-precipitation)	7	10-50	-	14.2	[33]
M-GO	6.5	5-100	14.3	17.1	This Work

Table 5: Parameters of Langmuir and Freundlich isotherm model for Co^{2+} ions at pH 7.0(± 0.2) at different temperature.

T (K)	Langmuir			Freundlich		
	$Q_{\text{max}}(\text{mg.g}^{-1})$	$b(\text{L.mg}^{-1})$	R^2	K_2	n	R^2
298.15	18.9	0.13	0.96	5.19	0.3	0.8
318.15	23.3	0.19	0.94	7.24	0.28	0.77
338.15	28.5	0.52	0.98	12.3	0.23	0.83

Table 6: Parameters of Langmuir and Freundlich isotherm model for Sr^{2+} ions at pH 7.0(± 0.2) at different temperature.

T (K)	Langmuir			Freundlich		
	$Q_{\max}(\text{mg.g}^{-1})$	$b(\text{L.mg}^{-1})$	R^2	K_2	n	R^2
298.15	13.7	0.07	0.99	2.9	0.36	0.84
318.15	17.6	0.11	0.97	4.55	0.33	0.85
338.15	22.3	0.18	0.97	7.4	0.28	0.74

Table 7: Values of Thermodynamic Parameters for Co^{2+} and Sr^{2+} Sorption on the M-GO.

Ions	ΔG^0 (kJ.mol ⁻¹)			ΔS^0 (J.mol ⁻¹ K ⁻¹)	ΔH^0 (kJ.mol ⁻¹)
	298.15	318.15	338.15		
Co^{2+}	-18.1	-20.9	-24.2	151.7	27.1
Sr^{2+}	-16.1	-17.6	-19.1	138.5	25.2