Novel Technology for the Removal of Brilliant Green from Water: Influence of Post-Oxidation, Environmental Conditions, and Capping

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ABSTRACT: Chemical dyes are used in a wide range of anthropogenic activities and are generally not biodegradable. Hence, sustainable recycling processes are needed to avoid their accumulation in the environment. A one-step synthesis of $\text{Fe}_{\text{core}}$-$\text{maghemite}_{\text{shell}}$ (Fe-MM) for facile, instantaneous, cost-effective, sustainable, and efficient removal of brilliant green (BG) dye from water has been reported here. The homogenous and monolayer type of adsorption is, to our knowledge, the most efficient, with a maximum uptake capacity of 1000 mg g$^{-1}$, for BG on Fe-MM. This adsorbent was shown to be efficient in occurring in time-scales of seconds and to be readily recyclable (ca. 91%). As iron/iron oxide possesses magnetic behavior, a strong magnet could be used to separate Fe-MM coated with BG. Thus, the recycling process required a minimum amount of energy. Capping Fe-MM by hydrophilic clay minerals further enhanced the BG uptake capacity, by reducing unwanted aggregation. Interestingly, capping the adsorbent by hydrophobic plastic (low-density polyethylene) had a completely inverse effect on clay minerals. BG removal using this method is found to be quite selective among the five common industrial dyes tested in this study. To shed light on the life cycle analysis of the composite in the environment, the influence of selected physicochemical factors ($T$, pH, $\nu$, $O_3$, and NO$_3$) was examined, along with four types of water samples (melted snow, rain, river, and tap water). To evaluate the potential limitations of this technique, because of likely competitive reactions with metal ion contaminants in aquatic systems, additional experiments with 13 metal ions were performed. To decipher the adsorption mechanism, we deployed four reducing agents (NaBH$_4$, hydrazine, LiAlH$_4$, and polyphenols in green tea) and NaBH$_4$, exclusively, favored the generation of an efficient adsorbent via aerial oxidation. The drift of electron density from electron-rich Fe$^{3+}$ to maghemite shells was attributed to be responsible for the electrostatic adsorption of N$^+$ in BG toward Fe-MM. This technology is deemed to be environmentally sustainable in environmental remediation, namely, in waste management protocol.

1. INTRODUCTION

Dye molecules usually consist of complex aromatic frameworks and exhibit bright colors. Such aromatic frameworks also exhibit long-term stability, preventing biodegradation. For extensive and versatile usage of dye generates serious pollution problems in environmental water bodies. Dyes mainly enter food products via industrial emissions (beverage industries, waste water of textiles, printing practices, etc.), causing serious health hazards. Moreover, the great visibility of dyes, even at trace concentrations, is generally related to less-dissolved oxygen in aquatic habitats, decreasing the penetration of sunlight along with photosynthetic activities. In this way, ecological harm may spread downstream to agricultural or aquaculture regions, affecting aquatic flora and fauna. It is, therefore, obligatory for some places to exercise proper treatment before the disposal of such wastewater.

Brilliant green (BG) products include a group of dye compounds which have many uses, namely, biological staining, dermatological agent, veterinary medicine, and inhibitor of mold/intestinal parasites/fungus propagation. Global demand for coatings and paints is predicted to rise 3.7 percent per year to $4.7$ million metric tons in 2020, valued at $193$ billion. The growing consumer demand for dye compounds in various end-use segments (such as plastics, textiles, food, and paints & coating) is projected to act as a major growth factor for the global market over the following few years. Accumulation of dyes in the environment, as nearly indestructible toxicants, is thereby a great concern. BG, a widely used dye, travels to incorporate itself in aquatic systems (highly soluble, $100$ g/L) and in the atmosphere (because of high volatility of the aromatic compound). Thereby, the development of green recycling processes are warranted.

In the past decade, there have been considerable efforts to remove BG from water. Biological molecules, zinc oxide, and...
activated carbon are very common in comparison to other sorbents. We have summarized the results of BG removal capacities of different groups in Table S1, Supporting Information. The use of iron oxide in this context is rare (Ishaq et al.9) and magnetite impregnated bentonite, reported by Ishaq et al., is probably the most efficient BG adsorbent (877 mg·g⁻¹) so far.9 However, maximum uptake capacity, time, recyclability, applicable conditions/versatility, cost, and simplicity of operation are some major challenges for the prototype/industrial use.10

Highly environmentally available iron and iron oxide (a major component of airborne dust particles)11 have also been found to be of great interest in environmental remediation and understanding of atmospheric processes.12−14 The surface morphology and passivation/capping of the nanoparticles can be manipulated to obtain a fruitful remediation application. The property of water affinity (hydrophobicity/hydrophilicity) of the surface is also noteworthy in this regard.12−16

To have versatile applicability of a proposed remediation technique, the effect of environment and co-contaminants in environmentally available conditions should be accounted for carefully, along with the rate, sustainability, efficiency, cost, and simplicity of the designed method.12,17,18

This research is aimed at the development of a recyclable and sustainable protocol for BG dyes. As such, an efficient synthesis process of maghemite (γ-Fe₂O₃), hematite (α-Fe₂O₃), and magnetite (Fe₃O₄) are all vastly commercially and environmentally available.19−21 However, unlike Fe−MM, they could not at all adsorb BG [Figure 1a]. We used nanopowders of maghemite (<50 nm), hematite (30−50 nm), magnetite (50−70 nm), and Fe (35−45 nm) from Sigma-Aldrich. However, they could not at all decrease the absorbance of BG in water. Hence, the synergism between maghemite and Fe in Fe−MM made Fe−MM an efficient adsorbent of BG.

It is to be noted that such commercially available Fe/Fe-oxides enhanced the absorbance of BG, probably because of the breakage of self-aggregation of the dye molecules.22,23 The %removal (PR) was ~77.2 for 10 mL of 100 mg/L BG with 1.0 mg of Fe−MM and insignificant with the same mass of efficiency. We will herein discuss the potential of a new reagent for recycling of the anthropogenic dye in the environment. We also explore the role of reducing agents during the synthesis of Fe−MM and the strength and limitation of the green method.

2. RESULTS AND DISCUSSION

We performed complementary synthesis, characterization, and adsorption studies. The following section explores all systematic steps related to our results and the implication of this research.

2.1. Fe−MM: A Highly Efficient Adsorbent for BG. We found Fe−MM to be the most efficient and a fast adsorbent to adsorb BG at room temperature, and absorbance (at 623 nm) of the BG solution was dramatically decreased in the presence of Fe−MM. We have compared our maximum adsorption capacity (Qₘ) of 1.00 g·g⁻¹ with 47 other adsorbents in Table S1, Supporting Information. To the best of our knowledge, Qₘ ≥ 1 has not been reported so far.

Fe powder, maghemite (γ-Fe₂O₃), hematite (α-Fe₂O₃), and magnetite (Fe₃O₄) were all natural, nontoxic, and widely available in the airborne dust particles and soil. The process was found not only to be fast, cost-effective, and facile, but also the most efficient, to the best of our knowledge. We studied the effect of environmental conditions, surface manipulations, and the effect of coating on adsorbent
other Fe/Fe-oxides, as obtained from absorption spectra [Figure 1b].

\[
\text{\% removal} = 100 \times \left( \frac{C_0 - C_e}{C_0} \right)
\]

(1)

where \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of BG in the solution, respectively.

We also replaced BG dye by other commonly available industrial dyes (safranin-O, malachite green, methylene blue, and rhodamine B) and discovered that PR was insignificant for other dyes. Even though the chemical structure of BG (triarylmethane dye) is closely related to malachite green, Fe\(^{\text{III}}\) could remove BG selectively, indicating the specificity of Fe\(^{\text{III}}\) as a BG adsorbent [Figure 1c].

The concentration of BG was varied (25–130 mg/L) with a fixed mass (1.0 mg) of Fe\(^{\text{III}}\) and PR was decreased gradually with the increased concentration of BG, as shown in Figure 1d.

Fe\(^{\text{III}}\) was shown to be an efficient adsorbent for BG, and the adsorption process was determined to be physisorption. In physisorption, the electronic structure of the atom or molecule is hardly perturbed upon the process of adsorption. It is mainly caused by van der Waals forces. Such intermolecular forces depend on the nature of molecules and the distance between them. Thus, selectivity comes in physisorption. Leed et al.\(^{24}\) have reported the relation of electronic structure in physisorption and chemisorption. Fe\(^{\text{III}}\) was selective to BG because of the specificity of the electronic structure in binding sites of the adsorbents and interaction sites of the adsorbates.

2.2. Characterization of Fe\(^{\text{III}}\). To extensively understand the properties of Fe\(^{\text{III}}\), we characterized Fe\(^{\text{III}}\) using several spectroscopic and microscopic techniques [Figure 2]. X-ray diffraction (XRD) analyses indicated that Fe\(^{\text{III}}\) was a mixture of Fe (47.60%) and maghemite (52.40%) [Figure S1, Supporting Information]. As X-ray photoelectron spectroscopy (XPS) analysis indicated the property of the surface, we found \( \sim 100\% \) Fe in Fe\(^{\text{III}}\) at +3 oxidation states. The binding energies (\( \sim 710.78 \) eV for Fe\(^{\text{III}}\) 2p\(_{3/2}\) and \( \sim 724.42 \) eV for Fe\(^{\text{III}}\) 2p\(_{1/2}\); respectively) correspond to Fe(III) of maghemite.\(^{25}\)

Likewise, the positions of the satellite peaks for the Fe 2p\(_{1/2}\) and Fe 2p\(_{3/2}\) peaks are also very sensitive to the iron oxidation states and are often considered for qualitative determination of the ionic states of Fe [Figure 2]. They clearly indicated that the surface of Fe\(^{\text{III}}\) was maghemite, because of the aerial oxidation of Fe. The in situ-produced maghemite, covering the Fe core, was likely the main adsorbent. Thus, Fe\(^{\text{III}}\) was Fe\(_{\text{core}}\)–maghemite\(_{\text{shell}}\).

For further characterizations of Fe\(^{\text{III}}\), we performed transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) analysis. Fe\(^{\text{III}}\) was composed of nanowires with \( \sim 30 \) nm diameter, consisting of linearly arranged nanospheres. A lattice fringe of 0.29 nm is the indication of the (220) plane of maghemite.\(^{26}\) In another region, we found the indication of the (111) plane of inverse spinel maghemite [fringe spacing of 0.470 nm] as well as the (101) plane of goethite [fringe spacing of 0.409 nm].\(^{27,28}\) Such an observation, again, supported that Fe\(^{\text{III}}\) was Fe\(_{\text{core}}\)–maghemite\(_{\text{shell}}\).

Figure 2. (a) Compositional analysis from XRD of Fe\(^{\text{III}}\); (b) wide-range and high-resolution XPS spectra of Fe\(^{\text{III}}\); (c) TEM and HRTEM image of Fe\(^{\text{III}}\); and (d) high- and low-resolution SEM image of Fe\(^{\text{III}}\).
ginger has been disclosed to be a highly efficient adsorbent for BG in this paper.

### 2.3. Adsorption Isotherm for Maximal Uptake

To evaluate the efficacy of BG removal from water via Fe−MM nano-ginger, a nano-trap, a fixed amount of BG (10 mL of 100 mg/L) was added to various masses of Fe−MM. After that, our data were fitted using three adsorption isotherms (Langmuir, Freundlich, and Elovich) to obtain the value of maximum adsorption capacity [Figure 3]. For the case of the Langmuir adsorption isotherm, homogenous adsorption sites and monolayer coverage are assumed, and the following equation is followed.

\[
\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}
\]

(Ce and qe denote the equilibrium concentration of BG (mg L\(^{-1}\)) in solution and adsorbed BG (g) per gram of Fe−MM, respectively. The maximum adsorption capacity (Q_m) was calculated from the slope of the best-fitted straight line of Ce/qe against Ce.)

Heterogeneous adsorption sites are considered in the Freundlich adsorption isotherm, homogenous adsorption sites and monolayer coverage are assumed, and the following equation is followed.

\[
\log(q_e) = \log(K_F) + \frac{1}{n} \log(C_e)
\]

The slope of the best-fitted straight line of log(qe) versus log(Ce) gives the adsorption intensity (n) and Freundlich constant (K_F). Q_m can be found by substituting Ce by C_0 (initial BG concentration in solution).

The Elovich adsorption isotherm describes multilayer adsorption, with the following equation.

\[
\ln\left(\frac{q_e}{C_e}\right) = -\frac{q_e}{K_E Q_m} + \ln(K_E Q_m)
\]

The data of adsorption, closer to 100%, were excluded during the plotting of adsorption isotherms, as isotherms are valid, when there is equilibrium between BG in the solution and the adsorbent. The Q_m for Langmuir was calculated to be 1.00 g g\(^{-1}\) and R\(^2\) (the coefficient of determination) was 0.997. This adsorption procedure did not really follow Freundlich and Elovich adsorption isotherms (R\(^2\) were 0.732 and 0.667, respectively). Therefore, homogeneous and monolayer coverage of BG on Fe−MM with Q_m of 1.00 g g\(^{-1}\) was inferred.

The crucial characteristics of the Langmuir isotherm are expressed by a dimensionless constant, equilibrium parameter R_L.

\[
R_L = \frac{1}{1 + K_L C_0}
\]

where K_L and C_0 denote the Langmuir constant and the highest initial dye concentration (mg L\(^{-1}\)), respectively. The value of R_L specifies the kind of isotherm, that is, to be unfavorable (R_L > 1), linear (R_L = 1), favorable (0 < R_L < 1), or irreversible (R_L = 0). The absolute R_L value (0.0086) in our experiment is in between zero and one, signifying that the adsorption of BG onto Fe−MM is favorable. Moreover, the value of R_L is closer to zero, indicating that the process is as favorable as a spontaneous process (K_L is 1.155 L mg\(^{-1}\)).

### 2.4. Rate of Adsorption

The adsorption process, reported here, was very fast. BG got adsorbed within 30 s of coming in contact with Fe−MM nano-ginger. According to the previous literature, adsorbents have needed a significant time for the adsorption process, often a couple of hours. The slow adsorption process is a major limitation for the prototype and industrial usage.

The fast adsorption made the Fe−MM surface highly useful to remove BG from water bodies, in the context of environmental remediation. It is a pseudo-first-order heterogeneous reaction. Because of the rapidity of the reaction, a
rate constant could not be measured. Easy separation of the adsorbed dye on magnetic particles using only a magnet was an extra facility.

2.5. Recovery of BG. The adsorption of BG on the Fe-MM surface was likely physisorption in nature, because the adsorbed BG was readily recovered by washing Fe-MM with copious amounts of water. We were able to recover 91% of BG by aging Fe-MM-BG (obtained by shaking 1 mg of Fe-MM with 10 mL of 100 mg/L) in 8 L of water for 2 h. The spectroscopic signature of BG remained unaltered after recovery. As such, the experimental protocol used in this study is seemingly sustainable and requires minimal energy. By mild heating (40 °C), the process of 89% recovery of BG can be done within 0.5 h.

2.6. Recyclability of Fe-MM. We performed the BG adsorption experiment for several cycles using the same Fe-MM after washing with water. The values of PR were found to be 77.2, 67.2, 55.2, and 41.8 for the 1st cycle, 2nd cycle, 3rd cycle, and 4th cycle, respectively [Figure 4a]. Because of the high affinity of BG, complete removal of BG from the Fe-MM surface was a slow process, requiring many washes. Active sites of Fe-MM might be blocked/changed to some extent because of the aggregation of the nano-ginger or for being immersed in water for a long time, exhibiting a gradual decrease of adsorption capacity. It is interesting to state that Fe and maghemite in Fe-MM were converted to magnetite (100%) after a few cycles of the BG removal process [Figures 4b and S2, Supporting Information]. In other words, BG adsorption was physisorption, but Fe-MM changed its composition during the process of recovery of BG from Fe-MM.

There were some practical reasons for the gradual decrease in the uptake capacity of Fe-MM. They include:

(a) During the BG recovery process, Fe-MM was sonicated in water for ~2 h. Thus, rusting of elemental Fe and some inactivation of active sites might take place.
(b) Fe-MM had a strong affinity for BG. Hence, complete recovery of BG was not possible in a green and energetically efficient way (no heat or no chemicals). Consequently, further BG uptake capacity was decreased by Fe-MM.
(c) Because of the presence of copious amounts of water during BG recovery, collection of suspended Fe-MM by a magnet was not quantitative and the chances of loss of Fe-MM were expected to be higher.

Oxidation of iron in water is well established. In our experimental conditions, the maghemite coating of iron and BG in water changed the formal potential to generate magnetite at the end. We found a similar adsorption spectrum of pure BG and recovered BG after the first and fourth cycles, indicating the purity of recovered BG.

2.7. Life Cycle Analysis: Evaluation of Environmentally Relevant Physicochemical Conditions on BG Removal Technology. To understand whether the protocol of water decontamination of water from BG was applicable in various environmental conditions, we tested the uptake capacity of BG in selected environmentally relevant physicochemical conditions and established the versatility and limitation of the process.

2.7.1. Effect of Temperature. We investigated the effect of temperature by gradually increasing the temperature. The extent of adsorption and PR decreased gradually. PR was 79.9 at 0 °C, 77.2 at 20 °C, 72.4 at 40 °C, and 60.9 at 60 °C [Figure 4c]. For the case of physisorption, an equilibrium between the fluid and the adsorbent is expected. The target molecules
are captured on the surface of the adsorbent via van der Waals forces, with low heat of adsorption.

Chemisorption demands binding sites on the surface, where the target molecules are attracted, forming a covalent chemical bond with a higher heat of adsorption, roughly identical to the heat of reaction. Adsorbents with lesser heats of adsorption are much more sensitive to temperature. Enhanced temperatures facilitate desorption in the case of physisorption and efficient collision (between targets and binding sites because of the enhanced Brownian motion) in the case of chemisorption. Thus, our observation of temperature dependence supports physisorption processes, under experimental conditions used in this study.

2.7.2. Effect of pH. Investigating the effect of pH is a matter of interest for the pollution control protocol, as the earth water reservoirs depict diverse acidity. BG solution was found to have different absorbances (with similar $\lambda_{\text{max}} = 623$ nm) depending on the pH. The BG solution was green, blue, and cyan (with suspending sulphur as colloid) at acidic, neutral, and alkaline pHs, respectively.

We found that lower pHs (pH 2) had the highest removal capacity of BG in the presence of Fe-MM. The PR at variable pHs were as follows, as shown in Figure 4d:

- $2 (84.7\%) > 4 (70.0\%) < 6 (77.2\%) > 8 (58.2\%) < 10 (66.6\%)$.

It is mentionable that aging of BG at high pH (pH 10) for over an hour produced a colorless solution, probably because of the irreversible oxidation of BG. It is important to note that we obtained a similar colorless BG solution by prolonged bubbling of O$_3$ gas in BG solution at neutral pH. Removal of such oxidized BG could not be monitored by absorption spectroscopy.

After treating colorless BG solution with Fe-MM, washing of Fe-MM with water, and decreasing the pH could not bring back the colored solution of BG, implying the conversion to be likely an irreversible redox process. It is to be noted that we adjusted the pH of the solution using only HCl and NaOH.
2.7.3. Effect of $h\nu$, $O_2$, and $NO_2$. Iron (Fe\textsuperscript{0}) and maghemite, the main constituents of the adsorbent Fe–MM, are widely available in the earth’s atmosphere.\textsuperscript{36,39} They have been classified as sustainable materials by different groups.\textsuperscript{40,41} Dust particles are very often formed via the aggregation of such iron particles with clay materials.\textsuperscript{22} In this context, we investigated the effect of several environmentally available physicochemical conditions on the adsorption of BG on Fe–MM [Figure 5a].

As mentioned in 2.7.1 and 2.7.2, enhancement of temperatures increased the desorption capacity of BG from Fe–MM and lowering of pH enhanced adsorption, whereas increasing the pH favored oxidation of the dye.

The sun is the fundamental source of radiation to our planet, including ultraviolet rays. Seasonal variation of exposure levels of UV radiation has been demonstrated by Rafshepour et al.\textsuperscript{43} Yet, the energetic UV will be removed in substantial amounts in the atmosphere by ozone molecules. As such, predominantly the ultraviolet radiation, reaching the earth surface, is UV A (∼315–400 nm). To mimic solar radiation, we performed experiments in which we exposed 15 W UV A light (Hitachi) to dry solid Fe–MM for 5–60 min. It was found that the PR of the exposed Fe–MM decreased (%) slightly, even after 1 h of exposure, indicating that the Fe–MM adsorbent was robust for UV exposure, under experimental conditions. There was also an insignificant change of PR, when Fe–MM in BG solution was exposed to radiation, as shown in Figure 5.

Ozone and NOx (NO and $NO_2$) are produced from natural and anthropogenic sources and are present in the environment in a significant quantity.\textsuperscript{34} O$_3$ is a greenhouse gas (mainly formed via photochemical oxidation of carbon monoxide and volatile organic compounds).\textsuperscript{45} $NO_2$ is also a source of O$_3$ via photochemical reaction.\textsuperscript{46}

$$NO_2 + h\nu (\lambda < 420 \text{ nm}) \rightarrow NO + O^* (\text{P})$$

and

$$O_3 + O^* (\text{P}) (+M) \rightarrow O_2 (+M)$$

Furthermore, ozone-initiated reactions are known to start a series of secondary reactions, which lead to the formation of reactive radicals, such as OH and HO$_2$ in the troposphere.\textsuperscript{47}

OH radicals were produced via the reaction

$$O_3 + h\nu (\lambda \leq 320 \text{ nm}) \rightarrow O_2 + O^* (\text{I})$$

followed by the reaction

$$O^* (\text{I}) + H_2O \rightarrow 2^*\text{OH}$$

We bubbled ozone in the BG solution with Fe–MM for 5 s. We also aged Fe–MM with $O_3$ (100 ppb) gas for 1 h in a gas-tight three-neck round bottom flask in the dark and under UV- A (315–400 nm). For all the cases, an insignificant change of PR was observed. The adsorbent Fe–MM could efficiently withstand exposure to $O_3$ [Figure 5b].

We performed additional sets of experiments using $NO_2$ gas. Bubbling and aging had an insignificant effect on BG adsorption capacity, under our experimental conditions. On the contrary, aging under UV A light greatly reduced the adsorption capacity of Fe–MM. Consequently, the potential in situ-generated NO changed the surface and composition of Fe–MM, diminishing BG adsorption efficiency.

Composition analysis of Fe–MM after ($NO_2 + UV\ A$) treatment indicated 9.8% magnetite and 90.2% Fe. Fe–MM with only UV A treatment produced 92.5% magnetite and 7.5% Fe [Figure 5c, Figures S3 and S4, Supporting Information]. Hence, Fe present in the core is not the adsorbent. Synergism of Fe and iron oxide was responsible for the adsorption process.

It is to be noted that Fe–MM possessed wire-like morphology after ($NO_2 + UV\ A$) treatment, as confirmed from SEM and TEM analysis. The HRTEM image showed ∼0.2 nm fringe spacing, characteristic of the (110) plane of Fe

2.7.4. Effect of Co-Contaminating Metal Ions: A Limitation. Natural water may be composed of various metal ions. The influence of co-polluting metal ions was hence investigated. We sonicated 10 mL of BG (100 mg/L) with 1.0 mg of Fe–MM. The solution became colorless as Fe got adsorbed on Fe–MM (Fe–MM–BG), and 1 mL $10^{-3}$ M of different metal ions (Al$^{3+}$, Ca$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Fe$^{3+}$, Hg$^{2+}$, K$^+$, Mg$^{2+}$, Na$^+$, NH$_4^+$, Pb$^{2+}$, Sn$^{2+}$, and Zn$^{2+}$) was added and sonicated with Fe–MM–BG.

After 10 min, we measured the absorbance of the supernatant. It was found that Al$^{3+}$, Ca$^{2+}$, Fe$^{3+}$, Hg$^{2+}$, and Pb$^{2+}$ caused significant desorption of BG in solution after 10 min, being adsorbed on the Fe–MM surface [Figure 6]. Thus, the presence of some specific metal ions in the aqueous medium limited the application of the technology.

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Recovery of BG from water Fe–MM–BG, using different metal ions.

The high charge density of Al$^{3+}$ was attributed to be the main reason for the highest rate of releasing BG from Fe–MM. We shall refer to the solid obtained after a 10 min sonication of Fe–MM–BG with Al$^{3+}$ as Fe–MM–BG–Al. Thus, the replacement reaction, based on affinity of the metal ions toward Fe/maghemite, generated free BG in the solution.

The metal ions remained hydrated in the solution and thereby the hydrodynamic radii of the metal ions were responsible for the desorption of BG. Thus, effective surface charge density and diffusion ability (mobility) would be related to hydrodynamic radii. Tourinho et al.\textsuperscript{48} have reported the role of hydrodynamic radii and mobility of the ions. Al$^{3+}$, in our case, was found to be likely the best BG recovering cations, considering all the factors under the environmental conditions used in this study.

As the adsorption process was much faster in comparison to some metal-induced desorption process, this protocol could be useful in the textile industry. Moreover, the used concentration of metal ions in Figure 6 was elevated ($10^{-3}$ M). Industry
effluents usually have metal ion concentrations less than that as co-pollutants. This study evaluated the effect of metal ions to understand the extreme situations, along with relative diffusion ability and mobility, and hydrodynamic radii, from a fundamental point of view. Masking of metal ions can also be performed before BG removal. Miura have indeed reported the masking protocol of metal ions during spectroscopic analysis.

The present protocol can also be an efficient platform for the sensing of metal ions in the effluents.

2.7.4.1. Characterization of Fe−MM−BG and Fe−MM−BG−Al. As depicted in Figure 7, XPS studies indicated that Fe in Fe−MM−BG was in an Fe(III) oxidation state [binding energy of 711.00 eV corresponds to Fe(III) 2p3/2], supporting the magnetite phase of iron oxide. Slightly higher binding energy was due to the capture of electron density of iron by N+ of BG, suggesting a clue for the mechanism of the adsorption process. The wire-like morphology of Fe−MM was extensively aggregated in Fe−MM−BG, as obtained from SEM and TEM images. The lattice fringe of 0.289 and 0.295 nm indicated the (220) plane of magnetite [Figure 7].

XPS studies indicated that Fe in Fe−MM−BG−Al was in the Fe(III) oxidation state [binding energy of 710.47 eV corresponds to Fe(III) 2p3/2]. Decrease of binding energy was due to the release of electron density of iron by N+ of BG. The morphology of Fe−MM−BG−Al was mostly wire-like, as obtained from SEM and TEM images. The lattice fringe of 0.489 and 0.247 nm indicated the (111) and (311) planes of magnetite, respectively [Figure 7].

2.8. Environmental Water Analysis. The removal of BG from environmental water samples was investigated using water from Saint Lawrence river (Montreal, Canada), tap water (McGill University, Canada), melted snow (near Burnside Hall, McGill University), and rain water (Montreal). Each environmental aquatic sample of 50 mL was studied by adding different quantities of BG. Then, Fe−MM was added to decontaminate water from BG. We found that BG removal was satisfactory for all the samples, supporting the usefulness of this technique for real environmentally available samples [Table S2, Supporting Information].

The compositions of natural snow and water are quite diverse around the world and include wide ranges of trace and ultratrace components. There is also a significant variability in the compositions of snow and water samples. In this study, similar samples were taken for another field research in this laboratory. As such, elemental analysis, total organic carbon, and dissolved organic carbon analyses were performed. Triple quad-induced coupled plasma mass spectrometry (QQQ-ICP-MS/MS) analysis, along with total carbon and dissolved organic carbon determination of molten snow samples indicated a suite of elements, which are shown in the Supporting Information (Table S3). These analyses led to the quantification of a significant organic carbon presence (2.30 g/m^3 including 1.17 g/m^3 of dissolved organic compounds) as well as metals such as Al, Cr, Mn, Fe, Co, Ni, Cu, As, Sr, Cd, Ba, Pb, U, and Hg. The quantification of metals is given in the Supporting Information. More detailed measurements of various snow and natural water samples around the city of Montreal have been shown previously.

2.9. Effect of the Capping Agents on the Adsorbent.

2.9.1. Clay Minerals: Hydrophilic Capping Agent. Iron, in various forms, was found to be in clay minerals. We synthesized kaolin-, montmorillonite-, and sepiolite-capped Fe−MM composites, KaFe−MM, MtFe−MM, and SpFe−MM. Such passivation was also helpful to decrease the possibility of unwanted aggregations of the nanoparticles, increasing the surface area of the adsorbent and such passivated adsorbents were hydrophilic. One milligram of

![Figure 7](https://example.com/figure7.png)

Figure 7. (a1−a4) represent wide-range and high-resolution (Fe) XPS, SEM, TEM, and HRTEM images of Fe−MM−BG, respectively; (b1−b4) represent wide-range and high-resolution (Fe) XPS, SEM, TEM, and HRTEM images of Fe−MM−BG−Al, respectively.
KaFe, MtFe, and SpFe had PR of 80.2, 79.9, and 73.1%, whereas it was 77.2% for Fe\textsuperscript{−} MM (in 10 mL of 100 mg/L BG solution). It is noteworthy that the main adsorbents, that is, Fe compounds, were almost half in clay material-passivated adsorbents, in comparison to Fe\textsuperscript{−} MM.

In our previous study,\textsuperscript{20} we have reported clay mineral (namely kaolin)-passivated Fe\textsuperscript{−} MM during the synthesis of Fe\textsuperscript{−} MM. From contact angle measurement, we also concluded\textsuperscript{20} that such clay mineral-passivated Fe\textsuperscript{−} MM was hydrophilic in nature. We herein found that such clay mineral-passivated Fe\textsuperscript{−} MM enhanced the removal of BG.

2.9.2. Plastic: Hydrophobic Capping Agent. One of the most alarming and emerging contaminants in water is plastic in various forms such as nanoplastics, microplastics, and in bulk. Though plastics are not soluble in water, yet micro- and nanoplastics can be suspended in water, and are recognized to be potential hazards. Yet, there is some technological advancement to recycling plastic, and easy recognition of plastic in water is still a challenge.
We performed a suite of additional experiments to decipher the role of a hydrophobic coating of common plastic on Fe-MM adsorbent efficiency. A piece of transparent low-density polyethylene (plastic) bag of 25 mg was kept inside 200 mL of tetrahydrofuran (THF) solvent for 48 h and then the piece of plastic was removed from THF. As such, THF was saturated with plastic (p-THF). Fe-MM (2 mg) was sonicated separately in different volumes of p-THF (0.1–1.6 mL) and dried to obtain plastic-capped Fe-MM. The aqueous solution of 10 mL of 100 mg/L BG was sonicated and we observed that Fe-MM treated with more p-THF had lesser PR. Figure 8 denotes a monotonous inverse relation of p-THF and PR. Our BG recycle protocol is, thus, a promising technology of suspended plastic particles in water. The inefficient BG adsorption of plastic-coated Fe-MM was due to the increased hydrophobicity and inactivation of the active sites of the adsorbent.

We observed that the common plastic was insoluble in common organic solvents and water, but sufficiently soluble in THF (confirmed from adsorption spectroscopy). Subsequently, p-THF was added in water, leading to the formation of a white colloidal stable suspension. Our plastic recognition protocol could be a potential colorimetric sensing platform of plastic in water. Future studies are recommended to evaluate the applicability of this discovery, as environmental sensors for the detection of plastic contaminants in aquatic systems.

2.10. Role of a Reducing Agent in Post-oxidation.
During the synthesis of Fe-MM, a reducing agent was required to reduce Fe(II) to Fe(0). Aerial oxidation was responsible for subsequent surface oxidation. To investigate the role of reducing agent in post-oxidation processes, we used several well-known reducing agents, namely, sodium borohydride (NaBH₄),−57 hydrazine (N₂H₄),−58 polyphenol in green tea extract,−59 and lithium aluminium hydride (LiAlH₄).−60

All of these reducing agents produced black-colored Fe(0) as soon as they were added to the Fe(II) solution. Subsequently, aerial oxidation produced different products. However, NaBH₄ produced the efficient adsorbent (Fe−maghemite composite) of BG. We found that 77.2, −50, −24.1, and −3.9 were the PRs for NaBH₄, LiAlH₄, N₂H₄, and polyphenols, respectively [Figure 9a].

The constituents of Fe−MM, produced from NaBH₄, were Fe (47.6%), and maghemite (52.4%) [Figure 2a]. The constituents of Fe−MM, produced from N₂H₄, were lepidocrocite (40.8%), akaganeite (3.3%), magnetite (16.8%), and goethite (8.6%) [Figures 9a and S5, Supporting Information].

The constituents of Fe−MM, produced from polyphenols in green tea, were goethite (10.0%), akaganeite (19.2%), and bernalite (70.8%) [Figures 9c and S6]. The constituents of Fe−MM produced from LiAlH₄ were akaganeite (100.0%) [Figures 9d and S7, Supporting Information].

Except for NaBH₄, all reducing agents caused complete post-oxidation of Fe in different ways. Thereby, the post-oxidation depended on the employed reducing agent, as found from compositional analysis of XRD. Only NaBH₄ directed proper post-oxidation, forming an excellent adsorbent.

Notwithstanding that, the observed negative data in Figure 9a had occurred as we found that the absorbance of pure BG was set as 100%. However, some iron compounds made a complex with BG, rendering a higher absorbance than pure BG, leading to negative removal efficiency. However, negative adsorption efficiency conclusively indicated that they were insignificantly adsorbent for BG.

Pal et al.−61 have clearly proposed the relation between the nucleophilicity of BH₄⁻ and the oxidation of Ag nanoparticles. Similarly, BH₄⁻, a strong nucleophile, adsorbed on the surface of zero-valent iron and decreased its reduction potential. Thus, Fe might react rapidly with oxygen, making a coating of maghemite on Fe. Therefore, further contact of Fe with oxygen could be hindered, forming Fe(core)−maghemite(shell) compounds, an efficient adsorbent.

2.11. Potential Mechanism. The reduction of Fe(II) by NaBH₄ followed by aerial oxidation, produced Fe(core)−maghemite(shell) particle, an efficient adsorbent of BG. When we used other reducing agents in lieu of NaBH₄ during the synthesis of Fe-MM, the obtained product did not possess any elemental Fe (as confirmed from XRD). Such treatments significantly decreased adsorption capabilities.

Fe (being covered by iron oxide of a specific phase) is important for BG adsorption and exclusive employment of NaBH₄ dictates such post-oxidation in a perfect manner. Further research is still needed to understand the insight into post-oxidation from morphological and electronic ground.

(UVA + NO₂) treatment greatly enhanced the contribution of Fe in Fe-MM, destroying BG adsorption ability. Consequently, Fe with a surface coating of iron oxide (maghemite) was important for it being an efficient adsorbent. The drift of electron density−62,63 from electronically rich Fe to maghemite helped to attract N⁺ of BG. The enhancement of binding energy after BG adsorption on the Fe-MM surface supports the excess electron density on maghemite, before the BG adsorption.

Homogenous, monolayer, and Langmuir type of physisorption might cause repulsion of closely placed N⁺ in BG dye. HSO₃⁻, as counter anions, prevented repulsion, favoring the adsorption process, as depicted in Figure 9.

In this paper, to our knowledge, we have disclosed one of the most efficient inorganic adsorbents for decontamination of water from BG. The adsorbent is inexpensive and sustainable, as iron oxides are largely available in the environment, in soil, and in airborne dust particles, which are found commonly in our planet. Furthermore, this method is fast, does not require energy, and is shown to be recyclable.

Further experimentations and modeling studies are warranted to establish the unequivocal mechanism, relating to oxidation states, phase, morphology, composition, and crystal plane.

2.12. Sustainable Technology. We are here presenting a new material, Fe-MM, with nano-ginger morphology, for BG recycling technology with plastic recognition. The constituents of Fe-MM were maghemite and Fe(0), both of which are ubiquitous in the environment, and commonly observed in airborne dust particles. Moreover, iron and iron oxide nanoparticles have been shown to be biocompatible nanomaterials, having abundant applications in various biomedical activities.−64−66 In our procedure, no other toxic coating/passivating agent was used for BG removal.

We synthesized Fe-MM by reducing FeCl₂ with NaBH₄. It is important to note that NaBH₄ was used for the synthesis of Fe-MM, but not for the adsorption process. Sodium metaborate (produced during NaBH₄-induced reduction) could be quantitatively collected and could be converted to NaBH₄ using a previously described method.−67
NaBO₂ + 4H₂ → NaBH₄ + 2H₂O \quad (10)

The proposed procedure is relatively simple, fast, recyclable, highly efficient for BG removal and recovery, energetically convenient, and cost-effective. Because of the suite of experiments to evaluate its life cycle analysis upon relative environmental conditions such as radiation, T, pH, co-pollutants, and atmospheric oxidants, the proposed technology is sustainable.

A magnetic adsorbent is helpful for facile and rapid separation, without centrifugation or dialysis unlike other biocompatible adsorbents.⁶⁸ All these features of our technique help to make our technique effective for industrial applications as well as academic research.

Adsorbents used in this study are iron-containing compounds, and sodium borohydride was washed away during the course of synthesis. Though sodium borohydride is a fairly active reducing agent, it can also be recycled from sodium metaborate.⁶⁷ The involvement of NaBH₄ in the synthesis is often considered green by several groups.⁶⁹,⁷⁰ As such, one could easily recover the adsorbed BG from Fe−MM. The adsorbent was thereby recyclable and sustainable.

The Fe−MM, loaded with BG, can be separated from water by a magnet (as both Fe−MM and Fe−MM−BG were magnetic). BG was recovered from Fe−MM, loaded with BG, by shaking it in copious amounts of water. BG could thus be retrieved back, as mentioned in 2.5. The protocol included the recycling of the dye. Moreover, elevated temperature also released BG, although the thermal method is not suitable energetically.

3. CONCLUSIONS

A cost-effective, fast, recyclable, efficient, sustainable, and simple protocol has been stated for the removal of BG to purify water. The process is Langmuir-type physisorption and recyclable. The efficient maximum adsorption is observed to be 1000 mg·g⁻¹. The drift of electron density from core to shell is responsible for such efficient adsorption. The adsorbent will open up a new area of environmental remediation, using the constituent of airborne dust. Not only BG, but also other toxic/hazardous materials may be eliminated from the environment using a similar mechanism. The additional advantage of magnetic adsorbents, like ours, is that they are easily separable by a magnet. Instead of just removing the BG, this protocol allows the removal of BG and recycling it with practically no energy and high efficiency. Furthermore, in the course of this protocol, we synthesized new materials, which can be used as added value, rendering our method desirable for sustainable industrial applications. Our technology has the potential to be an asset for waste management at industrial scales. Such a protocol can also be used in fabric, food processing, and water purification industries. Moreover, our colorimetric plastic recognition strategy may open up a new mechanistic understanding of environmental remediation and in finding a novel adsorbent for myriad applications.

4. EXPERIMENTAL SECTION

4.1. Materials and Supplies. All the reagents were of analytical reagent grade and Milli-Q water was used throughout the experiment. All metal salts, iron dust, and all iron oxides were purchased from Sigma-Aldrich. Sodium borohydride, hydrazine, and lithium aluminum hydride were obtained from Alfa Aesar. Hydrochloric acid, different organic solvents, sodium hydroxide, and BG were purchased from Fisher Scientific. All glassware were cleaned with freshly prepared aqua regia, subsequently rinsed with copious amounts of distilled water, and were dried well before use. All the reagents were used without further purification.

4.2. Synthesis of Fe−MM. A yellow solution of 5.2 g of FeCl₂·4H₂O (60 mL) was prepared in a 4:1 ethanol/water mixture. A solution of 200 mL of a 1 M NaBH₄ solution was made by dissolving required solid NaBH₄ in ice-cold Milli-Q water. The cold NaBH₄ solution was slowly added into the FeCl₂·4H₂O solution in an ice-bath through constant shaking. An instant color change from yellow to black was observed. After adding all of the NaBH₄ solution, the reaction mixture was shaken for another 30 min and left for 24 h. After 24 h, the supernatant was decanted, leaving the solid inside the container, using a strong magnet. The black solid was washed thoroughly with Milli-Q water and then with ethanol. To dry it completely, the black solid was then kept in a vacuum oven at 65 °C. The obtained grayish-black solid was crushed with a mortar and pestle to obtain the Fe−MM.

4.3. Analytical Techniques for Physical and Chemical Characterization. 4.3.1. Production and Exposure of Ozone. An ozone generator (Yanco Industries Ltd.) was used to obtain O₃ by flowing O₂ with a flow rate of ~60 mL/min to create O₃ with a concentration of ~46 000 ppm/mL. O₃ was bubbled slowly (one bubble/3 s) in 10 mL of 100 mg/L solution of BG with 1 mg of Fe−MM for 30 s and two parts of it were made. One was aged in the dark and the other under UV A light for 30 min. Subsequently, the absorbance of BG in solution was measured (after centrifugation) by employing a UV−vis spectrophotometer (Cary 50 Bio).

We also treated two sets of solid 1 mg Fe−MM with 100 ppb O₃ in three-neck gas-tight containers for 30 min, one in the dark and another with UV A light. Then, the BG adsorption experiment was performed. The concentration of ozone (100 ppb) was calculated by employing a UV−vis spectrophotometer (Cary 50 Bio).

4.3.2. Exposure of NO₂ Gas. A solution of BG (10 mL, 100 mg/L) with 1 mg of Fe−MM was bubbled with NO₂ gas (60 mL/min) for 10 s from an NO₂ cylinder (TC-3ALM-139/Dot 3AL). It was divided into two parts and one was aged in the dark and the other under UV A light for 30 min. Then, the absorbance of BG was measured (after centrifugation) by employing a UV−vis spectrophotometer (Cary 50 Bio).

We also treated two sets of solid 1 mg Fe−MM with NO₂ gas (60 mL/min) for 3 s in a three-neck gas-tight container and aged them for 30 min, one in the dark and another with UV A light. The adsorption experiment was subsequently performed.

4.3.3. XRD Spectroscopy. XRD was recorded with a Siemens D500 X-ray diffractometer (Cu source, λ = 1.79 Å). XRD patterns were recorded for 10° ≤ 2θ ≤ 90°. The samples were vacuum-dried at room temperature at 20 psi before taking the measurements.

4.3.4. X-ray Photo Electron Spectroscopy. XPS measurements were carried out with the Thermo Scientific K-Alpha XPS. The samples were loaded onto a carbon tape to be placed on a grid for the analysis. Samples were vacuum-dried at room temperature before measurement.

4.3.5. Scanning Electron Microscopy. Particle morphology was examined using a FEI Helios NanoLab 660 DualBeam (focused ion beam) extreme high-resolution scanning electron microscope. The microscope contains Leica Microsystems EM 12117

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VCT100 cryo-transfer system, MultiChem gas injection system, and EDAX Octane Ultra 100 mm² SDD, and TEAM 3D EDS analysis system. Samples were vacuum-dried at room temperature before measurement. The samples were put on a carbon tape before SEM analyses.

4.3.6. Transmission Electron Microscopy. Samples were vacuum-dried at room temperature before measurement. The samples were put on a carbon tape before TEM analyses. Then, 20 mg of each sample was dispersed in 4 mL of Milli-Q water. Then, 10 µL of each sample solution was deposited on glow-discharged carbon film-coated copper electron microscopy grids and dried. The samples were imaged using a FEI Tecnai 12 BioTwin TEM microscope (FEI Electron Optics) equipped with a tungsten filament at 120 kV, containing an AMT XR80C CCD camera system.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00757.

Comparison of Q₈ of BG by several absorbents; comparison of PR of BG; composition of water from snow; and XRD spectrum of Fe–MM (PDF)

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**Notes**

The authors declare no competing financial interest.

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### REFERENCES

(1) Calvete, T.; Lima, E. C.; Cardoso, N. F.; Dias, S. L. P.; Ribeiro, E. S. Removal of brilliant green dye from aqueous solutions using home made activated carbons. *Clean: Soil, Air, Water* 2010, 38, 521−532.

(2) Ahn, D.-H.; Chang, W.-S.; Yoon, T.-I. Dyestuff wastewater treatment using chemical oxidation, physical adsorption and fixed bed biofilm process. *Process Biochem.* 1999, 34, 429−439.

(3) Ghedi, M.; Negintaji, G.; Karimi, H.; Marefali, M. Solid phase extraction and removal of brilliant green dye on zinc oxide nanoparticles loaded on activated carbon: new kinetic model and thermodynamic evaluation. *J. Ind. Eng. Chem.* 2014, 20, 1444−1452.

(4) Dahri, M. K.; Lim, L. B. L.; Kooh, M. R. R.; Chen, C. M. Adsorption of brilliant green from aqueous solution by unmodified and chemically modified Tarap (*Artocarpus odoratissimus*) peel. *Int. J. Sci. Environ. Technol.* 2017, 14, 2683−2694.

(5) https://www.coatingsworld.com/issues/2016-07-01/view-market-research/world-paint-amp-coatings-demand-to-reach-54-7-mill (accessed June 13, 2016).

(6) https://www.grandviewresearch.com/press-release/global-colorants-market (accessed March 2017).

(7) http://www.latimes.com/world/europe/la-fg-russia-opposition-2017-story.html (accessed May 3, 2017).

(8) CID 12449 from PubChem.

(9) Ishaq, M.; Sultan, S.; Ahmad, I.; Saeed, K. Removal of Brilliant Green Dye from Aqueous Medium by Untreated Acid treated and Magneitte Impregnated Bentonite Adsorbents. *J. Chem. Soc. Pak.* 2017, 39, 780−787.

(10) Anjum, M.; Miandad, R.; Waqas, M.; Gehany, F.; Barakat, M. A. Remediation of wastewater using various nano-materials. *Arabian J. Chem.* 2016, DOI: 10.1016/j.arabjc.2016.10.004.

(11) Tavares, F. V. F.; Ardisson, J. D.; Rodrigues, P. C. H.; Brito, W.; Macedo, W. A. A.; Jacomino, V. M. F. Characterization of iron in airborne particulate matter. *Hyperfine Interact.* 2014, 224, 109−119.

(12) Ganguly, M.; Dib, S.; Ariya, P. Fast, Cost-effective and Energy Efficient Mercury Removal-Recycling Technology. *Sci. Rep.* 2018, 8, 16255.

(13) Jang, M.-H.; Lim, M.; Hwang, Y. S. Potential environmental implications of nanoscale zero-valent iron particles for environmental remediation. *Environ. Health Toxicol.* 2014, 29, e2014022.

(14) Ganguly, M.; Dib, S.; Kurien, U.; Rangel-Alvarado, R. B.; Miyahara, Y.; Ariya, P. A. Influence of Environmentally Relevant Physicochemical Conditions on a Highly Efficient Inorganic Ice Nucleating Particle. *J. Phys. Chem. C* 2018, 122, 18690−18704.

(15) Leventis, N.; Chidambareswarapattar, C.; Bang, A.; Sotiriou-Leventis, C. Cococon-in-Web-Like Superhydrophobic Aerogels from Hydrophilic Polyurea and Use in Environmental Remediation. *ACS Appl. Mater. Interfaces* 2014, 6, 6872−6882.

(16) Mattsson, K.; Hansson, L.-A.; Cedervall, T. Nano-plastics in the aquatic environment. *Environ. Sci.: Processes Impacts* 2015, 17, 1712−1721.

(17) Wang, K.; Zhu, Z.; Huang, H.; Li, T.; He, Z.; Yang, X.; Alva, A. Interactive effects of Cd and PAHs on contaminants removal from co-contaminated soil planted with hyperaccumulator plant Sedum alfredii. *J. Soils Sci. 2012, 12, 556−564.

(18) Patil, S. S.; Shedbalkar, U. U.; Truskewycz, A.; Chopade, B. A.; Ball, A. S. Nanoparticles for environmental clean-up: A review of potential risks and emerging solutions. *Environ. Technol. Innov.* 2016, 5, 10−21.

(19) Wang, Y.; Deng, L.; Caballero-Guzman, A.; Nowack, B. Are engineered nano iron oxide particles safe? an environmental risk assessment by probabilistic exposure, effects and risk modeling. *Nanotoxicology* 2016, 10, 1545−1554.

(20) Ganguly, M.; Dib, S.; Ariya, P. A. Purely Inorganic Highly Efficient Ice Nucleating Particle. *ACS Omega* 2018, 3, 3384−3385.

(21) Moteki, N.; Adachi, K.; Ohata, S.; Yoshida, A.; Harigaya, T.; Sato, Y.; Ikuhara, Y.; Koike, M.; Kondo, Y. Anthropogenic iron oxide aerosols enhance atmospheric heating. *Nat. Commun. 2017, 8, 15329.

(22) Ganguly, M.; Mondal, C.; Pal, A.; Pratik, S. M.; Pal, J.; Pal, T. Aggregation of nitroaniline in tetrahydrofuran through intriguing H-bond formation by sodium borohydride. *Phys. Chem. Chem. Phys.* 2014, 16, 12865−12874.

(23) Ganguly, M.; Pal, A.; Pal, T. Intriguing fluorescence behavior of diiminic Schiff bases in the presence of in situ produced noble metal nanoparticles. *J. Phys. Chem. C* 2011, 115, 22138−22147.

(24) Leed, E. A.; Sofo, J. O.; Pantano, C. G. Electronic Structure Calculations of Physiosorption and Chemisorption on Oxide Glass Surfaces. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2005, 72, 155427.

(25) Radu, T.; Iacovita, C.; Benea, D.; Turcu, R. X-ray photoelectron spectroscopic characterization of iron oxide nanoparticles. *Appl. Surf. Sci.* 2017, 405, 337−343.

(26) Cao, D.; Li, H.; Pan, L.; Li, J.; Wang, X.; Jing, P.; Cheng, X.; Wang, W.; Wang, J.; Liu, Q. High saturation magnetization of γ-Fe₂O₃ nano-particles by a facile one-step synthesis approach. *Sci. Rep.* 2016, 6, 32360.

(27) Salazar-Alvarez, G.; Sort, J.; Uheida, A.; Muhammed, M.; Surinach, S.; Baró, M. D.; Nogués, J. Reversible post-synthesis tuning of the superparamagnetic blocking temperature of γ-Fe₂O₃ nanoparticles by adsorption and desorption of Co(ii) ions. *J. Mater. Chem. 2007, 17, 322−328.*
Hockridge, J. G.; Jones, F.; Loan, M.; Richmond, W. R. An electron microscopy study of the crystal growth of schwertmannite needles through oriented aggregation of goethite nanocrystals. *J. Cryst. Growth* 2009, 311, 3876–3882.

Ganguly, M.; Jana, J.; Mondal, C.; Pal, A.; Pal, T. Green synthesis of highly fluorescent Au(i)@Ag2/Ag3-thiolate core-shell particles for selective detection of cysteine and Pb(ii). *Phys. Chem. Chem. Phys.* 2014, 16, 18185–18197.

Kurien, U.; Hu, Z.; Lee, H.; Dastoor, A. P.; Ariya, P. A. Radiation enhanced uptake of H2O(g) on iron (oxy)hydroxide nanoparticles. *RSC Adv.* 2017, 7, 45010–45021.

Kumar, R.; Ansari, M. O.; Barakat, M. A. Adsorption of Brilliant Green by Surfactant Doped Polylyamine/MWCNTs Composite: Evaluation of the Kinetic, Thermodynamic, and Isotherm. *Ind. Eng. Chem. Res.* 2014, 53, 7167–7175.

Chiang, H. I.; Priyantha, N.; Lim, B. L. B. Effective adsorption of toxic brilliant green from aqueous solution using peat of Brunei Darussalam: isotherms, thermodynamics, kinetics and regeneration studies. *RSC Adv.* 2015, 5, 34603–34615.

Grosoven, A. P.; Kobe, B. A.; McIntyre, N. S. Studies of the oxidation of iron by water vapour using X-ray photoelectron spectroscopy and QUASES. *Surf. Sci.* 2004, 572, 217–227.

Ali, I. New Generation Adsorbents for Water Treatment. *Chem. Rev.* 2012, 112, 5073–5091.

Berger, A. H.; Bhow, A. S. Comparing physisorption and chemisorption solid sorbents for use separating CO2 from flue gas using temperature swing adsorption. *Energy Procedia* 2011, 4, 562–567.

Ganguly, M.; Mondal, C.; Jana, J.; Pal, A.; Pal, T. Selective Dopamine Chemosensing Using Silver-Enhanced Fluorescence. *Langmuir* 2014, 30, 4120–4128.

Jofre-Meléndez, R.; Torres, E.; Ramos-Arroyo, Y.; Galván, L.; Ruiz-Cánovas, C.; Ayora, C. Reconstruction of an Acid Water Spill in a Mountain Reservoir. *Water* 2017, 9, 613.

Sanderson, P.; Su, S. S.; Chang, I. T. H.; Delgado Saborit, J. M.; Kepaptsoglou, D. M.; Weber, R. J. M.; Harrison, R. M. Characterisation of iron-rich atmospheric submicrometre particles in the roadside environment. *Atmos. Environ.* 2016, 140, 167–175.

Magiera, T.; Stryszcz, Z.; Jabłonska, M.; Bzowska, G. Characterization of magnetic particulates in urban and industrial dusts. In *Air pollution XVIII: Transactions on Ecology and the Environment*; Brebbia, C. A., Longhurst, J. W. S., Eds.; WIT: Southampton, 2010; Vol 176, pp 171–184.

Virkutyte, J.; Varma, R. S. Eco-friendly magnetic iron oxide-pillared montmorillonite for advanced catalytic degradation of dichlorophenol. *ACS Sustainable Chem. Eng.* 2014, 2, 1545–1550.

Gao, S.; Shi, Y.; Zhang, S.; Jiang, K.; Yang, S.; Li, Z.; Takayama-Küppers, M.; Lyer, S.; Alexiou, C. Strategies to optimize the biocompatibility of iron oxide nanoparticles from their intrinsic properties. *J. Magn. Magn. Mater.* 2013, 351–352, 229–2294.

Ambrosi, A.; Chua, C. C.; Bonanni, A.; Pumera, M. Lithium Aluminum Hydride as Reducing Agent for Chemically Reduced Graphene Oxides. *Chem. Mater.* 2012, 24, 2292–2298.

Pal, T.; Sau, T. K.; Jana, N. R. Reversible Formation and Dissolution of Silver Nanoparticles in Aqueous Surfactant Media. *Langmuir* 1997, 13, 1481–1485.

Ganguly, M.; Pal, A.; Negishi, Y.; Pal, T. Synthesis of highly fluorescent silver clusters on gold(1) surface. *Langmuir* 2013, 29, 2033–2043.

Ganguly, M.; Pal, J.; Das, S.; Mondal, C.; Pal, A.; Negishi, Y.; Pal, T. Green synthesis and reversible dispersion of a giant fluorescent cluster in solid and liquid phase. *Langmuir* 2013, 29, 10945–10958.

Wang, L.; Wang, Z.; Li, X.; Zhang, Y.; Yin, M.; Li, J.; Song, H.; Shi, J.; Ling, D.; Wang, L.; Chen, N.; Fan, C. Deciphering Active Biocompatibility of Iron Oxide Nanoparticles from Their Intrinsic Antagonism. *Nano Res.* 2018, 11, 2746–2755.

Janko, C.; Zaloga, J.; Pöttler, M.; Dürr, S.; Eberbeck, D.; Tietze, R.; Lyer, S.; Alexiou, C. Strategies to optimize the biocompatibility of iron oxide nanoparticles - *SPIO*Nes safe by design*. *J. Magn. Magn. Mater.* 2017, 431, 281–284.

Nadagouda, M. N.; Castle, A. B.; Murdock, R. C.; Hussain, S. M.; Varma, R. S. In vitro biocompatibility of nanoscale zerovalent iron nanoparticles ([NZVI] synthesized using tea polyphenols. *Green Chem.* 2010, 12, 114–122.
(67) Wu, Y.; Brady, J. C.; Kelly, M. T.; Ortega, J. V.; Snover, J. L. Synthesis of sodium borohydride for energy applications. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **2003**, *48*, 938.

(68) Mittal, A.; Kaur, D.; Mittal, J. Applicability of waste materials-bottom ash and deoiled soya-as adsorbents for the removal and recovery of a hazardous dye, brilliant green. *J. Colloid Interface Sci.* **2008**, *326*, 8−17.

(69) Pohl, N.; Clague, A.; Schwarz, K. Chiral Compounds and Green Chemistry in Undergraduate Organic Laboratories: Reduction of a Ketone by Sodium Borohydride and Baker’s Yeast. *J. Chem. Educ.* **2002**, *79*, 727−728.

(70) Zeynizadeh, B.; Setamdideh, D. Water as a Green Solvent for Fast and Efficient Reduction of Carbonyl Compounds with NaBH4under Microwave Irradiation. *J. Chin. Chem. Soc.* **2005**, *52*, 1179−1184.