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ORIGINAL PAPER

Adsorption studies of toxic metals and dyes on soil colloids and their transport in natural porous media

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Abstract Mobile colloids in soils and aquifers can act as carriers for adsorbed contaminants and thereby facilitate the transport of contaminants. In order to understand the problem, colloids isolated from soil were used as adsorbents for toxic metals such as Pb(II), Ni(II), Cu(II), Cr(VI) and dyes such as alizarin red and methylene blue. Column experiments were conducted to investigate the mobilization of in situ colloids from soil and their size distribution. Experiments were also conducted to study the transport of alizarin red dye through soil columns at different ionic strengths (0.01 and 0.001 M) and pH (pH 7.5, 9.5 and 11.5) and toxic metals at the ionic strength of 0.001 M. The colloids showed significant adsorption toward the contaminants with the adsorption of methylene blue reaching as high as 625 mg g^{-1}. The mobilized colloids had significant difference in their size distribution, and the cumulative mass curve of colloids followed a nonlinear pattern in contrast to the previously reported linear behavior on model systems. The dye and toxic metal transport experiments suggested their sensitivity to low ionic strength influent solution, with the capacity of colloids to transport the dye and toxic metals increasing at low ionic strength and the transport of dye at high pH. With decreasing ionic strength, the release rate coefficient of dye increased. This study represents an important step to understand colloid-associated contaminant transport in natural soils.

Keywords Adsorption · Dye contaminant · Flocculation · Ionic strength · Soil colloids

Introduction

It is imperative to understand the mechanisms of colloid and colloid-associated transport of contaminants in natural porous media, when addressing environmental issues (Mishurov et al. 2008). Earlier studies have described the ground water as a two-phase system in which contaminants partition between immobile solid matrix and the mobile aqueous phase. But it has been acknowledged now that colloids in the solid phase act as a third phase and are known to be mobile in subsurface environments (Aramrak et al. 2014; Gao et al. 2004; Honeyman 1999; Magal et al. 2011; McCarthy and Zachara 1989; Puls and Powell 1992; Zhang et al. 2010). Colloidal particles with diameters <10 µm in the soil include mineral fragments, oxides of Fe and Al, microbes, plant decay debris and macromolecular components such as humic substances among others (Murali et al. 2012). Mobile colloids which are ubiquitous in soil waters and ground waters adsorb the dissolved contaminants and act as carriers of these contaminants in subsurface environments. This process referred to as

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"colloid-facilitated contaminant transport" assumes importance because of their ability to carry low water-soluble hydrophobic organic contaminants (Cheng and Saiers 2010).

Many studies have reported the transport of strongly sorbing contaminants such as radionuclide's, transition metals, heavy metals, pesticides and hydrophobic organics among others in a saturated soil column (Cherrey et al. 2003; Dunnivant et al. 1992; Grolimund and Borkovec 2005; Grolimund et al. 1996; Howard and Sova 1993; Magee et al. 1991; Nelson et al. 1985; Sen et al. 2002a; Vinten et al. 1983). The co-transport and desorption of metals by colloidal particles have been studied using Zn-saturated soil (Barton and Karathanasis 2003). The study involving the transport of Ni(II) in a kaolin–sand bed showed that the kaolin colloids facilitate the transport of Ni(II) owing to their increased adsorption over sand (Sen et al. 2002b). The studies on the adsorption of Cu(II) and Ni(II) metal ions on iron oxide, kaolin and sand material has shown that the adsorption of Cu(II) and Ni(II) occurs preferentially on the colloidal materials and adsorption is favored at high pH (Sen et al. 2002a).

The colloid-facilitated transport of Pb as a model contaminant has been investigated in laboratory column experiments with sodium and calcium as major cations. It has been shown that colloid release could be prevented by infiltrating the sediment column with concentrated divalent cation, Ca^{2+} solution, thus preventing the contaminant transport (Grolimund and Borkovec 2005). The investigations into the ability of biosolid colloids on the transport of copper, lead and zinc performed in undisturbed soil monoliths have demonstrated their role as a potential contaminant carrier and the risk of ground water contamination by dumped biosolid wastes. The enhanced mobility of colloids and contaminants with decreasing pH and colloid size and increased soil macroporosity has been well reported (Karathanasis et al. 2005).

A number of studies have also described the release and transport of colloidal particles from the soil column (Grolimund and Borkovec 1999, 2006; Grolimund et al. 2001; Kretzschmar et al. 1999; Roy and Dzombak 1997; Pilgrim and Huff 1983; Swartz and Gschwend 1998). These studies typically investigate the influence of solution chemistry on colloid transport in porous media. The transport of colloids is influenced by surface chemical characteristics of natural porous media, solution chemistry, size and flow velocity (Grolimund et al. 1998). The transport of colloidal particles from the surface soil to the aquifer increases the risk of contaminant transport, thereby causing the water contamination. Thus, a quantification of transport of colloidal particles through soil assumes significance, for the estimation of leaching of contaminants (Barton and Karathanasis 2003).

The mobilization of soil colloids through natural porous media entirely depends on its size with the micrometer-sized colloidal particles are immobilized due to gravitational settling. But colloids of nanometer size range are considered to be highly mobile in subsurface environments, though the exact size range is not known for maximum mobility (Ranville et al. 2005).

In contrast to the large number of studies on colloidal particles release in model systems, systematic investigation into the mobilization of colloids in natural porous media and quantification of colloids released from soil are rather limited. Though studies on the transport of colloids and contaminants in porous media at variable flow rate and solution chemistry are available, our knowledge of size distribution of colloids mobilized from soil and contaminant transport at constant flow rate is limited. This study is distinguished from other published works through its focus on colloid release and colloid-associated contaminant transport at constant flow conditions.

The main objective of this study was to investigate the adsorption of alizarin red and methylene blue dye and toxic metals such as Pb(II), Ni(II), Cr(VI) and Cu(II) on colloidal particles isolated from soil and to study the transport property before and after adsorption. Experiments were conducted to investigate the influence of ionic strength and pH on the transport of in situ colloid-associated dye and Pb(II), Ni(II), Cr(VI) and Cu(II) at constant flow rate. These chemicals were chosen because of their strong adsorption to soil colloids and because these organic dye and inorganic toxic metals represent the two different category of contaminants in the natural environments.

Materials and methods

Porous medium

Sediment samples were collected at 0.25-m interval from the exposed late Quaternary sediment sequences dating back to 125 ka from the Mahi River basin of Gujarat, India. Prior to collection of sediment samples, the exposed surface was scraped clean, and polythene bags were used for collecting the samples. The collected sample was thoroughly mixed to get a homogenous mixture and sieved through a 2-mm sieve. The sediment material had a silt loam texture with an organic carbon content and cation exchange capacity of 5.1 g kg^{-1} and 40 mmol kg^{-1}, respectively. The organic carbon content was determined by wet oxidation method (Walkley and Black 1934) and cation exchange capacity by column technique (Cernik et al. 1994). The soil fraction was analyzed by the pipette method (Kilmer and Alexander 1949) and consisted of sand 25 %, silt 61 % and clay 14 %.

A first-order colloid release rate coefficient was calculated by fitting the decline in the colloid concentration in the breakthrough curve, i.e., from maximum to minimum colloid concentration to the Eq. (1).

$$C_t = C_{\max} e^{-K_{\mathrm{rel}} t} \tag{1}$$

where C_t is the colloid concentration with respect to time, $C_{\max}$ is the maximum colloid concentration in breakthrough curve and K_{rel} is the first-order release rate coefficient.

Contaminants

Solution of alizarin red, methylene blue (Chemdyes corporation), chromium(VI) oxide, nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), copper(II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) and lead(II) nitrate $Pb(NO_3)_2$ (Merck chemicals) were prepared and used in the experiments.

Colloid separation

Colloidal particles were separated from the sediment samples by mixing 200 g of sediment with 500 mL double distilled water in a beaker. The above mixture was stirred overnight using a mechanical stirrer. This mixture was centrifuged for about 15 min at 750 rpm. It has been reported that even 3.5 min of centrifugation at 750 rpm is sufficient to separate the native colloid particles from soil (Barton and Karathanasis 2003). The relative centrifugal force (RCF) was calculated by using the known formula (Upadhyay et al. 1993) and is an indication of the efficiency of separation, i.e., the separation of the non-colloidal particulates. The RCF value was 25.12 and sufficiently high to separate out all suspended matter except the colloidal dimensions. The supernatant solution was separated by decantation, and the colloidal particles present in the supernatant were separated by flocculation with 0.5 M $CaCl_2$ solution. These aggregated colloids were dried at room temperature (30 °C) and used for further analysis.

Characterization of colloids

The mineralogical composition of soil colloids was determined by powder X-ray diffraction analysis (Brucker DX). Elemental analysis of colloids was carried out by energy dispersive X-ray analysis. Size of the colloidal particles suspended in aqueous media was measured by static light scattering instrument (miniDAWN Tristar, Wyatt technology) equipped with Ga–As semiconductor laser with a operating wavelength of 690 nm. Transmission electron microscopy (Philips, Tecnai 20) images were taken to determine the shape of colloidal particles in the suspensions. ζ-potential was calculated from the ZetaSizer (Malvern).

Adsorption experiments

The structure of alizarin red and methylene blue dyes is shown in Figure S1, supporting information, and the properties are given in Table S2, supporting information. Adsorption of dyes from their aqueous solution by colloidal particles was measured by placing 50 mL of dye solution with a concentration range of 50–350 mg L^{-1} in contact with 20 mg of colloidal aggregates in a series of beakers at room temperature (30 ± 2 °C). Samples were stirred by using magnetic stirrer with constant speed to maintain the contents completely mixed for about 6 h. After equilibration, samples were centrifuged at 3,000 rpm for 15 min. The concentration of the supernatant solution was measured on a UV–Visible spectrophotometer (UV 2450, Shimadzu) at the wavelength of 520 nm for alizarin red and 665 nm for methylene blue. The quantity of adsorbed dye on colloidal particles was calculated as the difference between initial concentration and concentration at equilibrium.

In the case of toxic metals, the quantity of the native colloid adsorbent was 10 mg and the adsorbate taken was 50 mL with initial concentration range of 10–50 mg L^{-1}. The adsorption experiments were carried out at the pH of 2.75 for Cr(VI) and pH 6.5 for Pb(II), Ni(II), Cu(II) and dyes. The concentration of chromium was measured on a UV–Visible spectrophotometer (UV 2450, Shimadzu) at a wavelength of 372 nm, and the remaining toxic metals were determined using an Atomic absorption spectrometer (Electronic corporation of India Ltd. AAS 4141).

Column studies

Column setup and colloid mobilization

A chromatographic glass column with an internal diameter of 4 cm and length 50 cm was used to study the transport behavior of the colloidal particles. The bottom of the column had a porous disk to contain the sediment material. After packing the column with sediments, the column was gently tapped with a mechanical vibrator for 5 min to ensure a uniform packing of the column. The average packed height of the glass column was 15 cm. Typical pore volume was 35 mL, whereas the porosity and bulk density were 0.18 and 1.7 kg L^{-1}, respectively.

The colloids were mobilized from sediments with 0.001 M NaCl solution at a constant flow rate of 0.3 mL min^{-1}, and the effluent samples were collected at different pore volumes and analyzed for colloidal concentration by drying the solution at 100 °C as reported in the literature (Kjaergaard et al. 2004). This process was continued until a constant low concentration of colloids obtained in the effluent. The size distribution of colloidal particles mobilized out from sediments of separate set of column was also determined after centrifugation, as was done previously.

Transport experiments

This alizarin red dye transport experiments were carried out with the in situ released soil colloidal particles. Briefly, after packing, the soil columns were preconditioned with about 30 mL of 0.5 M NaCl solution. Then, 20 mL of the alizarin dye solution of 50 mg L^{-1} concentration was allowed to flow through it. This step ensured that the soil column gets sorbed with the dye so that the released colloidal particles would carry the dye.

After this sorption step, columns were leached with 0.01 M NaCl and 0.001 M NaCl solution at constant flow rate of 0.3 mL min^{-1}, and the effluents were collected. The total dye concentrations (dissolved and colloid associated) were determined using a UV–Visible spectrophotometer (UV 2450, Shimadzu) at a wavelength of 520 nm. Since the solubility of the dye in water is fixed, the total absorbance will depend only on the colloid adsorbed dye concentration. The effect of pH on the release of colloidal particles was investigated at different pH values. Saturation of soil column with dye was achieved after preconditioning it with 5 pore volume of 0.5 M NaCl solution. In these column experiments, contaminated sediments were exposed to influent solutions with ionic strength of 0.001 M NaCl of three different pH values of 7.5, 9.5 and 11.5. The collected effluent samples were analyzed for pH and total dye concentration.

In the case of toxic metals, the same procedure described above was performed with 50 mL of Cr(VI) having the initial concentration of 15 mg L^{-1} and 35 mL of other toxic metals having the concentration of 3 mg L^{-1} with the influent solution of 0.001 M NaCl.

Results and discussion

Colloid characterization

TEM images showed that the colloidal particles are highly irregular in shape and are shown in Figure S3. The hexagonal-shaped particles show the presence of kaolinite mineral in the suspension (Millot 1970). From the X-ray diffraction analysis (Figure S4), primary minerals identified were quartz, calcite, kaolinite and manganite from the 2θ values of these minerals reported in the literature and confirmed that the colloidal particles were highly heterogeneous in their mineralogical composition. The elemental content of colloids is given in Table S5 and its spectra are shown in Figure S6, supporting information, which shows that Si and Al are the major elemental constituent of colloids. The ζ-potential of the colloidal particles as a function of pH is shown in Fig. 1. The ζ-potential was positive at pH 3.5 and became more negative as pH increased from 7.5 to 11.5. This charge reversal increases the possibility of their transport, if sufficient amount of anions are present in subsurface environment (Bekhit et al. 2006).

Adsorption experiments

The effect of initial solution concentration on the adsorption of the dye on colloids was investigated at room temperature (30 ± 2 °C) with measurements made after an equilibration time of 6 h. The amount of the dye adsorbed with change in concentration is shown in Figure S7a. It can be seen that the adsorption of dye on colloid increases with increasing dye concentration in aqueous solution and attains equilibrium. At lower concentrations, all the dye

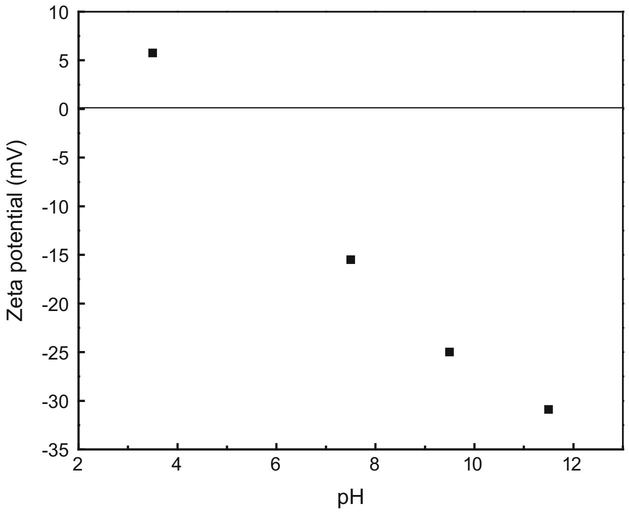

Fig. 1 Zeta potential of colloidal suspensions at different pH

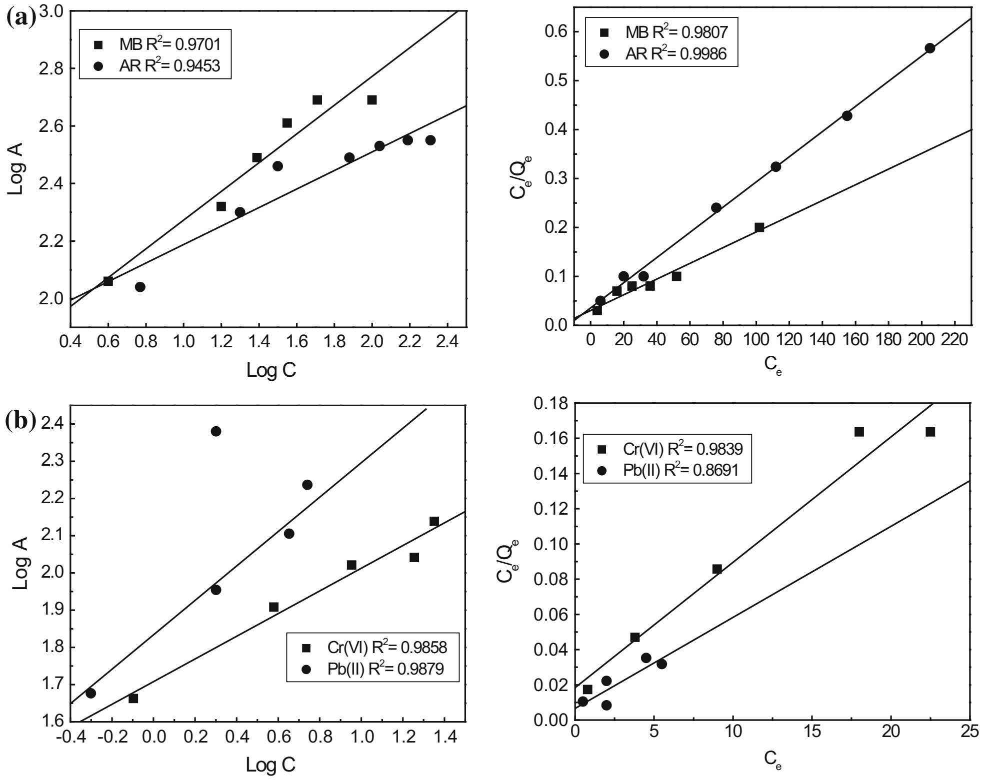

Fig. 2 Freundlich and Langmuir adsorption isotherm for **a** methylene blue (MB) and alizarin red (AR), **b** Pb(II) and Cr(VI) on colloids

molecules present in the aqueous media are able to interact with the adsorption sites on the colloids that are followed by the slow intraparticle diffusion into the interior of the particles at higher concentrations. As the colloid is crystalline material, intraparticle diffusion occurs through the space between the lattice layers. However, the amount of adsorption of alizarin red on colloid is lower than that of methylene blue.

The experimental data were fitted to the logarithmic form of the Freundlich equation as shown in Eq. (2), and the Log *A*/Log *C* plot for dyes is shown in Fig. 2a.

$$\text{Log}\, A = \text{Log}\, K_F + N\, \text{Log}\, C \qquad (2)$$

where *A* is the solid phase concentration (mg g^{-1}) and *C* is the liquid phase concentration (mg L^{-1}). The K_F indicates adsorbed amount [(mg g^{-1})/(L mg^{-1})] and *N* indicates isotherm nonlinearity.

Langmuir isotherm can be represented by the Eq. (3) as given below

$$C_e/Q_e = 1/Q_0 b + C_e/Q_0 \qquad (3)$$

where C_e is the equilibrium concentration (mg L^{-1}), Q_e is the amount adsorbed at equilibrium (mg g^{-1}). *b* is a constant related to the intensity of the adsorption process, Q_0 shows the adsorption efficiency (mg g^{-1}). The linear plots of C_e/Q_e against C_e suggest the applicability of Langmuir adsorption isotherm. A better fit with Langmuir model is obtained for alizarin red dye with Q_0 value of 400 mg g^{-1} and the correlation coefficient being 0.9986.

The amount of toxic metals adsorbed with change in concentration is shown in Figure S7b, and the Log *A*/Log *C* plot for Freundlich isotherm and C_e versus C_e/Q_e for Langmuir isotherm are shown in Fig. 2b. The Freundlich and Langmuir isotherm parameters for the adsorption of toxic metals are given in Table 1, and the adsorbed amount of Ni(II) on colloid was higher and decreased in the sequence Cu(II), Pb(II) and Cr(VI).

The adsorption at a colloid surface is mainly a result of electrostatic binding forces that exist between ions of toxic metals to the adsorbent surface as natural colloids are negatively charged (Puls and Powell 1992). The divalent cations such as Cu(II), Ni(II) and Pb(II) can interact with the available deprotonated surface sites on colloids, ≡SOH, where S represents Si and Al which are the main constituent of colloids and are shown in Eqs. (4) and (5).

$$\equiv \text{SOH} + \text{M}^{2+} \rightleftharpoons \ \equiv \text{SOM}^{+} + \text{H}^{+} \qquad (4)$$

$$\equiv \text{SOH} + \text{M}^{2+} + \text{H}_2\text{O} \rightleftharpoons \ \equiv \text{SOMOH} + 2\text{H}^{+} \qquad (5)$$

In the case of Cr(VI) adsorption, where the pH of the system is 2.75, the adsorbent surface contains a large number of protonated aluminol ($AlOH_2^+$) and silanol ($SiOH_2^+$) groups that bind electrostatically with the monomeric species of Cr(VI) which exist in solution as $HCrO_4^-$ to cause the adsorption.

Table 1 Freundlich and Langmuir adsorption isotherms for dyes and toxic metals

Contaminant	Freundlich isotherm			Langmuir isotherm		
	K_F (mg g^{-1})/(L mg^{-1})	N	R^2	Q_0 (mg g^{-1})	b (L mg^{-1})	R^2
Alizarin red	50.1	0.46	0.9650	400.0	0.0690	0.9983
Methylene blue	58.8	0.49	0.9701	625.0	0.053	0.9860
Cr(VI)	50.4	0.30	0.9858	140.8	0.0178	0.9839
Pb(II)	41.6	0.46	0.9879	196.0	0.0066	0.8691
Ni(II)	71.6	0.48	0.9752	263.1	0.0108	0.8872
Cu(II)	44.8	0.50	0.9839	222.2	0.0226	0.9724

The adsorption of dyes and toxic metals is found to be relatively higher on soil colloids than other adsorbents reported in the literature, and it is given in Table 2.

Table 2 Comparison of adsorption capacities of various adsorbents

Adsorbent	Contaminant	Adsorption capacity (mg g^{-1})	References
Montmorillonite	Basic green 5	127.6	Shiau and Pan (2004)
Activated clay		271.3	
Solid waste from leather industry	Methylene blue	80	Oliveira et al. (2007)
	Reactive red	163	
Granular ferric hydroxide	Cr(VI)	0.78	Asgari et al. (2008)
Goethite	Pb(II)	120.4	Mohapatra et al. (2010)
Sawdust-activated carbon	Cr(VI)	44.0	Karthikeyan et al. (2005)
Soil colloids	Methylene blue	625.0	Present study
Soil colloids	Ni(II)	263.1	Present study

Colloid mobilization

The experimental investigations involving the mobilization of colloidal particles from sediments have been carried out with 0.001 M NaCl solution. The concentration of colloids in the effluent and the mass balance of the colloids are given in Fig. 3. A significant amount of colloidal particles were found in the effluent at 0.14 pore volumes, and the breakthrough curve shows that the maxima of colloidal concentration appear at 0.42 pore volumes, and colloids kept eluting from the column to a low concentration. The increase in colloidal concentration with time is expected as the influent water soaks the soil for a longer time and so the dispersion of binding agents would be more. Despite the flow rate being constant, the decline in the concentration of colloids is caused by the finite supply of colloids, which is depleted in the progress of the experiment.

The mobilization of colloids by a change in solution chemistry depends on the alteration of forces such as double-layer attraction or repulsion, van der Waals attraction between surfaces of colloids and the aquifer grains to which they are attached (Ryan and Elimelech 1996). The change in solution chemistry causes repulsive forces between attached colloids and soil grains leading to their release and transport (Petosa et al. 2010).

The cumulative mass of colloids in the effluent turned out to be 174 mg at 1.12 pore volumes. It can be seen from Fig. 3 that the cumulative mass curve of colloids exhibits a nonlinear pattern. It has been previously reported that the cumulative mass of colloidal particles is flow rate dependent and shows linearity at low flow rate while at high flow rate it shows nonlinearity (Jacobsen et al. 1997). Our observations indicate nonlinearity similar to that at high flow rate though our flow rate was not as high. Diffusion limited colloid mobilization was explained to be the cause of linearity of cumulative mass at low flow rate. In contrast, the nonlinear trend in our experiments may be due to the non-equilibrium processes and physiochemical characteristics of the soil on colloid mobilization. One of the reasons for the non-equilibrium process could also be due to the size variation of the colloidal particles leading to different adsorption capacity of the colloid. This size distribution of the colloidal particles eluted from the sediments and measured by static light scattering is given in Fig. 4. While the initial samples had very small size range, the size of colloids after 0.7 pore volumes was high. Thereafter, the size of the colloids showed a decreasing trend and increasing again after 1.5 pore volumes. Such non-uniform and zigzag trend observed in the size distribution of colloids implies that the sediment contains particles of varying size, and these get detached and eluted out in a mixed manner.

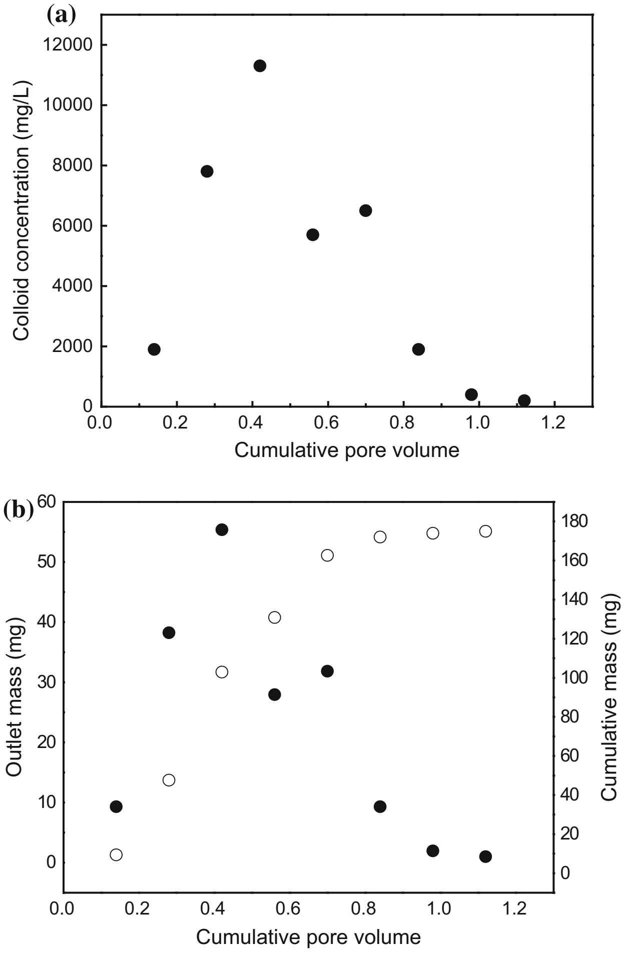

Fig. 3 Leaching of colloidal particles from soil column **a** colloid concentration versus cumulative pore volume. **b** (*dark circles*) Outlet mass of colloids (mg) and (*open circles*) cumulative mass (mg) versus cumulative pore volume

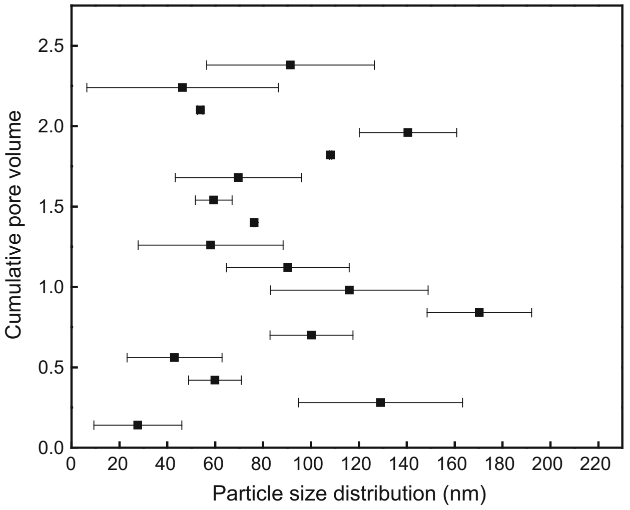

Fig. 4 Particle size distribution of colloids eluted from sediments

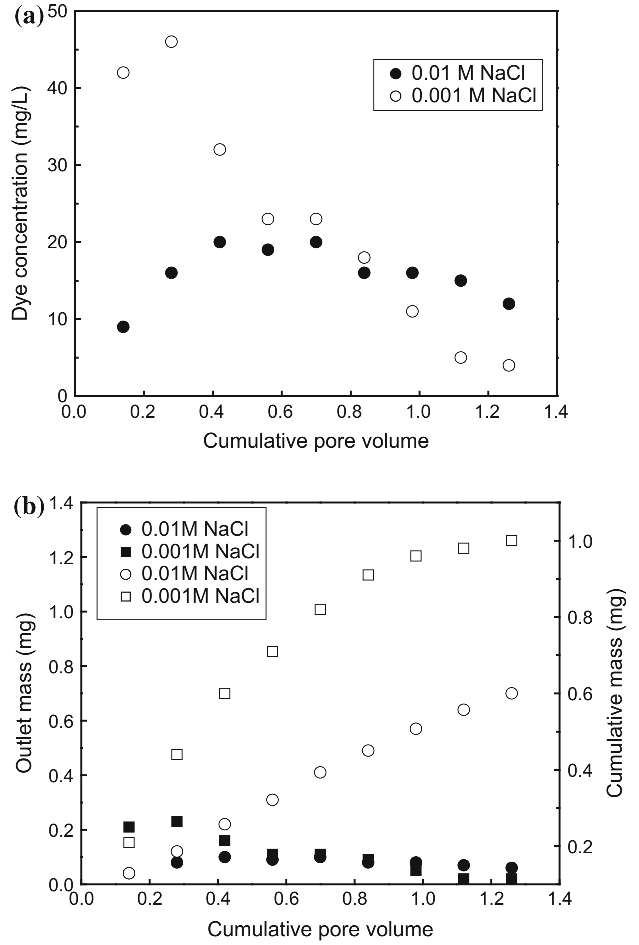

Fig. 5 Transport of the dye through the soil column. **a** Dye concentration at (*dark circles*) 0.01 M NaCl, (*open circles*) 0.001 M NaCl versus cumulative pore volume. **b** Outlet mass (mg) (*dark circles*) and cumulative mass (mg) (*open circles*) versus cumulative pore volume

A first-order colloid release rate coefficient (K_{rel}) determined by fitting the decrease in the colloid concentration of breakthrough curve for 15-min time interval to the Eq. (1) turned out to be 0.0451 min^{-1}.

Dye transport experiments

The breakthrough curves of dye at the ionic strength of 0.01 and 0.001 M NaCl and the mass balance for the dye are shown in Fig. 5. The strong correlation between the effluent dye concentration and colloid concentration was observed at low ionic strength. The peak in the dye concentration of 46 mg L^{-1} was observed when the effluent colloid concentrations were >8,000 mg L^{-1} and decreased to 4 mg L^{-1} when the colloid concentrations were <200 mg L^{-1}. These results suggest transport of dye when the concentrations of colloids mobilized are high.

At high ionic strength, the dye concentration peaked at 0.42 pore volumes to 20 mg L^{-1}, and the majority of the dye was present in the dissolved form, due to less mobility of colloids, leading to the decreased dye concentration in the effluent as against low ionic strength conditions. As the ionic strength increased from 0.001 to 0.01 M, approximately 2.5-fold decrease in peak dye concentration and mass was observed.

The breakthrough curves clearly show that low ionic strength condition facilitates the transport of dye more and faster than high ionic strength conditions. The high ionic strength influent solution reduces the excluded area of colloidal particles through the compression of its diffuse double layers, and this causes the decrease in particle mobility, which is in agreement with previous observations (Liu et al. 1995). At the ionic strength of 0.001 M, the stability of the colloidal particles is high due to the expansion of the double layer of the colloids. This double-layer expansion causes the colloidal particles to get easily released from the column along with the dye. The release rate coefficient of dye with respect to ionic strength is shown in Table 3. The higher release rate at 0.001 M suggests the high mobilization of colloids from the sediment column.

The mass balance of dye transport is given in Fig. 5. Total mass of the dye at the outlet is found to be 0.7 and 1.0 mg for the columns leached with 0.01 and 0.001 M influent solutions, respectively, as against the inlet mass of 1 mg. Thus, it becomes clear that the ionic strength influences the mass transport of dye through sediment-packed column and the mass of the dye retained within the column decreased as the ionic strength of the influent solution decreased.

Table 3 Release rate coefficient of colloids, alizarin red dye and toxic metals at constant flow rate

Experiment	Contaminant	Ionic strength	Flow rate (mL min^{-1})	Release rate coefficient (min^{-1})
1	Colloid	0.001 M	0.3	0.0451
2	Alizarin red	0.01 M		0.0048
3	Alizarin red	0.001 M		0.0387
4	Cr(VI)			0.0046
5	Pb(II)			0.0463
6	Ni(II)			0.0134
7	Cu(II)			0.0113

Effect of pH on dye transport

The effect of pH on the colloid-associated transport of dye and its mass balance calculations is given in Fig. 6. The increase in dye concentration at outlet was observed with increase in the pH of the influent solution and is shown in Fig. 6a–c. The peak in the dye concentration was observed at different pore volumes for the experiments carried out at different pH values. At pH 7.5 and 9.5, the difference in effluent dye concentration was relatively less with peak dye concentration reaching 11 and 12 mg L^{-1}, respectively. As the pH increased to 11.5, peak dye concentration increased to 29 mg L^{-1}. The 2.5-fold increase in peak dye concentration and mass in the effluent indicate that the colloid-facilitated transport of dye is sensitive to solution pH. The charge of colloids becomes more negative as the pH increased to 11.5 as shown in Fig. 1, and this contribute to the transport of dye.

It has been observed that the surface coating of iron oxide on the quartz-based colloids shifts the point of zero charge from a pH below 3 to approximately pH 8.1 and to a less extent for kaolinite (Hendershot and Lavkulich 1983). Thus, in our case also, this factor may have contributed to significant colloid release and dye transport above pH 8.1. Despite the effluent concentration of dye being slightly higher at pH 9.5 than at pH 7.5, which is above the point of zero charge value of 8.1, a large increase in dye concentration was observed for the pH of 11.5. And, these results establish the effect of pH on the colloid-facilitated transport dye in our experiments.

The effect of pH on colloid mobilization from natural sediments in laboratory columns has produced similar results, which is increase in pH causes increase in colloid mobilization. It has been hypothesized that the pH of the injection solution would have to exceed the pH_{pzc} of grain coatings to cause significant colloid release and transport (Bunn et al. 2002; Ryan and Elimelech 1996). The pH below the pH_{pzc}, the positively charged grain coatings, would bind electrostatically with the negatively charged colloids and above the pH_{pzc} surface charge of the coatings would be reversed resulting in electrostatic repulsion and release of colloids. The increase in dye transport at pH 11.5 is indicative of substantial increase in colloid release due to electrostatic repulsion between colloids and grains.

With an influent solution of pH 7.5, dye mass at the outlet was found to be 0.23 mg as against the inlet mass of 1 mg, and for pH 9.5 and pH 11.5, the dye mass at the outlet was 0.29 and 0.92 mg, respectively. The mass of the dye at the outlet was found to be threefold higher for the

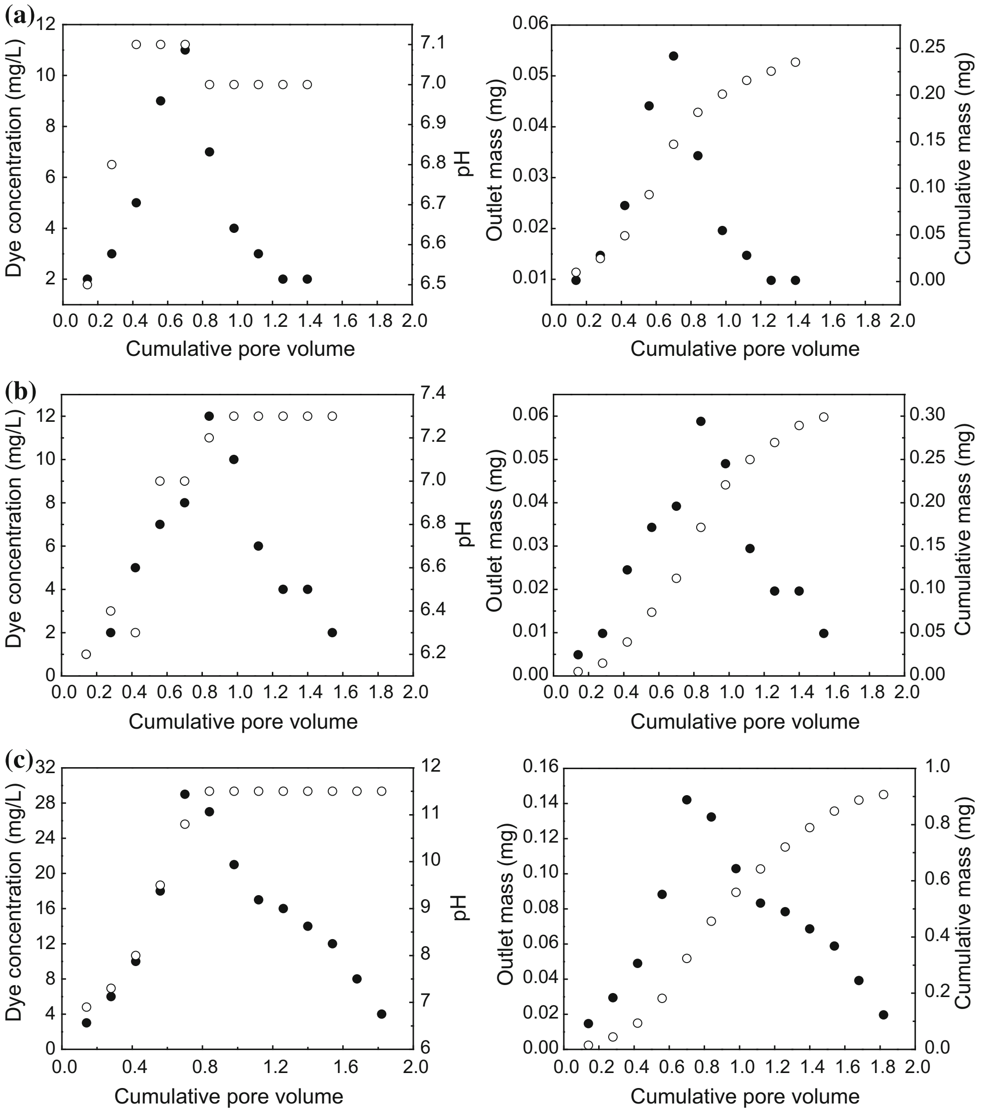

Fig. 6 Transport of the dye contaminant at elevated pH values **a** pH 7.5, **b** pH 9.5, **c** pH 11.5, (*dark circles*) dye concentration, outlet mass (*open circles*) pH, cumulative mass

pH of 11.5, suggesting that the retained mass within the column decreases with increased pH.

As shown in Fig. 6, there is a step-wise variation of pH of the effluent solution. For the pH 7.5, the effluent solution pH was found to be low after which the pH increases to 7. Where the influent pH was 9.5 and 11.5, the pH of the effluent was found to start at three to four pH units less than that of the influent solution. When the experiments were stopped, the effluent pH decreased to pH 7.3 for the influent solution of pH 9.5, but the effluent pH remained the same for pH 11.5. Ion exchange is one of the possible factors for the observed decrease in pH of the effluent solution. The exchange of ions for Al in the kaolinite during the preconditioning step and subsequent hydrolysis of exchanged Al with the influent solution of different pH values causes the release of proton leading to the decrease in pH of effluent solution.

Cr(VI), Ni(II), Pb(II) and Cu(II) transport

The breakthrough curves for Cr(VI), Ni(II), Pb(II) and Cu(II) transport are shown in Fig. 7. It was recorded as a plot of C/C_0 versus pore volume where C is the concentration of toxic metals in the effluent and C_0 is the initial concentration in solution. In all cases, the relative concentration in the effluent (C/C_0) increased and then decayed with time. The effluent chromium concentration peaks at 1.1 pore volume corresponding to 40 mL of salt

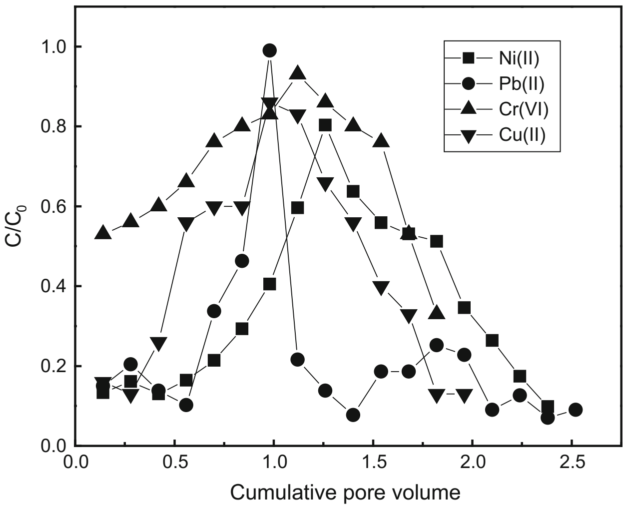

Fig. 7 Transport of Ni(II), Pb(II), Cr(VI) and Cu(II) at 0.001 M NaCl

solution percolating through the bed. After 1.5 pore volumes, there is a sharp decline in the chromium concentration, and after 1.8 pore volume, the measurements were stopped, by this time 89.73 % of the chromium added had eluted out from the column.

The investigations involving the transport of Ni(II), Cu(II) and Pb(II) show that the Ni(II) concentration attains maxima at around 1.26 pore volume, while the Cu(II) and Pb(II) peaked at 0.98 pore volume corresponding to 45 and 35 mL of salt solution passing though the bed, respectively. By the time the effluent concentration decreased to a low level, almost 89 % of Cu(II), 86 % of Ni(II) and 57 % of Pb(II) had eluted out from the column. The release rate coefficient of colloids, alizarin red dye and toxic metals is shown in Table 3. The total mass of Pb(II) eluted out from the column is less than other toxic metals, which increases in the sequence Ni(II), Cu(II) and Cr(VI). But the release rate coefficient of Pb(II) is high and decreases in the sequence Ni(II), Cu(II) and Cr(VI). This shows that release rate of Pb(II) is approximately ten times faster than Cr(VI) and 3.5 times faster than Ni(II) and approximately four times faster than Cu(II). As the effluent mass decreases, the release rate coefficient increases. Thus, it can be concluded that the transport of Pb(II) would be faster than other toxic metals in natural environments, though the mass at the outlet is less.

Conclusion

Batch experiments show that colloids have good adsorption capacity toward dyes and toxic metals. Low ionic strength enhanced the transport of dye. The significant increase in the transport of dye with increasing pH implies that the colloid-associated dye transport is sensitive to pH also. Though industrial effluents in general cannot be expected to be greater than pH 10, improper treatment would have a major effect, and the results presented here show the transport behavior of dye in response to effluent pH in natural environments. Colloid mobilization experiments showed that there could be considerable leaching of native colloidal particles from the sediments during rainy season runoff. These studies can be extended to other contaminants to understand their transport through the heterogeneous soil environments.

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