

1           **Simultaneous removal of heavy metals and dyes in water using a MgO-coated Fe<sub>3</sub>O<sub>4</sub>**  
2           **nanocomposite: Role of micro-mixing effect induced by bubble generation**

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19 **Abstract:**

20 This study focused on the development of a nano-adsorbent for contaminant removal  
21 without the use of any external energy. An eco-friendly  $\text{Fe}_3\text{O}_4@\text{MgO}$  core-shell nanocomposite  
22 was synthesized and tested for the removal of a heavy metal, lead ( $\text{Pb}^{2+}$ ) and a dye, rhodamine B  
23 (RhB). The addition of  $\text{H}_2\text{O}_2$  into the system enabled the self-mixing of the aqueous solution  
24 containing  $\text{Fe}_3\text{O}_4@\text{MgO}$  through the generation of bubbles. This system showed an excellent  
25 removal efficiency of 99% in just 15 min for  $\text{Pb}^{2+}$  and 120 min for RhB, which is far better than  
26 the control experiment (without  $\text{H}_2\text{O}_2$ ). The cation exchange mechanism dominated in the  
27 removal of heavy metals, while the adsorptive removal of dye proceeded through the H-bonding  
28 between  $\text{Mg}(\text{OH})_2$  and dye molecules. The removal efficiency increased exponentially with the  
29 increase of  $\text{H}_2\text{O}_2$  at the optimal concentration of 5% and it was effective over a wide pH range.  
30 Moreover, the performance of the  $\text{Fe}_3\text{O}_4@\text{MgO}-\text{H}_2\text{O}_2$  system was verified for other heavy metals  
31 such as Cd, Ni, Zn, Co, and Cu, demonstrating that the  $\text{Fe}_3\text{O}_4@\text{MgO}-\text{H}_2\text{O}_2$  system can be widely  
32 implemented in the treatment of real water matrices contaminated with heavy metals and organic  
33 dyes.

34 **Keywords:** *Water treatment,  $\text{Fe}_3\text{O}_4@\text{MgO}$ , bubble generation, adsorption, heavy metals, dyes*

35



36 ***Abbreviations***

37 RhB: rhodamine B, PEG: Polyethylene glycol, CTAB: Cetyltrimethylammonium bromide,  
38 SEM: scanning electron microscopy, EDX: Energy dispersive X-ray, XRD: X-ray diffractometer,  
39 XPS: X-ray photoelectron spectroscopy, ICP-OES: inductively coupled plasma–optical emission  
40 spectrometer, DO: Dissolved oxygen

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## 43 **1. Introduction**

44 Heavy metals such as arsenic, lead, cadmium, nickel, chromium, cobalt, and selenium are  
45 major environmental pollutants because of their toxic effects, even at trace levels (Nadeem et al.,  
46 2006; Qiu et al., 2021). All these elements are discharged directly from industries and agricultural  
47 fields into the aquatic system. Their adverse effects create negative impacts on all environmental  
48 compartments (Vakili et al., 2014). Although there are several sources of the exposure of humans  
49 to these pollutants, their intake via drinking water is the most prominent and thereby highlights  
50 the need for a proper treatment protocol. Another important category of water pollutants is dye  
51 waste (Nigam et al., 1996) which is introduced into water bodies from textile mills, leather, jute,  
52 and food industries. Previous reports showed that dyehouse effluent contains many heavy metals,  
53 which also increase the perilous situation of water pollution by this kind of waste (Chen et al.,  
54 2007; Ye et al., 2021b). However, traditional technologies such as ion exchange, biological  
55 degradation, reverse osmosis, coagulation and flocculation, membrane filtration, oxidation, and  
56 chemical precipitation are effective mostly in the removal of a single pollutant from various  
57 contaminated water (Dotto et al., 2019; Rasaki et al., 2019; Zazou et al., 2019; Iqbal et al., 2021).  
58 Therefore, recent studies have focused on the materials/methods that could remove both heavy  
59 metals and organic pollutants in water (Kim et al., 2018; Ghaedi et al., 2022; Malik et al., 2022).

60 Adsorption using various nanomaterials is the most frequently used technique for the  
61 removal of a majority of pollutants (Valix et al., 2004; Afroze and Sen, 2018; Abdullah et al.,  
62 2019; Joseph et al., 2019; Castro-Muñoz et al., 2021; Osagie et al., 2021). However, it was found  
63 not to be very effective, especially when dealing with a mixture of pollutants. Therefore, the  
64 selection of an adsorbent that is capable of removing both organic and inorganic pollutants is a  
65 typical challenge in this field. Another difficulty is the requirement of additional mechanical



66 forces to increase the mass transfer of the pollutant to enhance removal efficiency, which limits  
67 the practical implementation of adsorption materials. Recent advances in environmental  
68 nanotechnology have therefore focused on decontamination using self-propelled materials  
69 (Calvo-Marzal et al., 2010; Liu et al., 2010; Sánchez et al., 2015; Wang and Pumera, 2015; Chen  
70 et al., 2017; Xu et al., 2017). Pt/Fe-, MnO<sub>2</sub>-, and Ag-based materials have been widely deployed  
71 as self-propelled materials in the presence of certain chemicals for water purification (Ye et al.,  
72 2017; Chen et al., 2018; Lee et al., 2018; Ye et al., 2018). These materials decompose hydrogen  
73 peroxide fuel (H<sub>2</sub>O<sub>2</sub>) and generate bubbles to move the adsorbent through the aqueous  
74 environment. The bubble generating materials are therefore of considerable interest because of  
75 their enhanced micro-mixing capability owing to bubble propulsion, which increases pollutant  
76 transfer from the solution phase to the surface of the adsorbent and thereby improves the removal  
77 of pollutants through oxidation/adsorption processes (Gao et al., 2013b; Safdar et al., 2015;  
78 Vilela et al., 2016; Lee et al., 2018). However, the major difficulty in handling these adsorbents is  
79 the requirement for expensive supporting metals such as Pt, Au, and Ag, which can cause toxic  
80 effects when released into the aquatic system. Hence, current research is focused on  
81 environmentally friendly, stable, and easily accessible materials for such applications (Chen et  
82 al., 2018).

83 Metal oxide nanocomposites containing Fe<sub>3</sub>O<sub>4</sub> have attracted considerable interest for  
84 environmental remediation owing to their excellent magnetic and surface properties (Kim et al.,  
85 2013; Kang et al., 2019). MnO<sub>2</sub>-coated iron oxides have been demonstrated as an effective  
86 material for the removal of water pollutants. Kim et al. reported that these composite materials  
87 are effective for the removal of heavy metals, but require mechanical stirring (Kim et al., 2013).  
88 Moreover, Kang et al. utilized the same material in advanced oxidation processes and adsorptive



89 bubble separation of various dyes in the presence of a surfactant and H<sub>2</sub>O<sub>2</sub> (Kang et al., 2019).  
90 These materials have also been found effective for the simultaneous removal of organics and  
91 microplastics by the micro-mixing effect (Ye et al., 2021a). However, both studies used  
92 surfactants for the generation of bubbles and the subsequent micro-mixing effect (Kang et al.,  
93 2019; Ye et al., 2021a). Surfactants are also considered an important water pollution source all  
94 over the world (Sasi et al., 2021). Therefore, for practical uses, the present study attempted to  
95 utilize nanomaterials that are capable of removing both organic and inorganic contaminants from  
96 aqueous bodies without the use of surfactants or other fuels.

97 Mg, one of the most abundant elements in the world, is characterized by its high reactivity  
98 in water and air to form oxides and hydroxides. These reactions evolve H<sub>2</sub> gas to enable the  
99 propulsion of particles in water. Therefore, many studies have evaluated materials such as TiO<sub>2</sub>,  
100 Au/TiO<sub>2</sub>, Au, and Ag-doped with Mg, which are used for the removal of a variety of organic  
101 pollutants (Gao et al., 2013a; Mou et al., 2013; Li et al., 2014; Vilela et al., 2017). Instead, the  
102 lifetime of the H<sub>2</sub> generation reaction is relatively short because of the rapid corrosion reaction  
103 (Mou et al., 2013). The formation of a passivation layer of the corresponding hydroxide hinders  
104 the further reduction of water. Mg-based alkaline materials like MgO are considered an efficient  
105 material for the remediation of pollutants through adsorption owing to their high adsorption  
106 capacity (Gao et al., 2008; Yu et al., 2011; Kameda et al., 2018; Chinthala et al., 2021). The MgO  
107 nanoparticles are not expensive and environmentally benign, and can hence be easily used to  
108 scale up the removal process. Moreover, *in vivo* toxicity evaluations, it has shown that these  
109 particles are relatively less toxic than other metal oxides (TiO<sub>2</sub>, MnO<sub>2</sub>, ZnO, etc.,) and also  
110 biocompatible (Gao et al., 2008; Sasaki et al., 2011; Yu et al., 2011). Therefore, MgO in  
111 conjunction with other materials (graphene, graphene oxide and diatomite, Fe–Co–Mn



112 nanoparticles) has been widely utilized for the removal of heavy metals and many organic  
113 pollutants (Mohan et al., 2017; Rahdar et al., 2019; Liu et al., 2020; Guo and Bulin, 2021). A  
114 disadvantage of this process is the required mechanical stirring and separation of the material  
115 after the adsorption process. Thus, the key objective of the present study was the development of  
116 a MgO-based and easily separable/recoverable material for the removal of pollutants without  
117 external agitation.

118 Similar to MnO<sub>2</sub>, MgO decomposes H<sub>2</sub>O<sub>2</sub> to generate O<sub>2</sub> gas (Zeng et al., 2020), which is  
119 assumed to be helpful in the bubble-induced mixing of the particles. Thus, the combination of  
120 MgO with Fe<sub>3</sub>O<sub>4</sub> nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@MgO) was proposed as an efficient material for water  
121 treatment. All the previously reported micro-mixing and bubble generating systems used  
122 surfactants to induce bubble formation. In addition, they had focused on only one kind of  
123 pollutants (either organic or inorganic) in their removal. In contrast to the previous reports, this  
124 study tried to remove both kinds of pollutants simultaneously without the use of surfactants. In  
125 short, the objectives of the present study were i) to investigate the mechanism of bubble  
126 generation and the micro-mixing capacity, ii) to study the potential of Fe<sub>3</sub>O<sub>4</sub>@MgO  
127 nanocomposite for concomitant removal of Pb<sup>2+</sup> and rhodamine B dye without any mechanical  
128 stirring, and iii) to evaluate the applicability of the Fe<sub>3</sub>O<sub>4</sub>@MgO micro-mixing system to real  
129 contaminated water spiked with the selected model compounds.

## 130 **2. Experimental section**

### 131 **2.1. Materials and methods**

132 Ferric chloride (FeCl<sub>3</sub>), magnesium chloride (MgCl<sub>2</sub>), sodium acetate, ammonium  
133 hydroxide (NH<sub>4</sub>OH), rhodamine B (RhB), and H<sub>2</sub>O<sub>2</sub> were acquired from Merck (Seoul, South



134 Korea). Lead nitrate ( $\text{PbNO}_3$ ), polyethylene glycol (PEG), and cetyltrimethylammonium bromide  
135 (CTAB) were purchased from Sigma-Aldrich (Seoul, South Korea). Ultrapure water with a  
136 specific resistivity of  $>18 \text{ M}\Omega \text{ cm}$  was prepared using a Millipore (France) system.

## 137 **2.2. Synthesis of $\text{Fe}_3\text{O}_4@\text{MgO}$**

138  $\text{Fe}_3\text{O}_4@\text{MgO}$  was synthesized using a two-step process as reported earlier (Peng et al.,  
139 2016). First,  $\text{Fe}_3\text{O}_4$  nanoparticles were synthesized. In this step, 5 mM of  $\text{FeCl}_3$  was prepared in  
140 ethylene glycol. Sodium acetate (3.6 g) and PEG (1.0 g) were added to the previously prepared  
141  $\text{FeCl}_3$  solution and stirred well at  $50 \text{ }^\circ\text{C}$  for approximately 30 min. The mixture was then added to  
142 a 100 mL Teflon-lined autoclave and heated to  $200 \text{ }^\circ\text{C}$  for approximately 8 h. The obtained black  
143 product of  $\text{Fe}_3\text{O}_4$  was allowed to reach  $22\text{-}25 \text{ }^\circ\text{C}$  room temperature and was then centrifuged,  
144 washed several times with ethanol, and dried in a vacuum oven at  $60 \text{ }^\circ\text{C}$  for 6 h (Deng et al.,  
145 2005). Approximately 0.5 g of the previously prepared  $\text{Fe}_3\text{O}_4$  was dispersed in 100 mL of 0.025  
146 M CTAB and sonicated for 30 min. The solution was then mixed with 50 mL of 0.5 M  $\text{MgCl}_2$   
147 solution by constant stirring for another 1 h.  $\text{NH}_4\text{OH}$  was then added slowly to the solution to  
148 reach a temperature of  $70 \text{ }^\circ\text{C}$ . The solution was allowed to cool until room temperature was  
149 reached. The separated particles were then washed several times with ethanol and dried at  $50 \text{ }^\circ\text{C}$   
150 for 6 h. The  $\text{Fe}_3\text{O}_4@\text{MgO}$  nanocomposites were then obtained by the calcination of the dried  
151 particles at  $450 \text{ }^\circ\text{C}$  for 3 h (Peng et al., 2016).

## 152 **2.3. Characterization of $\text{MgO}@\text{Fe}_3\text{O}_4$**

153 The morphology and structure of the  $\text{MgO}@\text{Fe}_3\text{O}_4$  nanocomposites were determined through  
154 scanning electron microscopy (SEM) (JSM-7401F; JEOL, Tokyo, Japan). Energy dispersive X-  
155 ray (EDX) mapping was performed to obtain the surface composition of the materials. The





156 crystalline nature of the material was obtained using an X-ray diffractometer (XRD, MXP18 HF;  
157 MAC Science Co., Japan). The chemical composition of the particles was analyzed using X-ray  
158 photoelectron spectroscopy (XPS, K-Alpha; Thermo Scientific, USA). The bubble formation was  
159 monitored, and images were captured using an optical microscope (Olympus MX51).

#### 160 **2.4. Batch experiment and analysis**

161 Initially, a stock solution of RhB and  $\text{Pb}^{2+}$  with a concentration of  $500 \text{ mg L}^{-1}$  was  
162 prepared in deionized water. The pollutant solutions for the adsorption experiment were prepared  
163 from this stock solution. To study the removal efficiency in a real system,  $\text{Pb}^{2+}$  ions were spiked  
164 in real groundwater (from a rural area in South Korea) and river water (collected from Hyeongsan  
165 River, South Korea). Adsorption studies were conducted in a 20 mL glass vial. The solutions (10  
166 mL) containing  $10 \text{ mg L}^{-1}$  pollutants ( $\text{Pb}^{2+}$  and RhB), and  $\text{H}_2\text{O}_2$  were first prepared in the vial. A  
167 specific amount of  $\text{Fe}_3\text{O}_4@\text{MgO}$  was weighed and transferred into the vial. After a predetermined  
168 time interval, the materials were separated using a magnet, and approximately  $200 \mu\text{L}$  of the  
169 solution was pipetted out for the analysis of the remaining pollutant in the solution. The  
170 reusability of the  $\text{Fe}_3\text{O}_4@\text{MgO}$  nanocomposite was evaluated with the addition of  $10 \text{ mg L}^{-1}$  of  
171 the selected pollutants to the magnetically separated material after 15 min of each cycle.

172 The concentration of Pb, Mg, and Fe ions after each sampling was analyzed using an  
173 inductively coupled plasma–optical emission spectrometer (ICP-OES, iCAP6300; Thermo  
174 Scientific). The concentration of RhB was monitored using a UV spectrophotometer at a  
175 wavelength of 540 nm (Varian, Palo Alto, CA, USA). An Orion™ Versa Star advanced  
176 electrochemistry meter was used to monitor the changes in pH and dissolved oxygen (DO)  
177 concentrations during the reaction. The removal percentage was then calculated using the eqn. 1,

$$\% \text{ removal} = \frac{(C_0 - C_t) \times 100}{C_0} \quad (1)$$

178  
179  $C_0$  and  $C_t$  are the concentrations of the pollutants before and after the adsorption reactions  
180 in mg/L.

### 181 3. Results and Discussions

#### 182 3.1. Characterization of Fe<sub>3</sub>O<sub>4</sub>@MgO

183 As can be seen from Figs. 1A and 1B, the Fe<sub>3</sub>O<sub>4</sub>@MgO nanocomposite was spherical in  
184 shape. The EDX mapping showed that compared to Fe, Mg was the major contributor to the  
185 surface of the material (Fig. 1C).

186

187

**Fig. 1.**

188

189 The diffraction peaks at 30.2°, 35.6°, 42.9°, 53.7°, 57.2°, and 62.3° could be indexed to  
190 the cubic structure of Fe<sub>3</sub>O<sub>4</sub>; whereas those at 18.2°, 36.8°, 38.1°, 42.9°, and 62.3° represented  
191 the polycrystalline cubic structure of MgO. Moreover, the lack of extra peaks or peak shifts  
192 observed in the XRD spectrum confirmed that no direct interaction occurred between the core  
193 Fe<sub>3</sub>O<sub>4</sub> and the outer MgO layer (Peng et al., 2016). The XPS spectrum also showed the presence  
194 of Fe, Mg, and O in the material (Fig. S1). The high-resolution Mg 1s and O 1s spectra of  
195 Fe<sub>3</sub>O<sub>4</sub>@MgO are shown in Fig. 2. The deconvolution of Fe 2p spectra generated four major  
196 peaks which correspond to Fe<sup>2+</sup> (723.8 and 710.6 eV) and Fe<sup>3+</sup> (725.3 and 711.9 eV) (Fig. S2)  
197 (Grosvenor et al., 2004). Mg 1s spectra showed peaks at 1301.7 and 1304.7 for Mg(OH)<sub>2</sub> and  
198 MgO, respectively. This was further confirmed from the corresponding O 1s peaks at 530.1 and  
199 531.2 eV corresponding to the Mg oxide (Khairallah et al., 2012; Alla et al., 2016).

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**Fig. 2.**

### **3.2. Bubble generation and mixing phenomena**

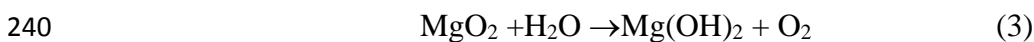
The prime objective of the study was to identify the micro-mixing phenomena by the generation of bubbles. The bubble generation was monitored without and with the addition of  $\text{H}_2\text{O}_2$ . The 1 mL of the aqueous solution containing different concentration of  $\text{H}_2\text{O}_2$  (0%, 0.05%, 0.5%, 1%, 2%, 5%, and 10%) was put in a petri dish and 1 mg of  $\text{Fe}_3\text{O}_4@\text{MgO}$  added. The bubbles are then monitored using the optical microscope. The  $\text{Fe}_3\text{O}_4@\text{MgO}$  nanocomposites were aggregated and settled at the bottom once it was added to the aqueous solution. However, self-movement of the particles was observed with the generation of bubbles in the solution when  $\text{H}_2\text{O}_2$  was added to the solution (Supporting Information Video S1). A small amount of surfactant (0.05%) was used to help monitor the bubble formation when using an optical microscope. The visual images of bubble formation in the solution containing  $\text{Fe}_3\text{O}_4@\text{MgO}$  with the addition of  $\text{H}_2\text{O}_2$  are shown in Figs. 3A–C. Initially, the bubbles were generated around the material, then spread through the solution after 60 s, and finally, the entire solution was covered by the bubbles. This process continued for more than 2 min (Video S1). The bubble formation with the addition of different concentrations of  $\text{H}_2\text{O}_2$  was monitored using an optical microscope and the results are shown in Figs. 3D–I. It can be seen from Fig. 3D that the bubbles were generated even in the presence of a low  $\text{H}_2\text{O}_2$  concentration of 0.05% and the bubble formation and mixing of the nanocomposite in the solution increased with the increase in  $\text{H}_2\text{O}_2$  addition. An interesting

222 observation was that the frequency of bubble generation in the medium increased until an H<sub>2</sub>O<sub>2</sub>  
223 concentration of 5%.

224

225 **Fig. 3.**

226 The mechanism for bubble generation in Fe<sub>3</sub>O<sub>4</sub>@MgO in the presence of H<sub>2</sub>O<sub>2</sub> can be  
227 explained as follows. The reaction of H<sub>2</sub>O<sub>2</sub> with MgO results in the formation of MgO<sub>2</sub> (Eq. 2)  
228 (Zeng et al., 2020). Peroxides are well known for their oxygen generation ability when they are  
229 hydrolyzed in an aqueous medium (Eq. 3). Therefore, we could not spot distinguishable peaks for  
230 O 1s spectra for the corresponding peroxides (532.4 eV for Mg-O<sub>2</sub>) (Deng et al., 2005). At the  
231 same time, the high-resolution Mg 1s spectra show an increase in the peak intensity at 1301.3 eV  
232 for Mg(OH)<sub>2</sub> after the reaction with H<sub>2</sub>O<sub>2</sub>. In addition, a small shift in the binding energy was also  
233 observed after oxidation. Further pieces of evidence for the generation of O<sub>2</sub> and Mg(OH)<sub>2</sub> were  
234 obtained by monitoring the pH and DO (Figs. 4A and B). The initial increase in DO of the  
235 solution in the medium is likely owing to the oxygen formation reaction. After the reaction was  
236 completed, the oxygen in the medium was removed and the DO decreased. Similarly, the pH of  
237 the medium increased from the initial 4.2 to 9.0 (Fig. 4). This is an indication of Mg(OH)<sub>2</sub>  
238 formation and its release into the water.



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242 **Fig. 4.**

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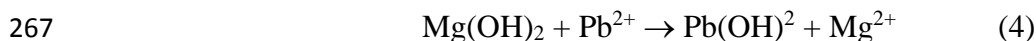
### 244 3.3. Applicability of the Fe<sub>3</sub>O<sub>4</sub>@MgO-H<sub>2</sub>O<sub>2</sub> system for the removal of contaminants

245 The second objective of the study was the evaluation of the micro-mixing system in the  
246 removal of water pollutants. To evaluate the applicability of the material for environmental  
247 remediation purposes, both organic and inorganic contaminants were selected. The inorganic  
248 contaminant described in this section was Pb<sup>2+</sup> and the organic contaminant selected was a dye,  
249 RhB. Fe<sub>3</sub>O<sub>4</sub>@MgO was added to the aqueous solution containing 10 mg L<sup>-1</sup> of pollutants (Pb<sup>2+</sup>  
250 and RhB), with H<sub>2</sub>O<sub>2</sub> (5 %). The removal efficiencies of Pb and RhB in the mixed environment  
251 are shown in Fig. 5. As shown by the results of this study, nearly 100% of the initial Pb<sup>2+</sup> and  
252 RhB were removed from the solution after 2 h. In particular, the removal of Pb<sup>2+</sup> was rapid in the  
253 initial stage of the process and slowed down after 30 min, likely owing to the competition for the  
254 adsorption sites with RhB.

255  
256 **Fig. 5.**

257 To better understand the mechanism of heavy metal removal, further investigation was  
258 performed with Pb<sup>2+</sup>. Using ICP-OES, a constant release of Mg<sup>2+</sup> to the solution was observed  
259 during the process of Pb removal (Fig. 6A). This indicates that the major mechanism for the  
260 removal of heavy metals would be the cation exchange process (Cao et al., 2012); the Mg<sup>2+</sup> ions  
261 on the surface of the material are replaced with the positively charged heavy metal ions. As  
262 described in the previous section, the surface of the material is covered with Mg(OH)<sub>2</sub> and can  
263 react with the heavy metal ions to form Pb(OH)<sub>2</sub> with the release of Mg<sup>2+</sup> to the solution (Eq. 4).  
264 The formation of Pb(OH)<sub>2</sub> on the surface of the material after Pb adsorption was confirmed by  
265 XPS analysis (Fig. 6B). The Pb 4f peaks located at 137.5 and 142.3 eV represent the lead oxides  
266 formed by the cation exchange process (Lai et al., 2019).





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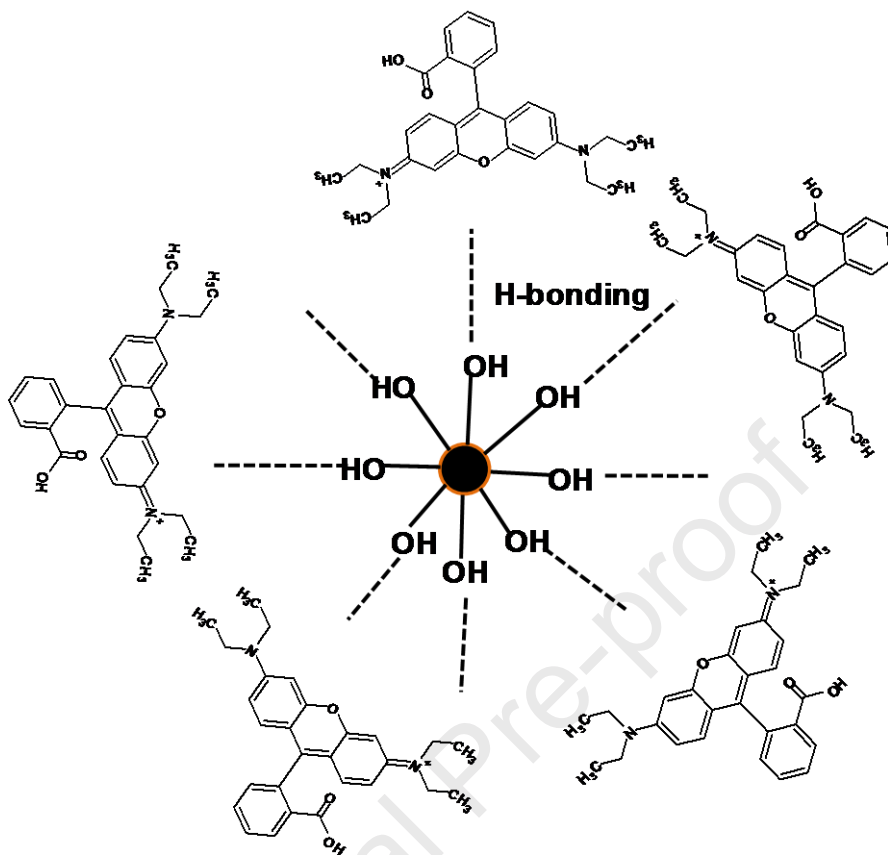
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**Fig. 6.**

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272 The organic dye removal process follows two possible mechanisms, either through the  
273 Fenton oxidation by released  $\text{Fe}^{2+}$  or by the adsorption on the surface of the nanocomposite. As  
274  $\text{Fe}_3\text{O}_4$  is present in the core, its direct reaction with  $\text{H}_2\text{O}_2$  (Fenton reaction) to generate reactive  
275 oxygen species is unlikely. To confirm this, the Fe concentration leached into the solution was  
276 monitored and a very small concentration of  $0.6 \text{ mg L}^{-1}$  of Fe was detected (Fig. S3). The  
277 homogeneous Fenton reactions with this particular Fe and Mg concentration show that the  
278 removal of RhB was insignificant (Fig. S4). Therefore, the removal of RhB is mainly through  
279 physical adsorption. As described in Eqs. 2 and 3, the first step is the formation of  $\text{Mg(OH)}_2$ . As  
280 reported for similar adsorbents, the hydrogen bonding between  $-\text{OH}$  present in the  $\text{Mg(OH)}_2$  and  
281 nitrogen in the dye molecule favors the adsorptive removal of these types of dyes (Scheme 1)  
282 (Lin and Wang, 2009).





283

284 **Scheme 1:** Mechanism for the adsorptive removal of RhB in the  $\text{Fe}_3\text{O}_4@\text{MgO}-\text{H}_2\text{O}_2$  system

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### 287 3.4. Effects of operational parameters

288 The removal efficiency of the process depends on various factors such as concentrations  
 289 of  $\text{Fe}_3\text{O}_4@\text{MgO}$ ,  $\text{H}_2\text{O}_2$ , and the initial pH. Hence, to obtain a better performance of the system,  
 290 the removal efficiency was evaluated at varying concentrations of the nanomaterial and  $\text{H}_2\text{O}_2$  and  
 291 pH. The results of  $\text{Pb}^{2+}$  removal under varying operating conditions are presented in Fig. 7 and  
 292 that of RhB are shown in Supporting Information (Fig. S5).

#### 293 *Effect of $\text{H}_2\text{O}_2$ concentration*



294 The  $\text{H}_2\text{O}_2$  concentration (0–10%) influenced the adsorption of  $\text{Pb}^{2+}$  (10 ppm) at a fixed  
295  $\text{Fe}_3\text{O}_4@\text{MgO}$  dose ( $0.8 \text{ g L}^{-1}$ ) (Fig. 7A). The removal efficiency of 20% was observed without  
296 the addition of  $\text{H}_2\text{O}_2$ , and the removal efficiency increased with the increase of reaction time.  
297 Interestingly, it is clear from Fig. 3H that even a small addition of  $\text{H}_2\text{O}_2$  (0.5%) resulted in 34%  
298 Pb removal after 15 min which increased to 89% after 60 min. When the concentration of  $\text{H}_2\text{O}_2$   
299 increased to 5% and 10%, more than 90% removal was attained within a short period of 15 min.  
300 Instead, for RhB, the removal was negligible in the presence of  $\text{Fe}_3\text{O}_4@\text{MgO}$  without  $\text{H}_2\text{O}_2$ .  
301 However, the removal of RhB increased to 75%, 85%, and 100% with the increase in  $\text{H}_2\text{O}_2$   
302 concentrations to 0.5%, 1%, and 10%, respectively.

303 It is clear from the XPS analysis that in the absence of  $\text{H}_2\text{O}_2$ , the adsorbent layer exists as  
304 MgO. Consequently, there will not be any bubble formation and thus, the system remains  
305 immobile. This implies that the bubble formation and subsequent mixing effect have a prominent  
306 role in the removal of pollutants. Moreover, when the concentration of  $\text{H}_2\text{O}_2$  increased, the  
307 material started moving through the solution to capture  $\text{Pb}^{2+}$  ions along with the generation of  
308 bubbles.

### 309 ***Effect of $\text{Fe}_3\text{O}_4@\text{MgO}$***

310 The effect of  $\text{Fe}_3\text{O}_4@\text{MgO}$  concentration ( $0.2\text{--}1 \text{ g L}^{-1}$ ) was evaluated at a fixed  $\text{H}_2\text{O}_2$   
311 concentration of 5% (Fig. 7B). A clear difference in the removal efficiency was observed during  
312 the initial period. Removal efficiencies of 0%, 46%, 63%, 80%, and 81% were observed with 0,  
313 0.2, 0.4, 0.8, and  $1 \text{ g L}^{-1}$  of  $\text{Fe}_3\text{O}_4@\text{MgO}$ , respectively. A similar removal pattern was observed  
314 for RhB. This difference could be correlated with the lack of adsorption sites at a low dose of the  
315 material. The adsorption sites increased with the increase in adsorbent concentration and reaction  
316 with  $\text{H}_2\text{O}_2$ .





### 317 *Effect of pH*

318 pH is another important parameter in the remediation process, and therefore experiments  
319 were conducted at different initial pHs such as 2, 5, 7.5, 9, and 11 with the optimized condition of  
320 H<sub>2</sub>O<sub>2</sub> concentration of 5% and Fe<sub>3</sub>O<sub>4</sub>@MgO dose of 0.8 g L<sup>-1</sup>. As in the previous cases, a  
321 noticeable effect was observed at the initial time of 15 min. The removal efficiencies were 62%,  
322 63%, 85%, 84%, and 83% at pH 2, 5, 7.5, 9, and 11, respectively for Pb<sup>2+</sup> ion removal (Fig. 7C).  
323 However, for RhB, removal efficiencies of 53%, 63%, 62%, 68%, and 89% were observed after  
324 45 min at these pHs.

325 Since the isoelectric point of MgO is 11, the difference in the adsorption could not be  
326 discussed in relation to the material property (Wang et al., 2017). Therefore, the removal  
327 efficiencies under varying pH could be due to the different speciation of Pb<sup>2+</sup>. The Pb species  
328 exist as Pb<sup>2+</sup>, Pb(OH)<sup>+</sup>, Pb(OH)<sub>2</sub><sup>0</sup>, and Pb(OH)<sub>3</sub><sup>-</sup> at pH < 6, 8, > 9, and > 12, respectively (Sheng  
329 et al., 2009; Mohan et al., 2017). When the pH is less than 6, the major species is Pb<sup>2+</sup>, and the  
330 competitive adsorption between H<sup>+</sup> and Pb<sup>2+</sup> on the surface of the material leads to a low  
331 adsorption capacity. Likewise, when the pH increases the precipitation of hydroxides occurs to  
332 enhance the removal efficiency. This is further supported by the lower solubility product of  
333 Pb(OH)<sub>2</sub> ( $k_{sp} = 1.43 \times 10^{-20}$ ) than that of Mg(OH)<sub>2</sub> ( $5.61 \times 10^{-12}$ ) (Ponomarev et al., 2019).  
334 Moreover, the electrostatic repulsion of RhB from the MgO surface at acidic pH results in  
335 reduced removal. Similarly, electrostatic attraction between the positively charged RhB and the  
336 negatively charged Fe<sub>3</sub>O<sub>4</sub>@MgO should enhance their removal at high pH (Liu et al., 2020).

337  
338  
339 **Fig. 7.**



### 340 **3.5. Evaluation of Fe<sub>3</sub>O<sub>4</sub>@MgO-H<sub>2</sub>O<sub>2</sub> practical application**

341 To attain our third objective, the performance of the Fe<sub>3</sub>O<sub>4</sub>@MgO-H<sub>2</sub>O<sub>2</sub> particles under  
342 environmentally relevant conditions, some supplementary experiments such as reusability,  
343 removal of other heavy metals, and removal efficiency in real groundwater (from a rural area in  
344 South Korea) and river water (collected from Hyeongsan River, South Korea) spiked with Pb<sup>2+</sup>  
345 were studied. The physicochemical characteristics of the ground and river water are listed in  
346 Supporting Information (Table S1).

347 The results of the reusability test are shown in Supporting Information (Fig. S6). It was  
348 found that more than 90% of the initial Pb was removed in the first cycle, and subsequently, the  
349 adsorption capacity was reduced. This is likely due to the leaching of Mg ions from the surface of  
350 MgO@Fe<sub>3</sub>O<sub>4</sub>. In addition, the capacity of MgO@Fe<sub>3</sub>O<sub>4</sub> for other heavy metals such as Cd, Ni,  
351 Zn, Co, and Cu was also investigated and the results are shown in Fig. 8A. As shown by the  
352 results, all the selected heavy metals could be removed effectively by the MgO@Fe<sub>3</sub>O<sub>4</sub>-H<sub>2</sub>O<sub>2</sub>  
353 system. The experiments with ground and river water spiked with Pb<sup>2+</sup> showed that there was no  
354 significant difference in the removal efficiencies between them even when they contained  
355 different co-existing or interfering ions (Fig. 8B), showing good environmental adaptation  
356 capability of the system.

#### 359 **Fig. 8.**

360 The Fe<sub>3</sub>O<sub>4</sub>@MgO nanocomposite-H<sub>2</sub>O<sub>2</sub> system possessed several advantages over other  
361 similar systems (Fe<sub>3</sub>O<sub>4</sub>@MnO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub>) (Kang et al., 2019; Ye et al., 2021a), the MgO based  
362 nanocomposites (Mohan et al., 2017; Rahdar et al., 2019; Liu et al., 2020; Guo and Bulin, 2021).

363 In contrast to other MgO-based materials and other adsorbents, the present system allowed  
364 superior activity for the removal of heavy metals concomitant with dyes without any external  
365 shaking. Most importantly, in comparison with the other micro-mixing systems, the present study  
366 doesn't require surfactants. We anticipate that the findings presented in this study will offer a  
367 promising strategy for the on-site removal of a variety of pollutants from contaminated water.  
368 Furthermore, it is proposed that the Fe<sub>3</sub>O<sub>4</sub>@MgO nanocomposite could be used along with other  
369 oxidants such as persulfate and ozone to induce the oxidation of pollutants. The increase of pH  
370 with the addition of Fe<sub>3</sub>O<sub>4</sub>@MgO to the aqueous solution will be beneficial for ozone activation.  
371 In the same way, polymeric membranes could also be fabricated with Fe<sub>3</sub>O<sub>4</sub>@MgO for water  
372 purification and other environmental applications.

373

#### 374 **4. Conclusions**

375 We have verified that the Fe<sub>3</sub>O<sub>4</sub>@MgO nanocomposite is very effective in the generation of  
376 bubbles in the presence of H<sub>2</sub>O<sub>2</sub>. As a result, the generation of oxygen bubbles in the presence of  
377 H<sub>2</sub>O<sub>2</sub> promoted the agitation of the solution containing Fe<sub>3</sub>O<sub>4</sub>@MgO. The bubble generation and  
378 the following self-mixing mechanism enhanced the simultaneous removal of both Pb<sup>2+</sup> and  
379 rhodamine B with exceptional stability. The effect of H<sub>2</sub>O<sub>2</sub> concentration and initial pH revealed  
380 that the adsorption was induced at a low H<sub>2</sub>O<sub>2</sub> concentration of 0.05% and is effective over a  
381 wide pH range (2.5 to 11). The data obtained from the XPS and ICP-OES analyses showed that  
382 the adsorption of Pb<sup>2+</sup> occurred via the cation exchange mechanism. The unfeasibility of the  
383 homogeneous Fenton reaction in this system showed that adsorption by Fe<sub>3</sub>O<sub>4</sub>@MgO is the  
384 predominant mechanism for the removal of RhB. The nearly similar removal efficiencies in pure,  
385 river, and groundwater matrices and for different heavy metals is an important advantage. Thus,



386 Fe<sub>3</sub>O<sub>4</sub>@MgO could be proposed as an efficient adsorbent for the removal of a variety of water  
387 contaminants from their sources.

### 388 **Conflicts of interest**

389 There are no conflicts to declare

### 390 **Acknowledgment**

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393

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561



## Figure captions

562  
563  
564 **Fig. 1.** Scanning electron microscopy images (A and B), energy dispersive X-ray spectra (C), and  
565 X-ray diffraction pattern (D) of Fe<sub>3</sub>O<sub>4</sub>@MgO nanocomposites.

566  
567 **Fig. 2.** Mg 1s X-ray photoelectron spectroscopy (XPS) spectra (A and C) and O 1s XPS spectra  
568 (B and D) of Fe<sub>3</sub>O<sub>4</sub>@MgO before and after H<sub>2</sub>O<sub>2</sub> treatment.

569  
570 **Fig. 3.** Photographic images of bubble formation with the addition of Fe<sub>3</sub>O<sub>4</sub>@MgO in the  
571 solution containing H<sub>2</sub>O<sub>2</sub>; 1 s (A), 60 s (B), and 90 s (C). Microscopic images (scale bar 10 μm)  
572 of bubble generation with the addition of 0.05% (D), 0.5% (E), 1% (F), 2% (G), 5% (H), and  
573 10% (I) H<sub>2</sub>O<sub>2</sub>.

574  
575 **Fig. 4.** Time-dependent changes in the pH (A) and dissolved oxygen (DO) (B) of deionized water  
576 in the Fe<sub>3</sub>O<sub>4</sub>@MgO-H<sub>2</sub>O<sub>2</sub> system. Experimental conditions: [Fe<sub>3</sub>O<sub>4</sub>@MgO] = 0.8 g/L, [H<sub>2</sub>O<sub>2</sub>] =  
577 5%.

578  
579 **Fig. 5.** Simultaneous removal of Pb<sup>2+</sup> and RhB by Fe<sub>3</sub>O<sub>4</sub>@MgO with the addition of H<sub>2</sub>O<sub>2</sub>.  
580 Experimental conditions: [Fe<sub>3</sub>O<sub>4</sub>@MgO] = 0.8 g L<sup>-1</sup>, [H<sub>2</sub>O<sub>2</sub>] = 5%, and [Pollutants] = 10 mg L<sup>-1</sup>.

581  
582 **Fig. 6.** Time-dependent release of Mg<sup>2+</sup> ions from Fe<sub>3</sub>O<sub>4</sub>@MgO during the adsorption reaction  
583 (A) and X-ray photoelectron spectroscopy of Pb 4f spectra of Fe<sub>3</sub>O<sub>4</sub>@MgO particles after the



584 adsorption of  $\text{Pb}^{2+}$  (B). Experimental conditions:  $[\text{Fe}_3\text{O}_4@\text{MgO}] = 0.8 \text{ g L}^{-1}$ ,  $[\text{H}_2\text{O}_2] = 5\%$ , and  
585  $[\text{Pb}^{2+}] = 10 \text{ mg L}^{-1}$ .

586  
587 **Fig. 7.** Effect of  $\text{H}_2\text{O}_2$  (A), TX-100 (B),  $\text{Fe}_3\text{O}_4@\text{MgO}$  dose (C), and pH (D) on the removal of  
588  $\text{Pb}^{2+}$  in the  $\text{Fe}_3\text{O}_4@\text{MgO}-\text{H}_2\text{O}_2$  system. Experimental conditions:  $[\text{Pb}^{2+}] = 10 \text{ mg L}^{-1}$ .

589  
590 **Fig. 8.** Removal of  $\text{Pb}^{2+}$  from deionized, ground, and river water (A) and removal efficiency of  
591 various heavy metals (B) by the  $\text{Fe}_3\text{O}_4@\text{MgO}-\text{H}_2\text{O}_2$  system. Experimental conditions:  
592  $[\text{Fe}_3\text{O}_4@\text{MgO}] = 0.8 \text{ g L}^{-1}$ ,  $[\text{H}_2\text{O}_2] = 5\%$ ,  $[\text{Pb}^{2+}] = 10 \text{ mg L}^{-1}$ , and pH 7.5

593

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# Figures

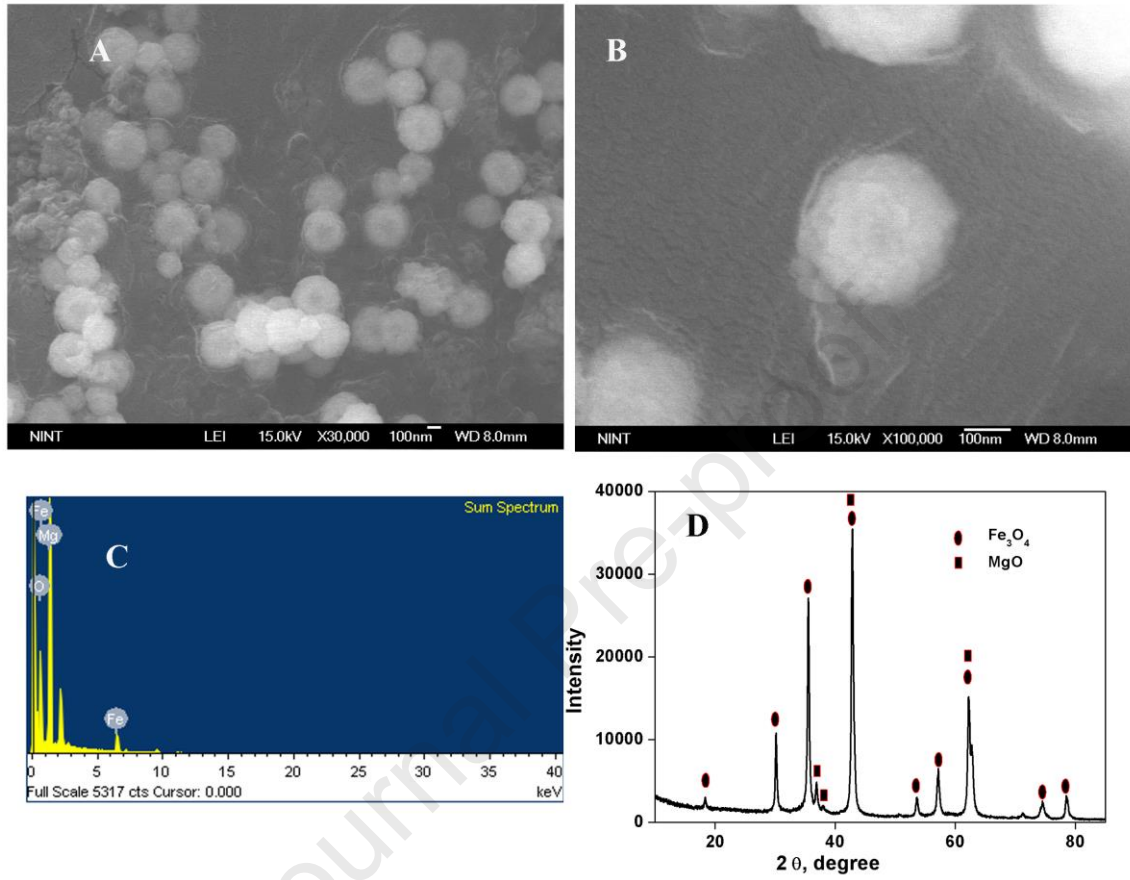


Fig. 1

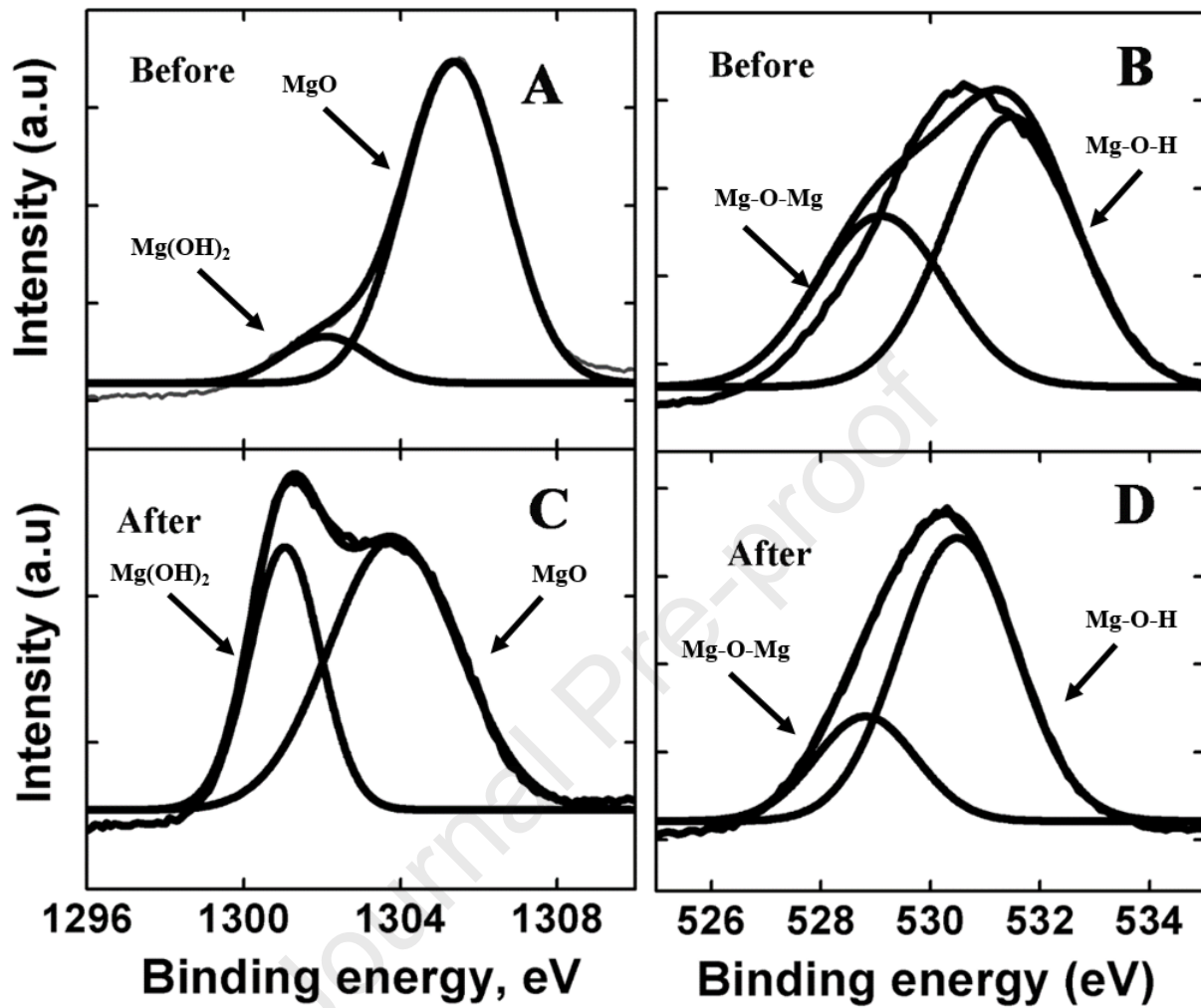
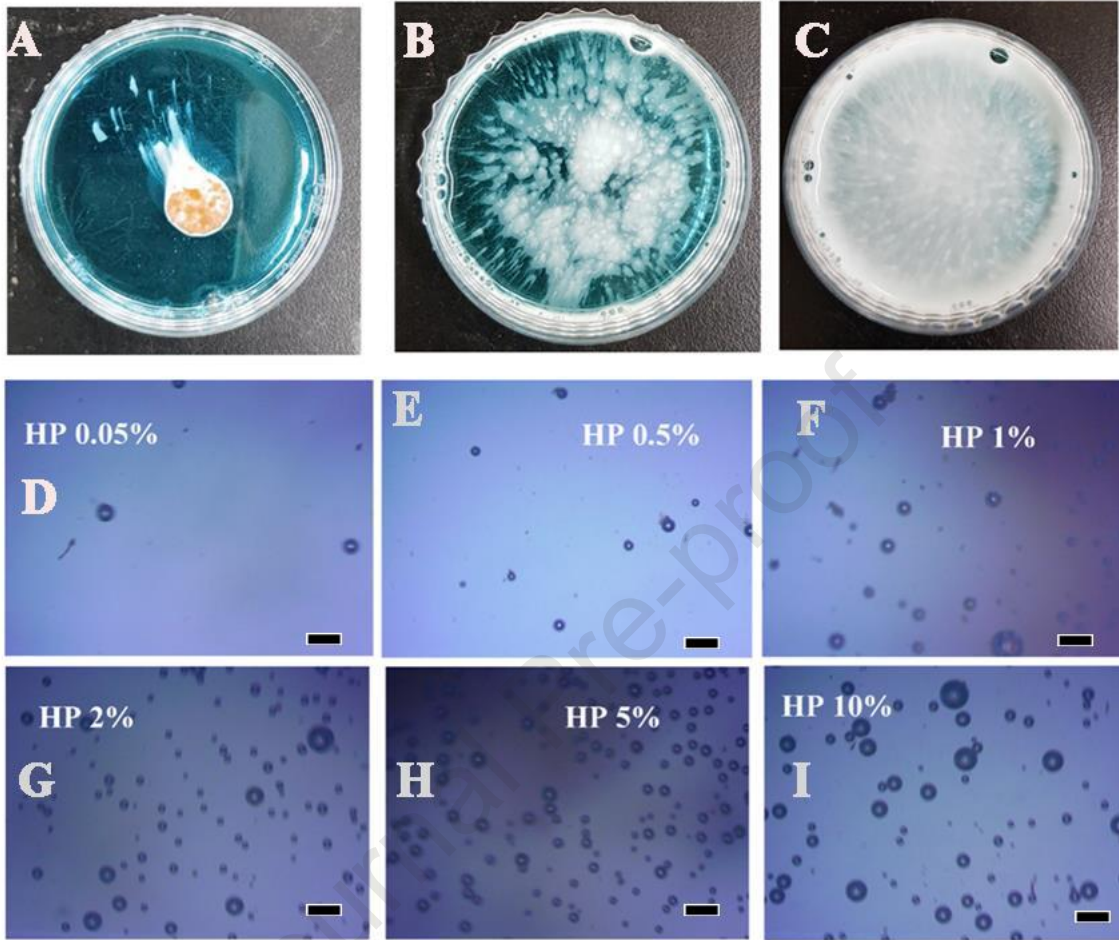


Fig. 2



**Fig. 3**



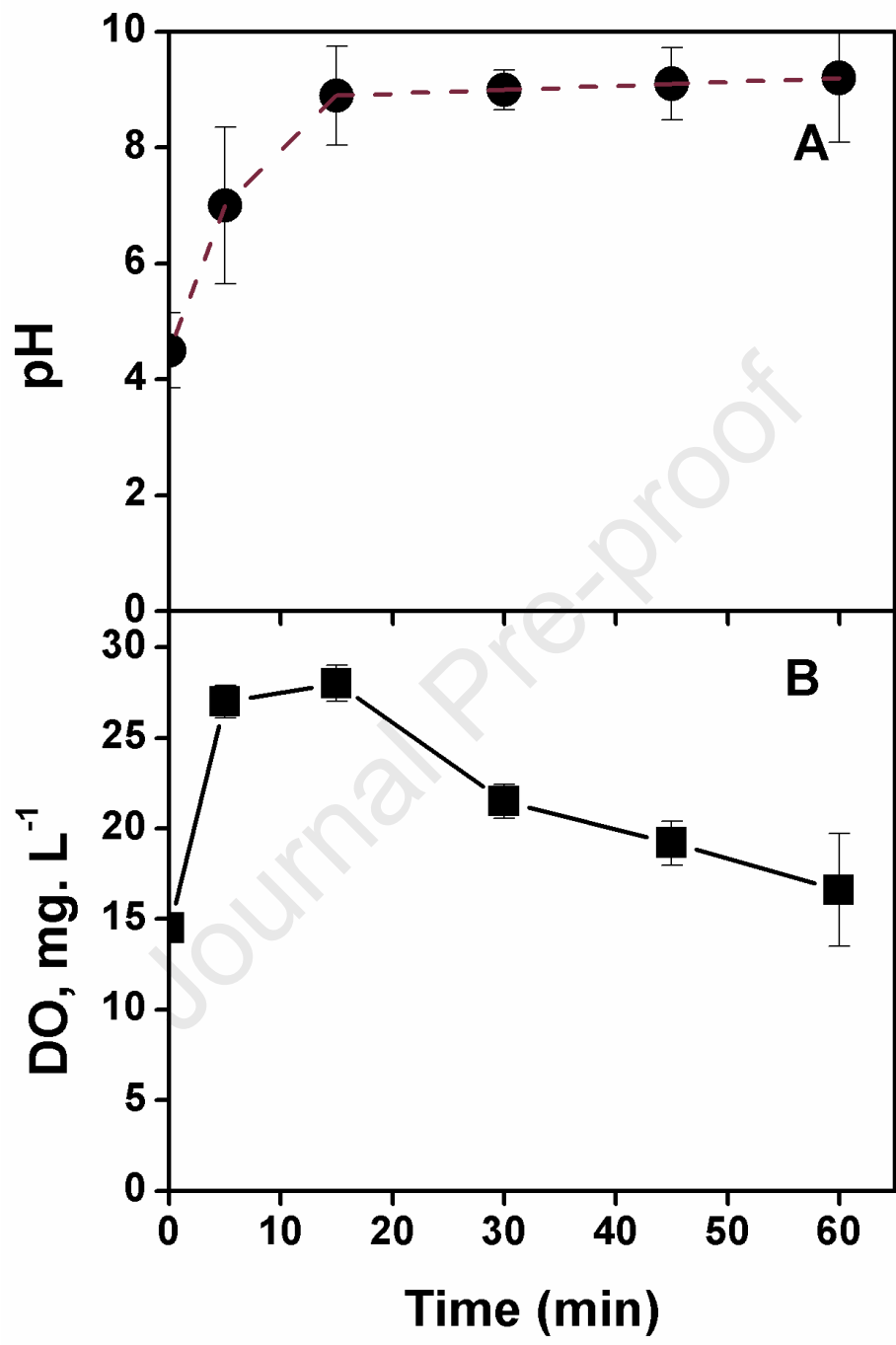


Fig. 4

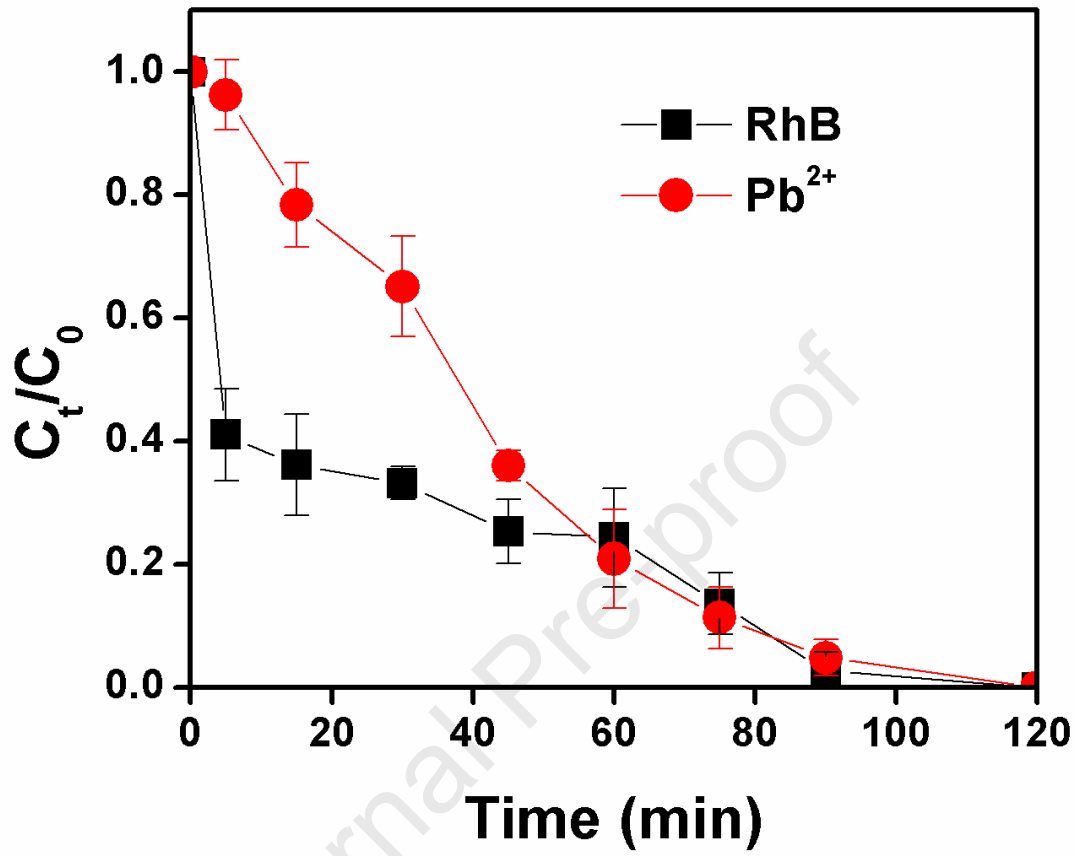


Fig. 5

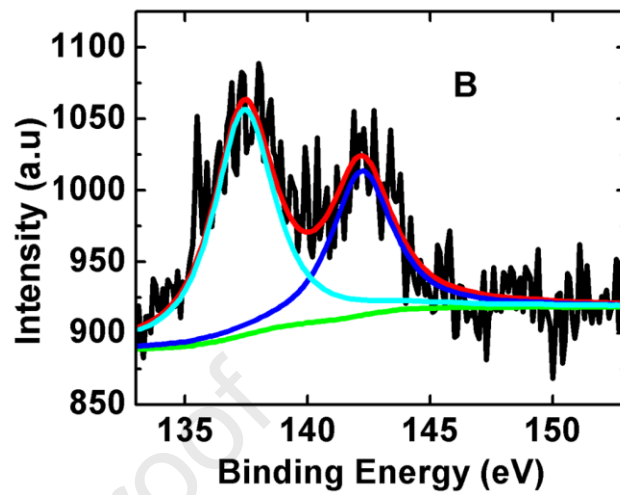
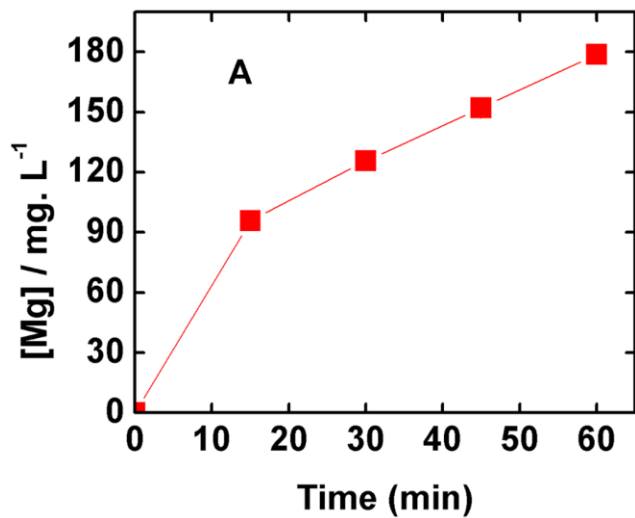


Fig. 6

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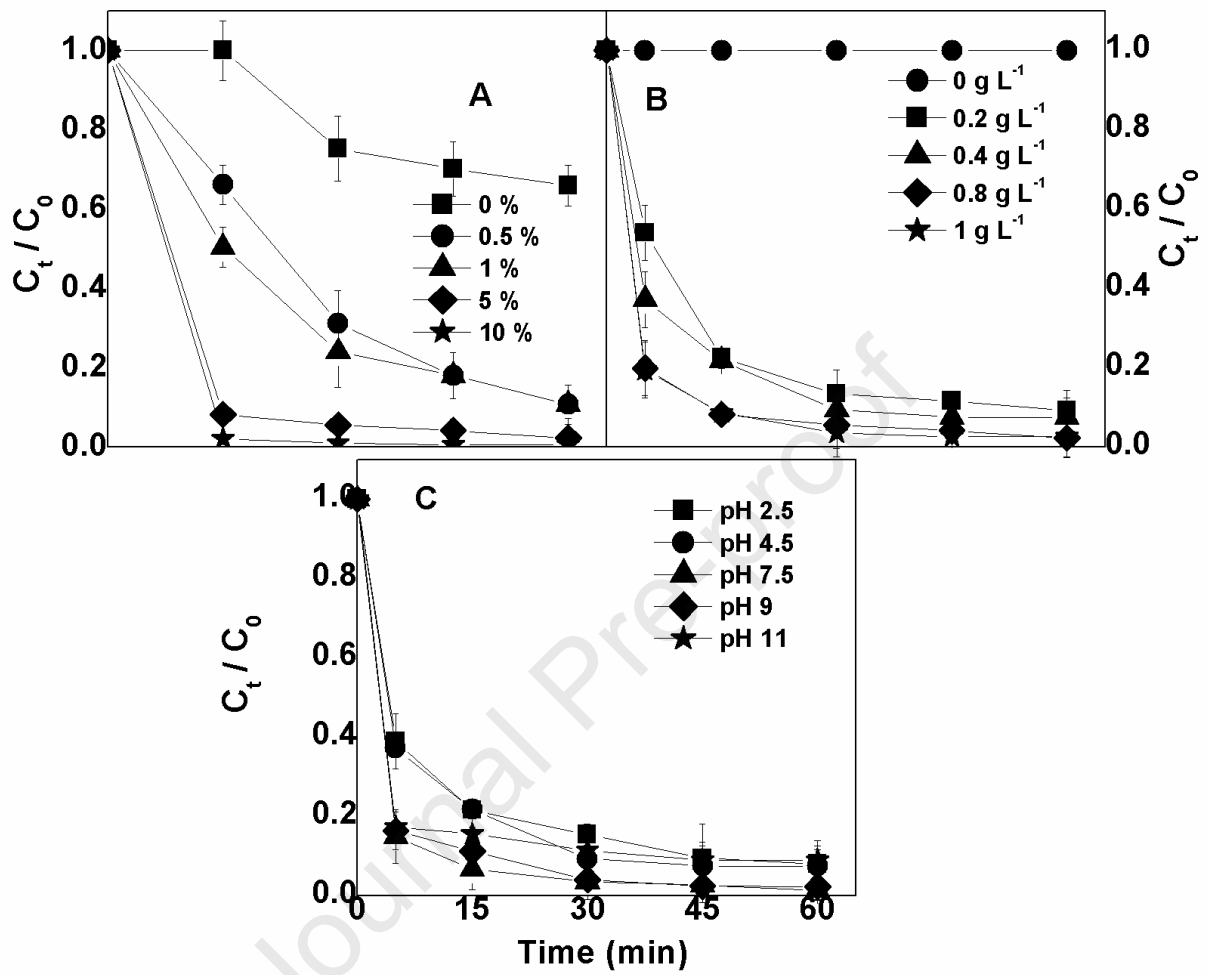


Fig. 7



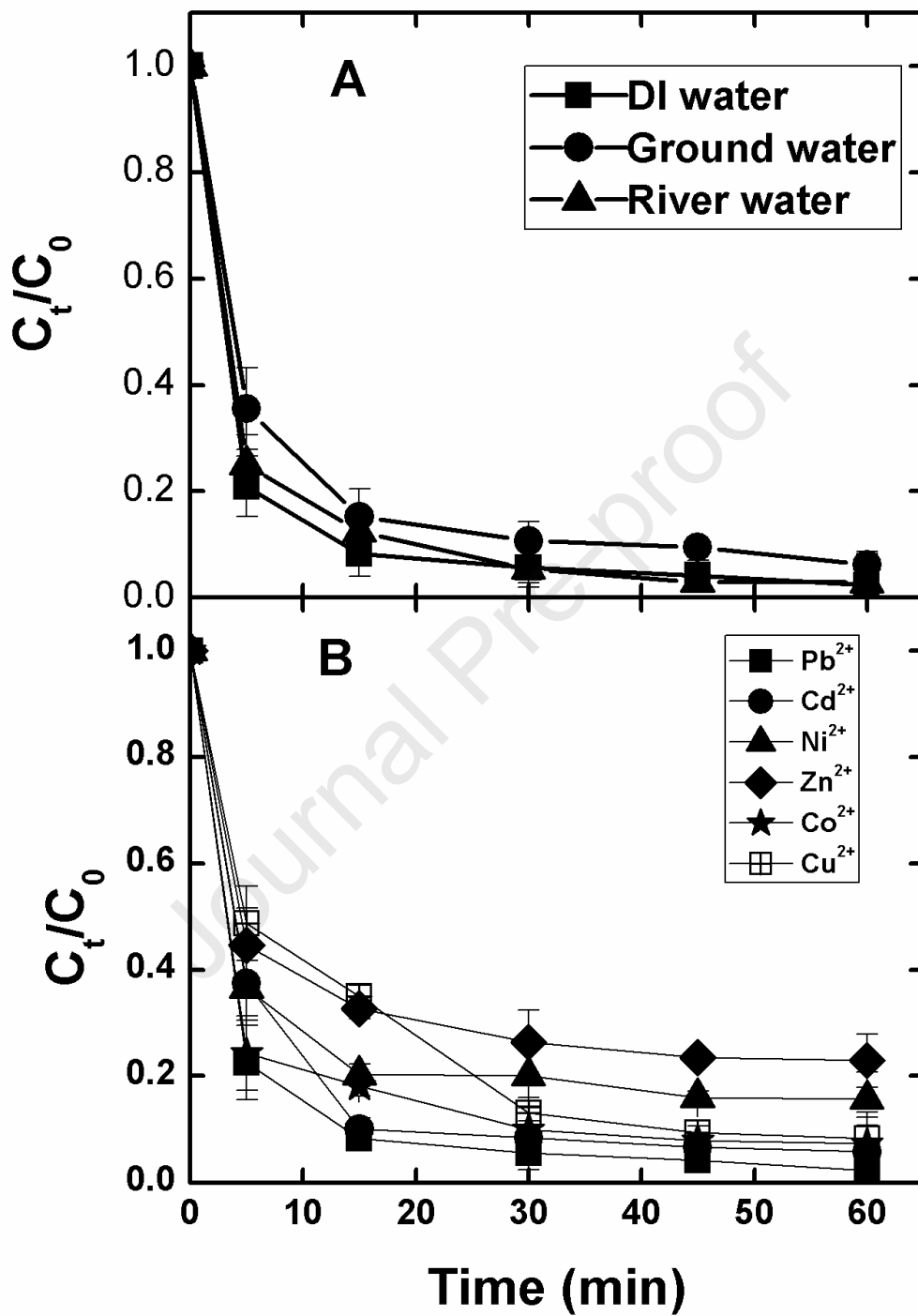


Fig. 8



## Highlights

- Heavy metal ( $\text{Pb}^{2+}$ ) and organic dye (Rhodamine B) removal with  $\text{H}_2\text{O}_2$  addition to the solution containing  $\text{Fe}_3\text{O}_4@\text{MgO}$ .
- Pollutants are removed by the adsorption mechanism.
- The bubble propulsion and self-mixing process enhanced the removal efficiency.
- $\text{Fe}_3\text{O}_4@\text{MgO}$  is efficient in environmentally relevant water matrices like ground and river water.

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