Experimental and Molecular Dynamics Simulation Study of Specific Ion Effect on the Graphene Oxide Surface and Investigation of the Influence on Reactive Extraction of Model Dye Molecule at Water–Organic Interface

Priyakshree Borthakur,∗,† Purna K. Boruah,‡,† Najrul Hussain,∗,‡ Bhagyasmeeta Sharma,† Manash R. Das,∗,‡,† Sara Matić,§ David Řeha,∥ and Babak Minofar∗,∥,‡,*

†Advanced Materials Group, Materials Science and Technology Division, CSIR-North East Institute of Science and Technology, Jorhat 785006, Assam, India
‡Academy of Scientific and Innovative Research (AcSIR), CSIR-NEIST Campus, India
§Faculty of Science, University of Zagreb, Roosevelt Sq. 6, 10000 Zagreb, Croatia
∥Center for Nanobiology and Structural Biology, Institute of Microbiology, Academy of Sciences of the Czech Republic, Zámeck 136, 373 33 Nové Hrady, Czech Republic
*Institute of Physics and Biophysics, Faculty of Science, University of South Bohemia, Branišovská 1760, 37005 ČeskéBudějovice, Czech Republic

Supporting Information

ABSTRACT: The influence of different inorganic anions (Cl−, Br−, SCN−, NO−, SO−, and CH3COO−) and cations (Ca2+, Mg2+, Na+, and NH4+) on the surface potential of graphene oxide (GO) suspension has been investigated both experimentally and computationally. The hydrophilic GO surface has negative surface potential (zeta potential) which can be varied by changing the pH of the suspension as well as by adding external inorganic ions. The surface of GO is hydrophilic in a basic medium and becomes hydrophobic in an acidic medium because of the protonation and deprotonation of the surface functional groups. The presence of inorganic ions affects the electrophoretic mobility of the dispersed phase within the GO suspension and influences its zeta potential. This is due to the formation of a double layer of charge at the interface of the GO and ionic salt solution. Molecular dynamics simulations were used to understand the interactions of ions within the slipping plane of GO, which influences its zeta potential in salt solutions. The results suggested that the influence of the various inorganic ions on the electrokinetic potential of GO is ion-specific and depends on the polarizability of the ions. Having high specific surface area and being amphiphilic and biocompatible, GO was successfully utilized in the reactive extraction technique of methyl blue (MB) dye molecule at the water–toluene interface. The present study demonstrates that the presence of highly polarizable ions increases the zeta potential as well as hydrophobicity of GO, which facilitates the extraction of MB from the aqueous to the organic phase.

INTRODUCTION

In recent years, colloidal systems have been widely used in various industrial, biological, and commercial applications, and the stability of the colloidal systems is a key factor influencing their application in different fields. Zeta potential, an important surface property, plays the key role in the study of stability of a colloidal system. The structure of the electrical double layer at the particle–dispersion medium interface influences the zeta potential and other surface properties of a colloidal dispersion. In colloidal science, the presence of salt solutions plays an important role in the variation of zeta potential at particle–electrolyte solution interface because of the variation of the distribution of ions near the interface and pH of the colloidal suspension, which are mainly a function of ionic charge and size. In the case of a colloidal dispersion of oxide materials, on addition of salt solutions, the acid–base surface functional groups of the oxide surface react with the ions of the salt and result in generation of electric charge at the interface.1,2 The magnitude of the electrical charge on the surface and the structure of the electrical double layer at the interface depend upon the concentration of the electrolyte solution as well as on the nature of the ions. The ionic species plays an important role in different chemical processes, such as electrochemical reactions at electrode surfaces, atmospheric chemistry on
aerosol surfaces, extraction processes between organic and aqueous phases, ion transfer through biological membranes, etc.\(^3\) In 1888, Franz Hofmeister discovered that the salting out efficiency of different ions on the precipitation of hen egg white proteins are different, and on the basis of this observation, he arranged the ions within a series known as the Hofmeister series (HS).\(^4,5\) From the earlier studies it was realized that the Hofmeister salts have significant ion-specific effect on the surface tension of water—air and oil—water interfaces, stability of emulsions, solubility of gases, catalysis of chemical reactions, etc.\(^6\) In colloidal systems, the HS ions show a distinguishable influence on the surface charge and polarity. Hydrophobic anionic colloids show direct HS effect, and the cationic colloids show reverse HS effect.\(^7,8\) In the case of hydrophilic colloids, the anionic colloids show reverse HS, but the cationic colloids show direct HS effect.\(^9\) The effect of Hofmeister ions on the colloidal systems can be discussed based on the variation of nonelectrostatic potentials between the ions and the surfaces and the ion hydration forces. Furthermore, the polarization of the ion also plays an important role in this study. Das et al. studied the effect of inorganic anions like NO\(_3^-(aq)\), I\(^-\)(aq), Br\(^-\)(aq), Cl\(^-\)(aq), SO\(_4^{2-}(aq)\), and S\(_2\)O\(_3^{2-}(aq)\) and cations Ca\(^{2+}\)(aq) and Mg\(^{2+}\)(aq) on the zeta potential and isoelectric point of α-alumina as well as their effect on adsorption density of the p-hydroxy benzoate on α-alumina in an aqueous medium.\(^10\) They observed that, at very low electrolyte concentration, the polarizability of ions plays an important role in the specific ion adsorption onto the α-alumina surfaces in addition to ion—ion and ion—solvent interactions in the presence of different salts.

Graphene oxide (GO) sheets have ionizable (−COOH and −OH) edge groups on the surface and produce a colloidal dispersion in an aqueous medium because of its hydrophilic nature. The specific ion effect on the stability of a GO colloidal system and the zeta potential are associated with the electrical charge formed at the GO—electrolyte solution interface. To best of our knowledge, there is no literature available on the discussion about the influence of HS ions on surfaces of GO. In this paper, we mainly focus on the measurement of the zeta potential value (ζ) of GO colloidal suspension in the presence of different anionic and cationic ions like Cl\(^-\)(aq), Br\(^-\)(aq), NO\(_3^-(aq)\), SCN\(^-(aq)\), SO\(_4^{2-}(aq)\), CH\(_3\)COO\(^-(aq)\), Na\(^+(aq)\), Ca\(^{2+}\)(aq), Mg\(^{2+}\)(aq), and NH\(_4^+(aq)\) of two different concentrations (0.01 M and 0.1M) in the pH range 2–10 of the medium. From the results obtained, it is found that with the variation of pH of the colloidal systems, the polarity of the GO surface is varied; hence, the effect of ions on the GO surface at different pH is also different, which depends on the surface polarity as well as on the polarizability of the ion.

Our objective is to investigate the specific ion effect on the GO surface both experimentally and through molecular dynamics (MD) simulation, which will play a major role in the reactive extraction of the dye molecules for environmental remediation. Reactive extraction technique refers to a liquid—liquid extraction technique in which a suitable carrier is used to extract toxic materials from the aqueous to the organic phase. The material and the carrier react with each other in the aqueous phase, and then the resultant complex is extracted to the organic phase. The reactive extraction technique is highly effective for biodiesel production, enantioselective separation, extraction of organic acids from the aqueous phase, etc.\(^11\) The reactive extraction technique also has attracted considerable attention for the removal of dye molecules from industrial waste before being discharged into the normal water stream. Among the various industrially utilized dye molecules, methyl blue (MB) is a toxic material for its carcinogenic and mutagenic effects;\(^16\) hence, removal of MB from industrial effluents is an important field of study. Our research group has recently utilized the reactive extraction technique for the removal of both the cationic and anionic dye molecules using GO as an efficient carrier.\(^17\) It was found that the variation of the zeta potential of the GO surface as a function of pH in the presence of different anionic and cationic ions shows significant effect on the reactive extraction analysis of dye molecules at the water—organic interface. The presence of both hydrophilic polar groups at the edges and the hydrophobic aromatic structure makes GO amphiphilic in nature. Because of the amphiphilicity, GO can be used as a surfactant in the formation of pickering emulsions consisting of an aqueous phase and an organic phase.\(^18\) In this paper we have explored how the zeta potential value of GO depends on the pH of the medium as well as on the presence of electrolyte ions. Thus, the influence of the presence of a series of inorganic ions and pH of the medium on the adsorption of methyl blue at the GO—electrolyte interface seems to be an uninvestigated topic which is yet to be explored. Our present work includes the variation of the surface properties in the presence of different electrolytes and the effect of surface charge on the reactive extraction analysis of carcinogenic methyl blue, an anionic dye, in toluene—water interface. The structure of MB is shown in Figure 1.

![Figure 1. Structure of methyl blue (MB) dye molecule.](image)
UV–vis spectra, thermogravimetric analysis, high-resolution transmission electron microscopy, etc.) were provided in our previous publications.\textsuperscript{19,20}

**Measurement of Zeta Potential of GO Suspension in the Presence of Different Electrolyte Solutions.** The potential difference between the two phases that are in contact with each other can be determined by four different techniques such as electrophoresis, electro-osmosis, streaming potential, and sedimentation potential. In the present study, the surface potential was determined by utilizing the electrophoresis method. In the electrophoresis method, the particles move under the influence of an applied electric field. The zeta potential of GO suspensions was calculated by measuring the electrophoretic mobility using a Zetasizer analyzer (Model: Nano ZS, Malvern, UK) instrument and the Smoluchowski equation.\textsuperscript{21} The relation between zeta potential and electrophoretic mobility is

$$\zeta = 4\pi \eta / D_e \times \mu$$  
(1)

where $\zeta$ is the zeta potential, $\eta$ the viscosity of the medium, $\mu$ the electrophoretic mobility at particular temperature, and $D_e$ the dielectric constant of the medium. Thus, the effect of different monovalent and divalent salts on the surface charge of particles can be studied by investigating the electrophoretic mobility as a function of pH in the presence of different salts. The effect of pH, electrolyte concentration, and presence of different ionic species on the zeta potential of the GO suspension was evaluated.

The specific ion effect on the zeta potential of GO (1 mg/mL) was evaluated by measuring the zeta potential at two different concentrations of salt solutions (0.01 M and 0.1M) separately with the help of a Zetasizer as a function of the pH in the range of 2–10. The GO suspension was prepared by ultrasonication of 1 mg/mL GO suspension with a fixed salt concentration at the desired pH value for zeta potential measurement. The pH of the suspension was adjusted with 0.1 M HCl and 0.1 M NaOH by using a pH meter. The 1 M stock solution of the various electrolytes (NaCl, Na\textsubscript{2}SO\textsubscript{4}, NaSCN, NaNO\textsubscript{3}, NaBr, CH\textsubscript{3}COONa, NH\textsubscript{4}Cl, MgCl\textsubscript{2}, and CaCl\textsubscript{2}) were prepared by dissolving in deionized water. The total volume of the GO suspension was adjusted to 5 mL with DI water in the presence of electrolyte solution at desired pH for the zeta potential experiment.

**Reactive Extraction Analysis.** The reactive extraction of MB at the water–organic interface was studied by using GO as carrier and toluene as model organic solvent in the pH range 2–10 and at 25 °C. The effect of time on the reactive extraction analysis was performed by stirring 5 mL of aqueous solution containing 1 mM MB dye solution and 1 mg mL$^{-1}$ GO with 5 mL of toluene for 10, 30, 40, 60, 80, 100, 120, 140, 160, 180, 200, and 220 s. The mixtures were then allowed to settle for another 1 h, and the bubbles were imaged using a microscope. The average size of the bubbles was measured using ImageJ software. The amount of dye molecules extracted from the aqueous phase to the organic phase was evaluated by determining the UV–vis spectra of the aqueous dye solution at $\lambda_{\text{max}} = 595$ nm. The adsorption capacity of the dye molecule at a particular time was determined by using the following equation

$$q_t = (C_0 - C_t) V / m$$  
(2)

where $C_0$ is the initial dye concentration and $C_t$ is the concentration of the dye molecule at time $t$. $V$ is the total volume of the aqueous phase, and $m$ is the mass of the GO.

The percentage of MB extraction at a particular time was calculated from the following equation

$$\text{Extraction} (\%) = \left( \frac{C_0 - C_t}{C_0} \right) \times 100$$  
(3)

The effect of different ions on the reactive extraction analysis of the dye molecule was investigated by adopting the same experimental procedure on the mixture containing 1 mg/mL GO, 1 mM MB dye, and 0.01 and 0.1 M salt solution in 5 mL of aqueous phase and 5 mL of toluene as organic phase.

**Computational Section.** To support experimental findings and understand at the molecular level the interactions of ions within the slipping plane influencing the zeta potential of GO in salts solutions, classical MD simulations have been employed. MD simulation is a powerful technique to identify the interaction of solute—solvent as well as solvent—solvent molecules in different solutions. For construction of GO C\textsubscript{34}H\textsubscript{4}O\textsubscript{24}, which has COOH and OH groups as functional groups, has been used. The ratio of COOH:OH is assumed to be 1:1, and no epoxy groups were used in the structure as the structure of GO used in experimental work was not identified in terms of different functional groups. MD simulations of a single GO molecule in both acidic and basic forms (protonated and deprotonated) solvated in pure water and aqueous solutions of NaCl, Na\textsubscript{2}SO\textsubscript{4}, NaSCN, NaNO\textsubscript{3}, NaBr, CH\textsubscript{3}COONa, NH\textsubscript{4}Cl, MgCl\textsubscript{2}, and CaCl\textsubscript{2} with the concentration of 0.1 M have been performed. For preparation of the solution boxes, Packmol package was used and the GO molecules have been placed in the center of the cubic box.\textsuperscript{22,23} Periodic boundary conditions in all three dimensions have been used for all simulations, and for simulated molecules and ions the general amber force field (GAFF) parameter set was employed.\textsuperscript{24}

Partial charges for all molecules and ions were obtained by ab initio quantum mechanical calculations based on geometry optimization by using the Gaussian 03 package\textsuperscript{25} by employing the density functional theory (DFT) method with B3LYP/ cc-pVDZ level of theory. Optimized structures were used to perform single-point calculations for further partial charges calculations with the restricted electrostatic potential (RESP)\textsuperscript{26} fitting procedure by applying the Antechamber program package.\textsuperscript{27} Prepared systems were energy minimized by a steepest descent minimization procedure to remove unfavorable contacts in the solutions then equilibrated by 100 ps restrained NVT (canonical ensemble) followed by 100 ps restrained NPT (isothermal–isobaric ensemble) molecular dynamics simulations. Linear constraint solver (LINCS) algorithm\textsuperscript{28} was employed for all bonds involving hydrogen atoms. The short-range nonbonded interactions were truncated to zero with the cutoff distance of 1.2 nm, and the long-range part of the electrostatic interactions was calculated by the particle mesh Ewald method.\textsuperscript{29} All the atoms in the systems were given initial velocities according to Maxwell–Boltzmann distribution at 300 K. V-rescale coupling algorithm was used\textsuperscript{30} with the coupling constant of 0.1 ps to maintain constant temperature and pressure for all simulated systems. All production runs were done in NPT ensemble for 20 ns at 300 K, and a time step of 2 fs was used for all simulations. Coordinates, velocities, and energies were saved for analysis every 5 ps. All simulations were performed employing Gromacs 4.5.5 program package.\textsuperscript{31} To quantify the distribution of
each ion species around the GO molecule in the solutions, the radial distribution function (RDF) of the GROMACS program package has been employed. Visual Molecular Dynamics (VMD) program was used for visualizations of the trajectory and preparation of snapshots.

### RESULTS AND DISCUSSION

**Influence of Monovalent and Divalent Ions on the Zeta Potential of GO Sheets.** In this study we have used GO as a base material which zeta potential value is found to be negative in the pH range 2–10. Without the effect of any monovalent and divalent ions the zeta potential has the lowest value, \(\sim -40 \text{ mV}\), in the pH range 4–10 and the highest value, \(\sim -23 \text{ mV}\), at pH 2 for GO surface. The variation of the zeta potential of GO in the presence of 0.01 and 0.1 M NaCl(aq), Na\(_2\)SO\(_4\)(aq), NaNO\(_3\)(aq), NaBr(aq), CH\(_3\)COONa(aq), NaSCN(aq), CaCl\(_2\)(aq), MgCl\(_2\)(aq), and NH\(_4\)Cl(aq) as a function of pH is shown in Figures 2 and 3, respectively. It is observed from Figure 2 that the zeta potential value is found to be negative in the pH range 2–10 in the presence of the 0.01 M Cl\(^-\)(aq), Br\(^-\)(aq), SCN\(^-\)(aq), NO\(_3\)^- (aq), SO\(_4^{2-}\)(aq), and CH\(_3\)COO\(^-\)(aq). With increasing the pH of the medium, the zeta potential of GO tends toward more negative values because of the increased ionization of the surface edge groups.\(^{35}\) At the low pH, the zeta potential of GO has low negative values due to the adsorption of H\(^+\) ions from the acidic media on the negatively charged surface.\(^{36}\) When a salt of Na\(^+\) ion is introduced into the GO suspension, the Na\(^+\) ions are adsorbed onto the GO surface by electrostatic interactions and formed a double layer. However, the polarizability of the anions of the salt affects the extent of adsorption of the cation on the negatively charged surface of GO. In Figure 2a, it is shown that at lower pH range, where the surface becomes hydrophobic as compared to the higher pH, a small number of positively charged cations (Na\(^+\)) are adsorbed on the GO surface and the anions and resting Na\(^+\) ions are distributed around the fixed layer of adsorbed cations on the GO surface. The hydrophobic GO surface attracts the smaller anions more strongly by electrostatic interactions than the larger anions. Hence, the zeta potential of the GO surface has a less negative value in the presence of lager anions (in comparison to without salt) than in the presence of the smaller anions.\(^{37}\) The polarizability of the anions plays the key role in the variation of zeta potential of GO in the presence of inorganic salts. Smaller anions are adsorbed on the hydrophobic positively charged GO surface more strongly than the larger ions. Hence, it is observed from Figure 2a that in acidic and also in basic pH range, the zeta potential of GO follows the order SO\(_4^{2-}\)(aq) < GO < Cl\(^-\)(aq) < SCN\(^-\)(aq) < Br\(^-\)(aq) < NO\(_3\)^- (aq) < CH\(_3\)COO\(^-\)(aq) at the background electrolyte concentration of 0.01 M. In the high pH range, the GO surface is hydrophilic in nature. When the salt solution is introduced into the GO suspension, Na\(^+\) ions are

![Figure 2](image1.png)

**Figure 2.** Variation of zeta potential of GO as a function of pH in the presence of 0.01 M solutions of (a) sodium salt of different anions and (b) chloride salt of different cations.

![Figure 3](image2.png)

**Figure 3.** Variation of zeta potential of GO as a function pH in the presence of 0.1 M solutions of (a) sodium salt of different anions and (b) chloride salts of different cations.
adsorbed on the GO surface; thus, it becomes positive. On the hydrophilic, positively charged surface, larger anions are more strongly adsorbed than the smaller anions.37 Hence, the surface potential of GO in the presence of Na2SO4 salt solution is more negative than the GO surface without salt. The other anions do not show considerable effect on the surface potential.

However, the zeta potential value of the GO shifted toward positive in the presence of the 0.1 M concentration of the background electrolyte solutions. It is observed from Figure 3a that in acidic pH range (e.g., pH 4) the zeta potential of GO follows the order GO < SO4^{2-}(aq) ∼ SCN^{−}(aq) < Br^{−}(aq) < NO3^{−}(aq) < Cl^{−}(aq) < CH3COO^{−}(aq) because of the adsorption of anions on the positively charged GO surface after formation of a double layer by Na+ ions at the GO−electrolyte interface which is mainly depend on the size and polarizability of the anions. The highly polarizable anions are adsorbed more strongly on the GO surface after formation of a double layer by Na+ ions at the interface because of higher surface-active properties; hence, the zeta potential of GO follows the as-mentioned order as a function of the polarizability of anions.38 The zeta potential value of the GO in the presence of the 0.1 M background electrolyte is found to be in the range of ~22 mV to ~16 mV, which is more positive than the original GO suspension. This phenomenon is observed because of the adsorption of more Na+ ions on the GO surface due to electrostatic interaction between the negative GO surface and positive Na+ ions. Almost similar zeta potential variation of GO is observed in the neutral as well as the basic pH range.

The variation of the zeta potential of GO in the presence of NH4Cl(aq), MgCl2(aq), and CaCl2(aq) at 0.01 and 0.1 M concentration as a function of the pH is depicted in Figures 2b and 3b, respectively. From Figure 2b, it is seen that the zeta potential values of GO suspension in the presence of different chloride salts, namely, NH4Cl(aq), NaCl(aq), MgCl2(aq), and CaCl2(aq) (same anion but different cations), are less negative than those in the absence of salt solution and follow the order Ca^{2+}(aq) > Mg^{2+}(aq) > Na^{+}(aq) > NH4^{+}(aq) because of the adsorption of cations on the negatively charged surface. Divalent cations are more strongly bound to the negative surface and hence give rise to a relatively small negative zeta potential value, whereas the monovalent cations Na^{+}(aq) and...
NH₄⁺(aq) are weakly bound to the surface. Moreover, the size of the hydrated ions in the Stern layer also influences the thickness of the layer as well as the zeta potential value. The Ca²⁺ ions have small hydrated ionic radii. As a result, Ca²⁺ ions can easily enter into the Stern layer, and the zeta potential of the GO dispersion as compared to the dispersions containing other salts was less negative. The same effect is seen in the case of monovalent Na⁺(aq) and NH₄⁺(aq) ions where weakly hydrated Na⁺(aq) can more easily enter into the Stern layer than the highly hydrated NH₄⁺ ions. The NH₄⁺(aq) ion can form hydrogen bonding with the H₂O molecules and hence get highly hydrated. The concentration of the salt solutions has a great influence in the variation of the zeta potential of GO. The zeta potential value of the GO suspension becomes less negative with an increase in concentration of the salt solutions from 0.01 to 0.1 M. This is because more counterions can accumulate on the GO surface; thus, the electrical double layer is compressed. The zeta potential value of GO is found to be ~−10 mV in the presence of the 0.01 M divalent cations of Ca²⁺(aq), Mg²⁺(aq), and NH₄⁺(aq). Interestingly, we have found the isoelectric point of the GO at pH ~7.5 and ~8.3 in the presence of the 0.1 M concentration of the divalent cations Mg²⁺(aq) and Ca²⁺(aq), respectively.

**Computational Section.** MD simulations were performed with both acidic and basic forms of GO solvated in water and aqueous salt solutions of NaCl(aq), Na₂SO₄(aq), NaNO₃(aq), NaBr(aq), CH₃COONa(aq), NaSCN(aq), CaCl₂(aq), MgCl₂(aq), and NH₄Cl(aq) to better understand the pH dependence of the interaction of ions with the surface of GO. The radial distribution function was used to demonstrate the distribution of ions around a single molecule of GO to quantify the interactions of ions with the surface of GO (Figure 4).

Snapshots of MD simulations (Figure 4) show the interactions of individual ions with either the hydrophobic surface or polar COOH and OH functional groups on the surface of GO. The interaction of Na⁺ cations with GO was observed to occur in a pH-dependent manner due to binding and electrostatic interaction to the anionic form of carboxylic groups on the surface of GO, which was also observed experimentally by zeta potential measurements. The binding of cations to the carboxylate groups causes a double layer of charged surface, which results in less negative total charge at the surface of GO.

Additionally, some anions showed specific interactions with the hydrophobic surface of GO. In all MD simulations, it was assumed that all carbons of the GO molecule have zero partial charge; thus, the surface of GO has hydrophobic character. Ions which prefer hydrophobic surfaces tend to be attracted to the surface of GO. Anions such as NO₃⁻(aq), SCN⁻(aq), and CH₃COO⁻(aq) showed surface propensity to the air–water interface, which has been observed both experimentally and theoretically in many studies. It seems that the behavior of these anions at the surface of GO is the same as at the air–water interface. Also, it is shown, both experimentally and theoretically, that by increasing the hydrophobicity of ions, their surface propensity at the air–water interface is enhanced, as is observed for benzene dicarboxylic diamions when CH₃ groups to benzene ring.⁵⁹–⁶⁸

From the comparison of RDFs of anions around acidic and basic forms of GO, it can be observed that more bulky, polarizable, and hydrophobic anions such as NO₃⁻(aq), SCN⁻(aq), and CH₃COO⁻(aq) show stronger affinity for binding to the acidic form of GO, which is hydrophobic and has a zero charged surface. However, they show weaker interactions with the basic and negatively charged form of GO. The reason for such phenomena is the interactions and ion pair formation of these ions with cations attracted to the CH₃COO⁻(aq) groups of GO. Thus, fewer anions are found close to the hydrophobic surface of GO. On the other hand, doubly negative charged SO₄²⁻(aq) anions are not bound to the surface of GO, but they do bind with high affinity to the anionic form of GO when the double layer with sodium cations is formed, which causes more negative zeta potential for the solution of GO with Na₂SO₄(aq). Singly charged Cl⁻ and Br⁻ anions show very low affinity for binding to either the hydrophobic surface of GO or to the Na⁺ cations in the double layer at the surface. However, the distribution of Cl⁻ shows a slight increase around the basic form of GO in RDF calculations.

The interaction of ions with the surface of GO is responsible for the changes of experimentally measured zeta potential. Therefore, to explain the pH dependence of zeta potential in different solutions of sodium salts (Figure 2), it is essential to investigate the nature of the ions binding to the surface. It was observed experimentally that in low pH values the GO surface has the most negative charge in aqueous solutions without any salt. At these low pH values the carboxylic groups are protonated; therefore, no sodium ions are binding to the surface of GO. However, the hydrophobic, bulky, and polarizable anions such as NO₃⁻(aq), SCN⁻(aq), and CH₃COO⁻(aq) can bind to the hydrophobic surface of GO, thus generating partial positive charge on the surface, which could lead to less negative zeta potential as is observed experimentally. Moreover, these polyatomic anions are increasing the bulkiness of the complex which is retarding the diffusion of the complex through the medium. Therefore, presence of these anions results in decreased mobility of complexes in the solutions, thus making the zeta potential values even less negative. Moreover, GO has the least negative value in aqueous solution of CH₃COONa, which is due to the binding of CH₃COO⁻ anions in a very specific manner at the surface of GO. The acetate anions are closely bound to the surface of GO in which the methyl group pointing to the hydrophobic surface and carboxylic group is oriented toward the solution. This propensity of the solution–vapor interface of acetate ions has previously been described by Minofar et al.⁴⁴–⁴⁶ The same manner of orientation of acetate anions at the interface of solutions to vapor or surface of GO confirms the affinity of their methyl moiety for the hydrophobic phase. This binding mode can especially influence the volume and mobility of the complex during the zeta potential measurement, resulting in the highest values of zeta potential observed in experiment (Figure 2).

Therefore, it is clear that the specific binding modes of anions are responsible for the observed variation of zeta potential of GO in sodium salt solutions even at low pH values in which the sodium ions are not contributing to the less negative charge of the GO surface. The generation of a positively charged double layer can be followed by binding of anions to the surface of GO at higher pH values, at which the carboxylic groups become deprotonated. This is especially favorable in the case of doubly charged SO₄²⁻(aq) anions, which was observed as a formation of a complex represented in Figure 4. The binding of doubly charged SO₄²⁻(aq) anions increases the amount of negative charge at the surface, therefore contributing to even lower zeta potential of GO in
the solutions of Na₂SO₄(aq). Other anions which are singly charged and not so closely bound to the double layer formed by sodium cations do not show such strong effect on zeta potential as sulfate ions. Cl⁻(aq) anions are weakly bound to Na⁺ cations, while Br⁻ anions are not found in the first solvation shell around GO. This is the reason for more positive surface potential of GO in NaCl(aq) and NaBr(aq) salt solutions. However, it must be taken into account that bromide anions have slightly stronger binding affinity to the hydrophobic surface of GO. Thus, the observed zeta potential is in agreement with computational findings.

The values of zeta potential obtained in higher concentrations of salts in solutions which are shifted to more positive values correspond to the presence of more Na⁺(aq) anions attracted to the carboxylate groups. However, one of the factors affecting the measurement of zeta potential is the viscosity of the medium. Accordingly, the presence of large anions close to the surface of GO can influence the obtained values even more in higher concentrations of salts. The interactions of cations with GO depend strongly on the deprotonation of carboxylic groups at higher pH values. However, the intensity of these interactions and the number of cations attracted to the surface of GO depend on their properties such as charge of ions, size, and solvation properties. At low pH values, cations are not very likely to interact with GO, as can be observed in Figure 5. However, at higher pH values, these interactions are increased significantly, especially in the case of Na⁺(aq) and Ca²⁺(aq) cations. Because of their similar size, they were found to bind to the carboxylic groups more closely and form more stable complexes than Mg²⁺(aq), which is a smaller cation. Therefore, the double layer of charge at the surface of GO is more positive in the solutions of NaCl(aq) and CaCl₂(aq). Positive charge at the interface of the double layer with the solution can also lead to attraction of Cl⁻(aq) ions into the outer solvation shell of GO. Polyatomic cation NH₄⁺(aq) is also closely bound to the carboxylic groups of GO forming a bulky complex on the surface. The electrostatic interactions of NH₄⁺(aq) cation with GO are additionally supported by the formation of hydrogen bonds.

Figure 5. Radial distribution function of ionic species around the surface of GO in (a) acidic and (b) ionic state in the aqueous solutions of NaCl(aq), MgCl₂(aq), CaCl₂(aq), and NH₄Cl(aq). Complexes formed at the surface of GO in ionic form by binding of cations: (c) Na⁺, (d) Mg²⁺, (e) Ca²⁺, and (f) NH₄⁺. (Color coding: Cl, green; Mg, tan; Ca, purple; Na, light blue).
bonds between the hydrogen atoms of NH$_4^+$ and oxygen of COO$^-$ group, which can be observed from the first peak at very low $r$ values in RDF for this cation with both acidic and basic forms of GO. Because of the hydrophobicity, NH$_4^+$ cations show surface propensity to the air–water interface, proposed by a recent publication of Tian et al.$^{41}$ NH$_4^+$ also showed affinity for binding to the hydrophobic surface of GO during MD simulations, which can contribute to even more positive surface charge.

The zeta potentials measured in chloride salt solutions containing different cationic species can be also explained by observing the nature of their binding to GO during MD simulations. As was previously mentioned, Cl$^-$ anions bind weakly to the first solvation shell of GO; therefore, they are not contributing significantly to the surface potential. This is due to high solubility of Cl$^-$ and its preference for staying in the aqueous solution. Therefore, the effect of cations to zeta potential of GO in chloride salts solutions can be attributed solely to their different binding affinities and charge contributions to the double layer formed at GO surface. As can be seen in Figure 3, the doubly charged cations, such as Ca$^{2+}$ and Mg$^{2+}$, significantly increase the zeta potential of GO, which even leads to positive values at very high pH values. These values are slightly higher for Ca$^{2+}$ because of higher preference for closer binding to deprotonated carboxylic groups, which was observed in RDF analysis of MD simulations. Singly positively charged Na$^+$ cations were shown to increase the zeta potential by only half of the values of difference between pure GO and solutions containing Ca$^{2+}$ and Mg$^{2+}$ (aq). Similar zeta potential values have been observed in high concentration solutions with NH$_4^+$ (aq) cations. However, the interactions of these cations with GO are not as strong as the ones of Na$^+$ (aq), which was observed in RDF analysis of MD simulations as well as the zeta potential measurements in lower concentrations of NH$_4$Cl(aq) solutions.

Reactive Extraction Analysis. In this study we have investigated the extraction of toxic carcinogenic and mutagenic MB dye molecules from aqueous medium using GO as suitable carrier and toluene as organic solvent. The MB adsorbed on the GO surface can be easily extracted from the aqueous phase to the organic phase; thus, the dye molecule can be easily separated and recovered for further applications. Because of the amphiphilic nature, GO has the ability to form stable bubbles at the water–organic interface and bind to the dye molecules through electrostatic and van der Waals interactions.$^{50-52}$ Apul et al. and Li et al. suggested that the $\pi$ electrons of the C=\text{C} bonds and aromatic rings of the adsorbed organic molecules can bind through $\pi-\pi$ bonding with the delocalized $\pi$ electrons of the benzene ring of graphene-like structures.$^{53,54}$ MB dye molecules contain $\pi$-electrons in their aromatic region, which facilitates the binding of dye molecules through $\pi-\pi$ interaction with the $\pi$ conjugation region of GO.$^{51,52}$ Sharma et al. reported that after adsorption of MB on GO, the intensity of the Fourier transform infrared bands due to C=C and –SO$_3$– groups decreased in comparison to the free dye molecule. This result suggested that the $\pi-\pi$ interactions took place between the dye molecule and the GO sheet.$^{20}$ Thus, $\pi-\pi$ coupling along with the electrostatic interaction are responsible for the adsorption of dye molecules on the GO sheets. Toluene is used as a model organic solvent because of strong $\pi-\pi$ interactions between the unoxidized GO basal plane and aromatic toluene molecules, which promote the transfer of GO from the aqueous phase to the organic phase, and the highest extraction was achieved.$^{50,55}$ Herein, we have investigated the effect of different reaction conditions such as pH of the medium and presence of electrolytes on the bubble formation at the water–toluene interface as well as on the extraction process.

Effect of pH. The effect of pH on the reactive extraction process was investigated by stirring a colloidal system consisting of 5 mL of aqueous phase containing GO (1 mg/mL) with 1 mM MB dye and 5 mL of toluene (organic phase) for 10, 30, 40, 50, 60, 90, 120, 150, 200, and 220 s at different pH (pH 2, 5, 7, 9) of the medium. Because of the amphiphilic behavior of GO, it can be used as a surfactant between the aqueous and the organic phase and results in the formation of bubbles at the interface which are stable up to 1 week. At low pH range, with increase in the hydrophobicity of GO, it can easily transferred to the organic phase, which facilitates the bubble formation; hence, more bubbles are formed at the water–toluene interface. It was also found that with increase in the pH of the medium, the bubble size decreases because of the decrease in tendency of aggregation of hydrophilic GO.$^{56}$ In our experiment, it is depicted in Figure 6 that the average bubble size was found to be around 443.5, 263.3, 206.54, and 143.3 $\mu$m at pH 2, 5, 7, and 9, respectively. We observed that (Figure 2) with increase of the pH of the medium, the surface of GO becomes more negative (the zeta potential of GO–water suspension was $\sim$39 mV in basic medium) because of the greater ionization of the $\text{COOH}$ groups present on the GO surface by the OH$^-$ ions present in the medium. Hence, the adsorption of the anionic dye molecules was retarded by the repulsion between the negative surface and the dye molecule. Moreover, in the high pH range, the GO sheet becomes hydrophilic; it tends to stay in the water phase, and the extraction of dye molecules from the water phase to the organic phase decreases. Whereas at low pH, the surface charge of the GO surface tends toward positive value (zeta potential of GO–water suspension was $\sim$23 mV in acidic medium) due to the presence of un-ionized $\text{COOH}$ groups; thus, the electrostatic attraction between the GO surface and the dye molecules increases. Hence, more adsorption takes place, and the extraction of dye molecules is also increased. The effect of pH on the reactive extraction
process is depicted in Figure 7. At low pH, the GO surface becomes hydrophobic and tends to stay in the organic phase; thus, the transfer of GO from water to organic phase becomes feasible. Hence, extraction of dye molecules to the organic phase is facilitated by the formation of larger size bubbles at the interface. The amount of dye molecule transferred from the aqueous phase to the organic phase was found to be about 85.19% at pH 2, whereas at pH 9 the extraction amount decreased to 76.45%.

It is observed from Figure 7 that the effect of stirring time also has significant influence on the extraction process. At pH 2, the GO surface becomes more positive and π−π interaction and electrostatic interactions between the three negatively charged SO3− parts with the oxygen-containing surface functional groups of GO are the driving forces for the adsorption. For the extraction process, formation of bubbles at the water–organic interface plays a significant role. Fewer bubbles are formed at the water–toluene interface at low stirring time. (The photographs of the bubble formation at the water–toluene interface after different stirring times are shown in the Supporting Information, Figure S1). Hence, the extraction efficiency is very low at low stirring time. With increase of the stirring time, more dye molecules come into contact with the GO sheets and more bubbles are formed at the interface; hence, extraction efficiency increases. Because of hydrophobicity, GO tends to remain at the organic phase and thus shows more extraction at pH 2 in comparison to higher pH. At high pH, although dye molecules can bind with GO through both electrostatic interactions and π−π interaction, because of the hydrophilicity of GO, it tends to remain at the aqueous phase. Therefore, the extraction efficiency is a maximum at the lowest pH (pH 2).

**Effect of Cations.** The effect of cations on the extraction of dye molecules was evaluated by analyzing the extraction of MB dye molecules from the aqueous phase to the organic phase in the presence of different salts NaCl(aq), MgCl2(aq), CaCl2(aq), and NH4Cl(aq) (same anion but different cations) at pH 2, 5, 7, 9. Figure 8 shows the effect of different cations on the extraction process of the dye molecules. It is seen from Figure 8 that the extraction efficiency of MB dye molecule in the presence of 0.01 M salt solutions follows the order GO(aq) < NH4Cl(aq) < NaCl(aq) < MgCl2(aq) < CaCl2(aq). This is because the surface potential (zeta potential) of GO in the presence of different cations increases from NH4+(aq) to Ca2+(aq) ions because of their polarizability effect. Because of the presence of positive surface charge, GO can bind more strongly with the negatively charged MB dye molecule, and the transfer of the dye adsorbed GO from water to organic phase is increased by the formation of more bubbles at the interface due to the more hydrophobic nature of GO (positive zeta potential). It was observed from Figure 8 that the percentage of extraction of MB was found to be 99.01% and 94.16% in the presence of Ca2+(aq) and NH4+(aq) ions, respectively, at pH 2 within 200 s, but at pH 9, the percentage of extraction decreases to 92.68% in the presence of Ca2+(aq) and to 86.43% in the presence of NH4+(aq) ions within 200 s because of the increase in the hydrophilic nature of the GO sheets in the basic medium. The binding of negative MB dye molecules with the GO sheet in the presence of different cations also depends on the polarizability of the ions. Highly polarizable cations bind more strongly with the negative dye molecules through electrostatic interactions and hence facilitate the extraction to the organic phase to a greater extent than the less polarizable cations. Hence, extraction of MB in the presence of divalent Ca2+(aq) and Mg2+(aq) ions is greater than that of the monovalent Na+(aq) and NH4+(aq) ions. The above experimental results show that the pH of the medium also plays an important role in the extraction process of negatively charged MB dye molecules on the GO surface in the presence of inorganic cations.

We also investigated the extraction of the MB in the presence of 0.1 M salt solutions, and it was observed that the extraction process is enhanced with increasing the concentration of the salt solutions. The effect of 0.1 M Na+(aq) and NH4+(aq) ions on the extraction process is similar to the effect of 0.01 M salt solutions (Figure 9). However, in the presence of 0.1 M Ca2+(aq) and Mg2+(aq) ions, the extraction of MB dye molecule from the aqueous phase to the organic phase increases with the increase of pH of the medium because of the greater hydrophobicity of GO in the basic medium (Figure 9). Both these cations show a significant effect before and after their isoelectric point. For the Mg2+(aq) ion, before its isoelectric point (pH ~7.5), the GO sheet remains slightly hydrophilic (negative zeta potential below ~−9 mV with decrease in pH), whereas after the isoelectric point, the GO surface becomes completely hydrophobic because of its positive surface charge (positive zeta potential above ~1 mV with increase in pH) (Figure 3b). Because of its strong hydrophobic nature, GO tends to remain at the organic phase; hence,

**Figure 7.** Extraction of MB (%) on GO surface at different pH.

**Figure 8.** Extraction of MB (%) on the GO surface in the presence of 0.01 M chloride salt solutions of different cations at pH 2, pH 5, pH 7, and pH 9 in 200 s.
Na2SO4(aq), CH3COONa(aq), and NaSCN(aq) (same cation the extraction with the presence of 0.01 M di
diff solutions, namely, NaCl(aq), NaBr(aq), NaNO3(aq),
the aqueous phase to the organic phase is also a
ions is due to the di
order Br
−
Figure 11 that the percentage of extraction increases in the
Similarly, the presence of Ca2+(aq) ions also plays a signi
point at pH 7.5 and 8.3, respectively, in 200 s.
Figure 10. Extraction of MB (%) on GO surface in the presence of 0.1
M chloride salt solutions of di
efferent salt solutions present in the mixture. The variation of
extraction of MB dye molecules (about 95.32%) was observed in the
presence of CH3COO
−
(aq) anions because of the low negative surface charge (∼−16 mV) and hence increase in hydro-
phobicity of GO; it easily transfer to the organic phase, whereas the
lowest extraction of dye (88.32%) was observed in the
presence of NaBr(aq) because of the hydrophilic nature of GO
with high negative surface charge (∼−20 mV), which is larger than the GO alone (extraction 85.19%) because of the presence of
Na+ of the salt solution and less negative surface charge of
GO. With a less negative the surface charge of GO (high zeta potential value), the electrostatic repulsion of the SO3
−
dye complex from the aqueous phase to the organic phase
increased. With the increase in pH of the medium, the
variation of surface charge in the presence of different salt solutions mainly depends upon the ion–ion interactions and polarizability of ions; hence, the extraction of MB is also significantly affected by the different ions at different pH. Figure
11 shows the variation of the extraction of MB dye molecules in the
presence of different anions at different pH. At high pH (pH 9), the extraction follows the order Na2SO4(aq) < GO(aq)
∼ NaSCN(aq) ∼ NaCl(aq) ∼ NaNO3(aq) < NaBr(aq) <
CH3COONa(aq), which is related to the surface potential of
GO in the presence of different salts. The extraction of dye
molecules in the presence of CH3COONa(aq) salt was about
86.27% (due to low negative surface charge of GO ∼−29 mV)
within 200 s. In the presence of Na2SO4(aq), the extraction decreases to 73.55% because of the greater hydrophilicity of
GO with surface charge ∼−42 mV and the presence of more
polarizable divalent SO3
2−(aq) ions and strong repulsions between the negative ions and the negative dye molecules. Thus, it is seen from the above observations that the pH of the medium as well as the presence of different anions affect the reactive extraction process because of the variation of the surface property of GO as a function of pH in the presence of different salt solutions. Similar observations were made in the presence of 0.1 M salt solutions, as shown in Figure 12. It was observed that the extraction process is facilitated to a greater

Figure 9. Extraction of MB (%) on GO surface in the presence of 0.1

Figure 10. Effect of 0.1 M chloride salt solution of Mg2+(aq) and
Ca2+(aq) ions on extraction of MB before and after their isoelectric
point at pH 7.5 and 8.3, respectively, in 200 s.

increase in hydrophobicity of GO with high surface charge, it
tends to remain in the organic phase, and GO completely
transferred to the organic phase through the formation of bubbles. In the presence of Ca2+(aq) ion, maximum extraction
(99.33%) takes place at pH 9 (Figure 10). The variation in the
extraction process in the presence of Ca2+(aq) and Mg2+(aq)
ions is due to the different polarizability of the cations.

Effect of Anions. The extraction of the dye molecule from
the aqueous phase to the organic phase is also affected by the
different salt solutions present in the mixture. The variation of
the extraction with the presence of 0.01 M different salt solutions, namely, NaCl(aq), NaBr(aq), NaNO3(aq),
Na2SO4(aq), CH3COONa(aq), and NaSCN(aq) (same cation and different anions) is shown in Figure 11. It is seen from
Figure 11 that the percentage of extraction increases in the
order Br
−
(aq) < Cl
−
(aq) < SCN
−
(aq) < NO3
−
(aq) <
SO3
2−(aq) < CH3COO
−
(aq) at pH 2, which depends on the surface potential of GO. Within 200 s, the maximum extraction of MB dye molecules (about 95.32%) was observed in the
presence of CH3COO
−
(aq) ions because of the low negative surface charge (∼−16 mV) and hence increase in hydro-
phobicity of GO; it easily transfer to the organic phase, whereas the
lowest extraction of dye (88.32%) was observed in the
presence of NaBr(aq) because of the hydrophilic nature of GO
with high negative surface charge (∼−20 mV), which is larger than the GO alone (extraction 85.19%) because of the presence of
Na+ of the salt solution and less negative surface charge of
GO. With a less negative the surface charge of GO (high zeta potential value), the electrostatic repulsion of the SO3
−
dye complex from the aqueous phase to the organic phase
increased. With the increase in pH of the medium, the
variation of surface charge in the presence of different salt solutions mainly depends upon the ion–ion interactions and polarizability of ions; hence, the extraction of MB is also significantly affected by the different ions at different pH. Figure
11 shows the variation of the extraction of MB dye molecules in the
presence of different anions at different pH. At high pH (pH 9), the extraction follows the order Na2SO4(aq) < GO(aq)
∼ NaSCN(aq) ∼ NaCl(aq) ∼ NaNO3(aq) < NaBr(aq) <
CH3COONa(aq), which is related to the surface potential of
GO in the presence of different salts. The extraction of dye
molecules in the presence of CH3COONa(aq) salt was about
86.27% (due to low negative surface charge of GO ∼−29 mV)
within 200 s. In the presence of Na2SO4(aq), the extraction decreases to 73.55% because of the greater hydrophilicity of
GO with surface charge ∼−42 mV and the presence of more
polarizable divalent SO3
2−(aq) ions and strong repulsions between the negative ions and the negative dye molecules. Thus, it is seen from the above observations that the pH of the medium as well as the presence of different anions affect the reactive extraction process because of the variation of the surface property of GO as a function of pH in the presence of different salt solutions. Similar observations were made in the presence of 0.1 M salt solutions, as shown in Figure 12. It was observed that the extraction process is facilitated to a greater
extent in the presence of 0.1 M salt solutions due to the presence of more cations at the interface and hence a less negative value of the surface charge of GO; hence, strong interaction between the GO and the dye molecules takes place which results in the greater extraction of the dye to the organic phase.

Reusability Study. The stability of the adsorbent has a great importance in the field of environmental remediation. To investigate the stability of the adsorbent, reusability of the adsorbent materials is carried out to study the adsorption behavior. The variation of the surface property of adsorbent in the presence of different inorganic ions has considerable effect on the adsorption efficiency of an adsorbent. Taking into consideration the importance of this investigation, the reusability of GO sheets toward the extraction of methyl blue was performed with the GO of concentration 1 mg/mL and 1 reusability of GO sheets toward the extraction of methyl blue was performed with the GO of concentration 1 mg/mL and 1 mM MB dye solution in the presence of 0.01 M solutions of CaCl₂(aq), NaCl(aq), Na₂SO₄(aq), and CH₃COONa(aq) inorganic salts at pH 2 and 25 °C. The reusability study was performed up to four cycles with stirring time 200 s. After each cycle, GO was separated by centrifugation and repeatedly washed with hot water and acetone and then dried in an air oven at 60 °C for 4 h. The extraction efficiency was found to be around 99.01%, 86.54%, 78.43%, and 72.76% for first, second, third and fourth cycle in the presence of CaCl₂(aq) salt solution whereas the efficiency of GO was about 95.72%, 84.54%, 75.54% and 67.43% for first, second, third and fourth cycles, respectively, in the presence of NaCl(aq) salt solution. Similarly, the extraction efficiency of GO was found to be about 95.45%, 73.75%, 70.43%, and 61.54% and 95.32%, 88.12%, 72.12%, and 63.45% in the presence of Na₂SO₄(aq) and CH₃COONa(aq) salt solution, respectively. It is found that the extraction efficiency of GO toward MB extraction in each repeated cycle is decreased. The adsorption of dye molecule on the GO surface may occupy the active sites of the adsorbent in each cycle and thus retard the adsorption of dye molecules on the adsorbent surface. The reusability study of GO toward MB dye molecule up to fourth cycle is shown in Figure 13.

■ CONCLUSIONS

This study investigated the effect of different inorganic ions on the surface charge of GO; hence, strong interaction between the GO and the dye molecules takes place which results in the greater extraction of the dye to the organic phase.

Reusability Study. The stability of the adsorbent has a great importance in the field of environmental remediation. To investigate the stability of the adsorbent, reusability of the adsorbent materials is carried out to study the adsorption behavior. The variation of the surface property of adsorbent in the presence of different inorganic ions has considerable effect on the adsorption efficiency of an adsorbent. Taking into consideration the importance of this investigation, the reusability of GO sheets toward the extraction of methyl blue was performed with the GO of concentration 1 mg/mL and 1 mM MB dye solution in the presence of 0.01 M solutions of CaCl₂(aq), NaCl(aq), Na₂SO₄(aq), and CH₃COONa(aq) inorganic salts at pH 2 and 25 °C. The reusability study was performed up to four cycles with stirring time 200 s. After each cycle, GO was separated by centrifugation and repeatedly washed with hot water and acetone and then dried in an air oven at 60 °C for 4 h. The extraction efficiency was found to be around 99.01%, 86.54%, 78.43%, and 72.76% for first, second, third and fourth cycle in the presence of CaCl₂(aq) salt solution whereas the efficiency of GO was about 95.72%, 84.54%, 75.54% and 67.43% for first, second, third and fourth cycles, respectively, in the presence of NaCl(aq) salt solution. Similarly, the extraction efficiency of GO was found to be about 95.45%, 73.75%, 70.43%, and 61.54% and 95.32%, 88.12%, 72.12%, and 63.45% in the presence of Na₂SO₄(aq) and CH₃COONa(aq) salt solution, respectively. It is found that the extraction efficiency of GO toward MB extraction in each repeated cycle is decreased. The adsorption of dye molecule on the GO surface may occupy the active sites of the adsorbent in each cycle and thus retard the adsorption of dye molecules on the adsorbent surface. The reusability study of GO toward MB dye molecule up to fourth cycle is shown in Figure 13.

Figure 12. Extraction of MB (%) on GO surface in the presence of 0.1 M sodium salt solutions of different anions at pH 2, pH 5, pH 7, and pH 9 in 200 s.

Figure 13. Reusability study of GO toward reactive extraction of MB in the presence of 0.01 M solutions of different inorganic salts NaCl(aq), CaCl₂(aq), Na₂SO₄(aq), and CH₃COOH(aq).
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b02787.

Images of bubble formation at water–toluene interface in the presence of GO (PDF)

AUTHOR INFORMATION

Corresponding Authors
*Tel: +91- 9957178399. Fax: +91-376–2370011. E-mail: mnshrdas@yahoo.com, mrdas@rrljorhat.res.in.
*Phone: +420 389 033 801. Mobile: +420 777 874 938. E-mail: minofar@nh.cas.cz, babakminoofar@gmail.com.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful to the Director, CSIR–NEIST, Jorhat, for his interest in carrying out the work. P.B. acknowledges DST, New Delhi, India for DST-INSPIRE Fellowship grant. N.H. acknowledges UGC, New Delhi, India for JRF grant. B.M. acknowledges support from the Grant Agency of the Czech Republic Czech Science Foundation (Project 13-08651S). Also, access to instruments and other facilities was supported by the Czech research infrastructure for systems biology C4SYS (Project LM2015055).

REFERENCES
