Transport and retention behavior of carbonaceous colloids in natural aqueous medium: Impact of water chemistry

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ABSTRACT

Carbon based materials are emerging as a sustainable alternative to their metal-oxide counterparts. However, their transport behavior under natural aqueous environment is poorly understood. This study investigated the transport and retention profiles of carbon nanoparticles (CNPs) and graphene oxide quantum dots (GOQDs) through column experiments in saturated porous media. CNPs and GOQDs (30 mg/L) were dispersed in natural river water (RW) and passed through the column at a flow rate of 1 mL/min, which mimicking the natural water flow rate. After every 10 min, the column effluents were collected and the mass recovery and retention profiles were monitored. Results indicated that the transport of both carbonaceous colloids was predominantly controlled by surface potential and ionic composition of natural water. The CNPs with its high surface potential (40 mV) exhibited more column transport and was less susceptible to solution pH (5.6–6.8) variation as compared to GOQDs (24 mV). The results showed that, monovalent salt (NaCl) was one of the dominating factors for the retention and transport of carbonaceous colloids compared to divalent salt (CaCl2). Furthermore, the presence of natural organic matter (NOM) increased the transport of both carbonaceous colloids and thereby decreases the tendency for column retention.

1. Introduction

Recently, a great deal of attention has been paid to the carbon-based nanomaterials because of their remarkable properties in various applications (Lotya et al., 2010; Parviz et al., 2012), which...
inevitably increase their incorporation into the natural aqueous medium. These materials interact with the aquatic system and cause damage to the objects they encounter (Oberdörster et al., 2006; Zhao et al., 2014). The consideration of these interactions is important not only to understand the fate and transport of these nano sized carbonaceous colloids, but also to predict their impact to the natural aquatic system. Despite widespread applications and utilization of carbon based nanomaterials, insufficient studies have been conducted to understand the behavior of these colloids under natural aqueous medium. Column transport experiments with granular packed materials such as quartz sand or glass beads have often employed previously to study the nanomaterials transport (El Badawy et al., 2013; He et al., 2017; Xia et al., 2017). Nevertheless, the investigations on transport and retention of nanomaterials concerning their unique properties such as, surface charge, surface to volume ratio, and surface reactivity are still largely incomplete. More precisely, systematic study on the case by case fate and transport of nanomaterials remains unexplored (He et al., 2008; Pelley and Tufenkji, 2008).

For instance, the general conclusion obtained from a number of previous studies on the effect of size of nanomaterials concluded that larger nanomaterials have higher retention ability (Phenrat et al., 2009). Nevertheless, it is difficult to draw a definite conclusion as nanomaterials easily get agglomerated under certain conditions, resulting their size variation during transport (Petosa et al., 2010). Thus, making it difficult to predict whether, how, and to what extent particle size played a role in their transport. Recently, a group of researchers (Hu et al., 2017) conducted a series of comprehensive, packed column experiment to understand the transport and deposition of CNPs under various ionic strength, particle sizes and concentration conditions. They concluded that, the retention of CNPs is highly sensitive to the salinity and particle concentrations. Similarly, another group (Kasel et al., 2013) demonstrates the concentration dependent transport of multi-walled carbon nanotubes with higher input concentrations in saturated porous media.

In another report a research group systematically described the transport, deposition and mobilization behaviors of multi-walled carbon nanotubes in saturated porous media (Tian et al., 2012). They found that the solution chemistry, particularly the solution ionic strength (1 mM) produced strong deposition or column attachment of multi-walled carbon nanotubes in quartz sand (> 43%) and glass beads (> 38%). Similarly, another study (Lanphere et al., 2013) investigated the effect of solution chemistry on the transport of graphene oxide nanoparticles (GONPs). They found that the transport of GONPs was insensitive to pH variation though ionic strength did play a role. Typically, the column retention was 7%–95% at KCl solution of concentration ranging from 10^{-2}–10^{-1} M, respectively. Thus, realizing a fact that the transport of GONPs was particularly a function of solution ionic strength.

Additionally, another group (Xia et al., 2017) described the cation inhibited transport of negatively charged GONPs in saturated porous media. They observed that, cations with larger ionic radii interact with GONPs more strongly than cations of smaller ionic radii. Hence, the significant deposition of GONPs via cation bridging or via enhanced straining effect may be possible due to the increased aggregation of GONPs. The study further demonstrated that the transport of GONPs was controlled by the complex interplay between GONPs surface functionalities and solution chemistry constituents.

In addition to the effects of solution chemistry such as, pH, ionic strength, and input concentration, another factor that deserves much more attention is the effect of dissolved natural organic matter (NOM) on the transport and retention of nanomaterials (Yang et al., 2014). Most of the previous reports concluded that NOM affect the nanomaterials transport by adsorption, surface complexation and some time by ligand-exchange phenomenon (Gu et al., 1996; Zhang et al., 2009). However, to the best of authors knowledge, consideration of these interactions with carbonaceous colloids are not very well explored. To date, several previous studies have investigated the transport of nanomaterials under water-saturated conditions using synthetic water (Jones and Su, 2014; Yang et al., 2014). However, the understanding of the transport and retention profiles of carbonaceous colloids using complex natural water has received less attention.

In this work, laboratory experiments were conducted to investigate the transport and retention behaviors of CNPs and GOQDs using natural river water of complex solution chemistry due to the presence of several anions and cations. The overarching objectives of this study were to investigate the transport, mobilization and retention behaviors of CNPs and GOQDs under natural aqueous media, and to understand the roles of pH, electrolytes, and natural organic matter by examining the breakthrough behavior under a series of column transport conditions. The model simulation was also carried out to interpret and compare the experimental data obtained.

2. Materials and methods

2.1. Synthesis of CNPs and GOQDs

CNPs was synthesized by following previous published report (Jahan et al., 2013). Firstly, 0.0927 g of boric acid was dissolved in 15 mL of deionized water and then mixed with 0.025 g of N-(4-hydroxyphenyl) glycine at pH 9 Scheme 1(A). The mixture was then allowed to hydrothermally with vigorous stirring at 6000 rpm at 300 °C for 2.5 h. The resulting brown solution of CNPs was dissolved in deionized water, rinsed thoroughly with anhydrous ethanol and centrifuged at 5000 rpm for 15 min. The precipitate was then washed with deionized water for several times to remove adsorbed ethanol.

GOQDs was synthesized by hydrothermal pyrolysis of sucrose molecules (Tang et al., 2012) at 400 °C for 4 h. Typically, 6 g of sucrose molecules were dissolved in 10 mL of deionized water and the pH of the solution was adjusted to 9 by adding sodium hydroxide (1 M). The resulting mixture was heated hydrothermally producing a pale yellow solution of GOQDs Scheme 1(B). Subsequently, the
solution was allowed to dry in an oven at 100 °C to remove the water molecule and the resulting product was stored at room temperature for further characterization.

2.2. Column transport

The column transport of CNPs and GOQDs were determined using Klang River (Malaysia) water as flowing medium. The water samplings were performed from three different sampling stations (RW: station 1/Stn-1, station 2/Stn-2 and station 3/Stn-3) in order to cover the change in solution chemistry due to the degree of industrialization and urbanization of that area. Each water sample was taken as triplicate and river water physical parameters were determined on the spot using portable meters (Table S1). The concentration of anions and cations were determined by ion chromatography (IC) and inductively coupled plasma mass spectrometry (ICP-MS) after 50-fold dilution of RW samples. The column experimental setup was described as described in our previous work (Jahan et al., 2017). After wet packing with Amberlite XAD4, 20–60 mesh size with an average diameter of 560–710 μM correspond to a total pore volume of 0.50 mL/g the column was pre-equilibrated with at least 10 pore volumes of each RW sample, or colloids-free salt solutions of desired ionic strength and pH to equilibrate the chemical condition and to establish steady saturate flow. Amberlite XAD4 was used as packing material because it is non-ionic cross-linked copolymer, with a large surface area and with a homogeneous pore distribution. It is the much use type of packing material in most of the previous studies (Zhang et al., 2016; Dos Reis et al., 2011) because of its good physical, chemical and thermal stability that are quite relevant to natural porous media (Lecoanet et al., 2004). Also because of its stability at wide range of acidic and basic media (Ozdemir et al., 2004).

The dispersed carbonaceous colloids (30 mg/L) were injected from the inlet, the column effluent was collected after every 10 min and the results were constructed using breakthrough curves (BTCs). The same set of column experiment was conducted using synthetic or deionized water (DW) and the individual effect of pH, ionic strength and dissolved natural organic matter was examined. For all the column experiments, the transport and column retention have been investigated in triplicate to permit the experimental variability to be assessed. All experiments were conducted at room temperature (28 ± 1 °C) with a laminar flow velocity of 1 cm/min which mimicking natural RW flow rate.

The transport and retention behavior of CNPs (column experiments: C1, C2, C3) and GOQDs (column experiments: G1, G2, G3) through porous medium was evaluated by introducing carbonaceous colloids dispersed in Stn-1, Stn-2 and Stn-3, respectively. After completion of the column experiments, the column effluents were collected and concentrations of carbonaceous colloids transported through the column were determined by using UV absorbance at 330 nm and 280 nm for CNPs and GOQDs, respectively. The breakthrough curve was constructed between the effluent volumes (mL) and normalized effluent concentration (C/C0). To explain the experimental results with the model equation, the transport of carbonaceous colloids was fitted using advection dispersion equation with terms for one-site kinetic deposition models (Kasel et al., 2015; Dong et al., 2017) and can be presented as equations below.

\[
\frac{\partial C}{\partial t} + \frac{p}{\partial S} = \frac{D_0^2 C}{\partial z^2} - k C (1 - S/S_{\text{max}})
\]  

where \( C \) is the reduced concentration of the colloid in effluent water (mg/L); \( t \) is time (min); \( p \) is the density of amberlite (mg/L); \( 0 \) is the volumetric water content (mL); \( S \) is the deposited particle concentration (mg); \( D \) is the hydrodynamic dispersion coefficient (cm²/min); \( z \) is the coordinate parallel to flow (L); \( r \) is pore velocity (cm/min); \( k \) is the kinetic deposition rate coefficient (min) and \( S_{\text{max}} \) is the maximum deposition capacity of colloids on to amberlite surface, a system-specific parameter that is associated with the available area for colloid attachment. The above equations were used to simulate the experimental breakthrough curves and column mass recovery of added CNPs and GOQDs was calculated. The values of \( k \) and \( S_{\text{max}} \) were determined by fitting the model to effluent breakthrough data using a non-linear least squares minimization algorithm (Becker et al., 2015).

In order to determine the column retention ability of both carbonaceous colloids, after completion of the experiment the column packing material (Amberlite) was carefully removed into 5 cm increments. The material was dissolved in 50 mL DW, centrifuged and the supernatant was collected to determine the concentration of retained carbonaceous colloids using UV–Visible absorption spectroscopy.

2.3. Effect of medium pH

The individual effect of RW pH on the transport and retention behavior of CNPs (column experiments: C4, C5, C6) and GOQDs (column experiments: G4, G5, G6) was also determined at pH values 5.6, 6.0 and 6.8, respectively. CNPs and GOQDs were dispersed in DW (10 mg/L) and pH was adjusted using HCl (0.1 M). The aggregation behavior of both carbonaceous colloids was determined by observing the change in surface plasmon resonance (SPR) through absorption spectroscopy and variation was recorded at their corresponding absorption maxima.

2.4. Effects of ionic strength and natural organic matter

To compare the individual effect of natural RW ionic composition with synthetic water, similar ionic strength solution were prepared using DW and transport, kinetic sedimentation or aggregation behavior of CNPs and GOQDs was determined. For this purpose, carbonaceous colloids (10 mg/L) were dispersed in a solution of desired monovalent or divalent salt concentration and column transport experiments were carried out in the same way as explained above. The effect of ionic salts concentrations (2–10 mM) on the transport behavior were elaborated using UV–visible absorption spectroscopy. To evaluate the effect of dissolved natural organic matters (NOM) on the transport behavior of carbonaceous colloids, two sets of column experiments were designed. In the first column experiment, dispersed carbon colloids were injected and RW sample (Stn-3) was flowed through the column. In the second experiment, the synthetic solution of RW (Stn-3) was prepared in deionized water of similar ionic composition and pH (except adding NOM) and column transport was carried out. In both set of experiments the % elution of carbonaceous colloids was determined using UV–visible absorption spectroscopy.

3. Results and discussions

3.1. Characterization of carbonaceous colloids

After synthesis, the CNPs and GOQDs were characterized by several techniques such as UV–visible, FTIR, FESEM and zeta-potential analysis. Fig. 1, represented the FESEM morphology (a, c) and UV–Visible absorption spectra (b, d) of synthesized CNPs and GOQDs respectively.

The average diameter of synthesized CNPs and GOQDs are approximately 20 nm and 50 nm in diameter. The typical
absorption spectra show peak maxima at 330 nm and 280 nm which are the corresponding peak of CNPs and GOQDs respectively (Tang et al., 2012; Liu et al., 2016).

Fig. 2; represent the FTIR spectra of CNPs and GOQDs. The FTIR spectra of CNPs showed the vibrations around 3293 cm\(^{-1}\) corresponds to the surface O-H group (Jahan et al., 2013). The vibrations centered at 1677 cm\(^{-1}\) and 1404 cm\(^{-1}\), ascribed to C=O and C-OH groups of COOH (Jahan et al., 2013). The FTIR spectra of the GOQDs showed an obvious absorption peak 1670 cm\(^{-1}\) which was due to the C=C stretching mode. The vibration at 779 cm\(^{-1}\) and broad absorption band at 3375 cm\(^{-1}\) were attributed to CH\(_2\) rocking and O-H groups. The absorptions bands at 1017 and 2930 cm\(^{-1}\) correspond to the C-O and C-H respectively (Tang et al., 2012).

The surface potential of both carbonaceous colloids was determined by zeta-potential analysis. Results revealed that both CNPs and GOQDs were negatively charged particles with surface potential of \(-40 \text{ mV}\) and \(-20 \text{ mV}\), respectively.

3.2. Column transport experiments

Fig. 3, represent the observed breakthrough curve (BTCs) for the transport of CNPs (C1, C2, C3) and GOQDs (G1, G2, G3) in RW samples of different ionic compositions. The experimental breakthrough curves described well with model equations (R\(^2\) > 0.90) and summary of model parameter were described in Table S2. As shown by the BTCs, the transport of CNPs was greater in all experiments as compared to GOQDs and more concentration of CNPs was eluted from the column.

If the size and zeta potential values of both carbonaceous colloids were compared (Table 1) it was notable that the particle size of CNPs is smaller whereas, the zeta potential value is higher than the GOQDs. It was reported in an earlier research (Zhou et al., 2016) that the less negative zeta potential value bound to induce weaker electrostatic repulsion forces between the particles and therefore more column retention was observed in GOQDs. This suggested that the transport behavior of both carbonaceous colloids is largely dependent upon the particle size and zeta potential value and more transport occurred with smaller particle size and higher zeta potential value.

From all these transport experiments, it was also observed that the elution concentration of CNPs and GOQDs decreased as the ionic composition of dissolved substances increased i.e., from RW Stn-1 \(<\) Stn-2 \(<\) Stn-3. The finding is in accordance with previous report (Zhou et al., 2016) in which graphene oxide was transported through the column and maximum column retention was observed.
in solution of higher ionic strength i.e., 100 mM. Typically in the BTCs, the peak effluent concentrations \((C/Co)\) max at Stn-1 was 1.5 times higher in the case of CNPs and 1.9 times higher in case of GOQDs compared to Stn-3. The peak effluent concentration \((C/Co)\) max was decreased from 0.12 to 0.09 and 0.1 to 0.06 for CNPs and GOQDs, respectively from Stn-1 to Stn-3. Whereas, the total mass recovery of added colloids were 85.8%, 78.6% and 64.3% for CNPs and 83.4%, 74.9% and 49.7% for GOQDs for Stn-1, Stn-2 and Stn-3, respectively. It means that the concentration of eluted carbonaceous colloids or the transport of colloids was largely controlled by the ionic composition and complexity of natural RW. This effect of decreased BTC plateaus due to increased ionic composition was also observed previously (Jiang et al., 2012) when ZnO nanoparticles were transported in saturated porous media. Basically, the increased ionic strength of solution resulted in column flocculation (Lin et al., 2010) leaving behind less space for particles to transport through the column surface and therefore more column retention observed as was also observed in this study.

To determine the retention of both carbonaceous colloids, after completion of the transport experiments the column dissections were performed to better understand the distribution of CNPs and GONPs. Fig. 4, represents the spatial distribution of retained CNPs and GOQDs in the column after the transport experiments. As shown by the figure, the retention of GOQDs was higher than the CNPs which are also evident from the results of a transport study (Fig. 3). The retention of both carbonaceous colloids decreased as the distance from the column inlet increased. Similar to column transport, the retention of CNPs and GOQDs into the column was strongly dependent upon the ionic strength of the solution. The higher the ionic strength the more will be the column retention such as at Stn-3 in our case. Typically the observed retention of CNPs and GOQDs were 0.9–2.4 mg and 0.5–2.5 mg in Stn-3, respectively.

These retention profiles were consistent with the previous work (Fan et al., 2015) which showed that the retention of graphene oxide was strongly dependent upon the ionic strength of the solution and high deposition rates was observed at solution of higher ionic strength. Therefore, it is anticipated that the retention profiles or column attachment of CNPs and GOQDs increased as the ionic strength of the solution increased.

### 3.3. Effect of pH

Fig. 5, revealed the effect of pH on the behavior of CNPs and GOQDs. Sharp BTCs were observed at 10 pore volume for all three solution pH i.e., \(pH = 5.6\) (a), \(pH = 6.0\) (b) and \(pH = 6.8\) (c). Similarly, during the rinse phase of column transport experiment, the normalized effluent concentration \((C/Co)\) decreased sharply to almost zero when particle free solution was fed to the column. The mathematical model closely matched the experimental BTCs of CNPs and GOQDs at all pH values with correlation coefficient \((R^2)\) higher than 0.92. As depicted by the figure, sharp BTCs were observed for CNPs at all tasted solution pH with low column retention. On the contrary, high column retention with small BTCs were observed in case of GOQDs, particularly at lowest pH (pH-5.6), this realizing the fact that, the transport of GOQDs was more susceptible to solution pH and more column retention was observed.

Typically, the peak effluent concentration \((C/Co)\) max for CNPs was \(0.5 \pm 0.02, 0.5 \pm 0.01\) and \(0.45 \pm 0.02\) for pH values 5.6, 6.0 and 6.8 respectively. While, \(C/Co\) values for GOQDs were in the order of \(0.2 \pm 0.01, 0.4 \pm 0.03\) and \(0.3 \pm 0.03\) for pH values 5.6, 6.0 and 6.8, respectively. The total mass recoveries were 94.2%, 94.3% and 94.1% and 44.5%, 66.7% and 78.8% for CNPs and GOQDs at pH values 5.6, 6.0, and 6.8, respectively.
6.0 and 6.8, respectively. Whereas, the retained profile calculated from the % mass recovery were 5.8%, 5.7% and 5.9% for CNPs and 55.5%, 33.3% and 21.2% for GOQDs, respectively (Table S2).

The pH dependent transport phenomenon was also observed previously when CeO₂ nanoparticles was transported through porous column transport (Li et al., 2011). According to this study, the transport of CeO₂ nanoparticles was inhibited which was evident from little to no BTCs, when solution pH was decreased from pH-9 to pH-3 indicating the stronger attachment of CeO₂ to the column surface. Similar trend was observed in this study when GOQDs was transported at pH values from pH-5.6 to pH-6.8. In addition to this, another recent report (Dong et al., 2017) concluded that pH has a significant influence on the transport of graphene oxide nanoparticles which was decreased from 51.7% to 40.3% when solution pH decreased from 9.5 to 4.5. The reason of low transport behavior of GOQDs compared to CNPs may be explain well by surface potential values. As presented in Table 1, the zeta-potential value for GOQDs was lower than CNPs which were $-24 \text{ mV}$ and $-40 \text{ mV}$ respectively.

The low transport of GOQDs at pH-5.6 is attributed to the fact that, GOQDs contains small amounts of surface hydroxyl (OH⁻) functional groups in contrast to CNPs, which can dissociate at relatively low pH values (pH 5.6) resulting in less negative surface charge, less electrostatic repulsion and more column deposition.
(Dong et al., 2017). Therefore, the surface potential has a strong influence on the transport behavior of carbon based colloids. CNPs with higher surface charge, was more stable towards all three solution pH with little to no column deposition. On the other hand GOQDs transport was retarded at lower pH value i.e., pH-5.6.

3.4. Effect of ionic strength

For the transport behavior study of both carbon based materials, the individual effect of monovalent salt (NaCl) and divalent salts (CaCl2) was also taken into consideration. For this purpose these two salts were selected because Na+ and Ca2+ are the two dominant cations present in most natural aqueous medium (Lanphere et al., 2014). Fig. 6 shows the breakthrough curves for the transport and retention behavior of CNPs and GOQDs in presence of NaCl and CaCl2. As depicted by figure, the transport of CNPs and GOQDs were more susceptible to column retention towards NaCl Fig. 6 (a, c). Whereas, the transport were less effected towards CaCl2 with low column retention behavior Fig. 6 (b, d). Typically, the increased NaCl concentration (2–10 mM) resulted in the maximum retention of both NMs which was evident from the concomitant decrease in breakthrough curves.

The peak effluent concentration (C/C0) max at maximum NaCl concentration (10 mM) was decreased from 0.8±0.02 to 0.4±0.01 in case of CNPs and from 0.78±0.02 to 0.20±0.03 in case of GOQDs (Fig. 6a and c), respectively. However, this significant decrease in peak effluent concentration (C/C0) max was not much prevalent in case of CaCl2 even at maximum concentration of 10 mM. The peak effluent concentration (C/C0) max was decreased from 0.8±0.02 to 0.6±0.01 in case of CNPs and from 0.78±0.03 to 0.45±0.01 in case of GOQDs (Fig. 6b and d). The total mass recoveries in presence of NaCl (10 mM) at pH value 6.8 were 40% and 20% in case of CNPs and GOQDs, respectively (Table S2: C7, G7). Whereas, the mass recoveries in presence of CaCl2 (10 mM) were 60% and 45% for CNPs and GOQDs (Table S2: C8, G8). Similarly, the retention of CNPs and GOQDs were 59.8% and 80.0% in presence of NaCl and 39.9% and 54.8 in presence of CaCl2, respectively (Table S2).

This suggested that the transport behavior of both carbonaceous colloids was strongly influenced by the concentration of monovalent salt (NaCl). While the effect of divalent salt (CaCl2) on the transport of CNPs and GOQDs was not prevalent. These results were consistent with previous report when gold nanoparticles was transported in saturated porous media in presence of NaCl (Afroz et al., 2016). According to this study the transport behavior of gold nanoparticles was significantly decreased as the concentration of NaCl electrolyte increases from 1 mM to 100 mM and lowest break through profile was observed at 100 mM NaCl concentration. The mechanism of CNPs and GOQDs decreased transport behavior in presence of NaCl can be describe well with previous report (Chowdhury et al., 2013) that this behavior was because of the cation bridging effect with increasing NaCl concentration. This cation bridging between surface hydroxyl groups of carbon based colloids and added NaCl, resulting in the progressive deposition of electronegative CNPs and GOQDs with increasing concentration of NaCl. Similar results were also observed in earlier reports for the transport of several other carbon-based materials (Saleh et al., 2008; Bouchard et al., 2009).

However, unlike several earlier reports (Xia et al., 2017; Zhang et al., 2017) the presence of CaCl2 (2–10 mM) produced less column retention and the BTCs for CNPs and GOQDs were higher as compare to NaCl. Typically, in our case the retention of both NMs was about 38%–22% lower than that of retention observed in presence of NaCl (2–10 mM). The lower column retention observed in presence of CaCl2 at similar ionic strength (2–10 mM) was due to the smaller diffusion coefficient of CaCl2 (Yang et al., 2014) which led to steric repulsion among particles (Liu et al., 2011) and more...
transport of CNPs and GOQDs were obtained. The steric repulsion particularly inhibit aggregation rate and thereby low column retention was observed.

3.5. Effect of natural organic matter (NOM)

Fig. 7, illustrates the effect of NOM on the transport behavior of CNPs and GOQDs. As figure represents, the percent elution of both NMs slightly enhanced in the presence of dissolved NOM in RW (Stn-3) compared to the synthetic water in the absence of NOM. The % elution of CNPs and GOQDs were 69% and 60% in absence of NOM, whereas, the % elution were 80% and 70% in presence of NOM.

Similarly, the retention profiles of CNPs and GOQDs in absence of NOM were observed as 31% and 40% and 20% and 30% in presence of NOM. This effect was may be due to the adsorption of NOM at the surface of carbon based NMs which increases the particle-particle repulsion between the negatively charged CNPs and GOQDs and dissolved NOM. This repulsion was also confirmed by less column attachment and more elution as was also observed in previous report (Afrooz et al., 2016). The increased % elution or mass recovery values obtained in this study correlate well with the stability characterization results obtained from the literature for the transport of NMs in the presence of NOM (Godinez et al., 2013; Wang et al., 2013).

According to these reports, as the NOM adsorbed at the surface of nanoparticles, decreased column attachment and increased relative mass recovery of nanoparticles were observed. This suggested that the presence of NOM enhanced the steric hindrance among the particles and subsequently increased particle stability during transport. This observation was in agreement with what observed in this study, when CNPs and GOQDs transport were investigated in presence of NOM. The interaction of graphene oxide nanoparticle with NOM was also observed in earlier study showing that graphene oxide exhibited specific interaction with NOM via functional group association under electrostatically unfavorable condition (Chowdhury et al., 2014). Hence, it is concluded that, presence of NOM in natural water play vital role in the transport of carbon based colloids as also observed in previous reports (Franchi and O’Melia, 2003; Qi et al., 2014). To confirm the adsorption of NOM at the surface of carbon based NMs, zeta potential analysis was performed. Fig. 8, displaying the effect of NOM attachment at the surface of carbon based NMs.

As shown by figure, the zeta-potential values of both NMs increased in the presence of NOM. Typically in case of CNPs, the surface potential change from $-40 \text{ mV}$ to $-44 \text{ mV}$ whereas, in case of GOQDs the zeta-potential value modified from $-24 \text{ mV}$ to $-27 \text{ mV}$. It means that the NOM adsorbed at the surface of carbon based NMs and provide stability via electrostatic repulsion among particles (Wang et al., 2015). This enhanced stability resulted in improved transport potential of both CNPs and GOQDs. Consequently, these results revealed that the transport behavior of both carbon based materials was largely controlled by factors such as, ionic composition of solution, solution pH and materials surface potential.

We also explored the zeta potential value of amberlite XAD4, since NOM would also affects the surface potential of XAD4 and may affects the transport of nanomaterials (Ferro-Garcia et al., 1998). The zeta potential of XAD4 in solution (pH 5.6, 6.0, and 6.8) were measured and the results are shown in Fig. S1. As shown if figure the zeta potential of XAD4 at all three solution pH are negative and no obvious change was observed. Furthermore, the charge attraction between negatively charged NOM and XAD4 could not be formed (Wang et al., 2009). Therefore, it is suggested that NOM would not adsorbed at XAD4 and would not contribute to the increased transport of CNPs and GOQDs.

4. Conclusion

In conclusion, this study demonstrated that the particle surface potential and ionic composition of water greatly affects the transport and retention behavior of carbonaceous colloids. For example, in presence of NaCl (2–10 mM) less column transport with small
BTCs were observed as compared to CaCl$_2$ (2–10 mM). Additionally, in most of the previous studies CaCl$_2$ has predominant effect on retention and transport of nanomaterials as compared to NaCl. However, in our case the effect of NaCl on transport and retention behavior was more prevalent as compare to CaCl$_2$. This is because of smaller diffusion coefficient of CaCl$_2$ which lead to more steric repulsion among the particles and hence less column retention was observed. Typically, the total mass recoveries of CNPs and GOQDs were 40% and 20% for NaCl and 60% and 45% for CaCl$_2$, respectively. The results of the NMs surface properties revealed that GOQDs with its low zeta-potential value (−24 mV) and large particle size (50 nm) were more susceptible to ionic strength and solution pH variation. While, CNPs with high zeta-potential value (−40 mV) and small particle size (20 nm) was less sensitive. The NOM increased the absolute surface potentials of CNPs and GOQDs by absorbing at the particle surface. As a consequence; the electrostatic repulsion among particles increased resulted in less retention. The findings obtained from this study will be significant in predicting the transport of NPs in a more realistic complex aquatic environment.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2018.11.015.

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