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Influence of pH on organic and inorganic colloids in stormwater

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ABSTRACT

Urban runoff usually contains significant amounts of organic and inorganic colloidal particles. Due to their high surface area and associated surface charges, these colloidal particles become a strong binding site and carriers to many contaminants found in the runoff. This paper presents our study on the physicochemical properties and behaviours of silica and humic colloidal particles found in urban runoff under different simulated pH conditions. Four optical characterisation techniques, namely (1) UV spectroscopy; (2) Fluorescence spectroscopy; (3) Size exclusion chromatography with UV detector and (4) Dynamic light scattering were used to examine and evaluate the colloidal properties and behaviours. It was found that the colloidal particles under both acidic and alkaline conditions exhibited a distinct bimodal characteristic in particle size distribution. Parallel interpretation of the four optical characterisation results revealed that the influence of pH on the colloidal particles were more prominent at alkaline conditions, where a strong growth of larger colloidal particles as a result of aggregation and/or dissolution of humics, fulvics as well as biopolymers and their precursors were observed. This study showed that the colloidal particles behave differently under acidic, neutral and alkaline conditions, which has an important implication on the water quality and its immediate water treatment processes required.

Keywords: urban runoff, colloidal particles, contaminants transport, silica, humic substance.

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INTRODUCTION

Urban runoff usually contains a wide range of chemical and biological contaminants. These contaminants include organics (e.g. oil, grease, humic substance, hydrocarbons), inorganics (e.g. metals, silica and nutrients) and pathogens, which often cause severe water quality problem that results in detrimental impacts on ecology and biodiversity of receiving water bodies (Schiff et al. 2003; Walsh 2004). The contaminants are usually present in either solid, colloidal or dissolved phases. The partition of contaminants between these phases depends on various environmental factors, and one of the more prominent factors is the pH condition. The degree to which the contaminants in stormwater are being partitioned to particles, colloidal and dissolved states has an important implication for their transport in receiving water bodies, as well as their

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bioavailability and inherent biological effects.

Among the partitioned phases, colloidal phase has been considered as the most important area in contaminants transport because of their high surface area and associated surface charge. In general, colloids are defined as particles of size in the range of 1 to 1,000 nm. Humic and silica colloidal particles are the major binding substrates for contaminants transport because of their associated surface charges. Awan et al. (2003) reported that silica particles can adsorb metal ions onto its surface. Similarly, He and Wang (2011) observed the adsorption of polycyclic aromatic hydrocarbons (PAHs) on humic colloidal particles. They observed that the aromatic properties of humic substances are the main underlying factors to transport PAH; where they are interacted via π-π electrons transfer mechanism. Sharma et al. (1985) found that the transport of bacteria in sandpacks increased when their negative surface charge also increased. Fletcher and Loeb (1979) found that positively-charged surface attracted more bacteria than negatively-charged surface.

As most of the contaminants in urban runoff are bound to colloidal particles, the bioavailability and inherent biological effects are likely to be strongly affected by the pH conditions. While the particle bound contaminants and their transport within the urban environment is reasonably well understood (Aryal et al., 2006; Kang et al., 2007; Badin et al., 2008), there has been limited understanding of colloidal particles in stormwater and the environmental influence of pH conditions on them (Grout et al., 1999; Zgheib et al., 2011). Existing stormwater literatures focuses mostly on particle-bound or dissolved phases of heavy metals, organics, pathogens or nutrients. Considering the limited available information on the colloidal particles in stormwater, this study aims at evaluating the physicochemical characteristics and behaviours of colloidal particles at different simulated environmental pH conditions. This knowledge will allows us to understand contaminants partition under different pH conditions which in turn, will inform the water treatment operators to optimise their removal efficiency in water treatment processes such as coagulation, filtration, ultraviolet disinfection and others.

MATERIALS AND METHODS

Stormwater samples were collected from urban drains at four different locations in South East Queensland during rainfall events. The four locations covered medium density residential area (S1), low-density residential area (S2), street runoff (S3) and green park runoff (S4). All the stormwater samples were collected in polypropylene tubes that were pre-washed with nitric acid (HNO_3) and milliQ water. This was followed by samples filtration through 1.2 μm glass fibre filter (GF/C Whatman). The pH of the solution was adjusted by adding HCl or NaOH into the filtrate to achieve the respective simulated pH conditions (pH 3, 5, 7, 9, and 11). Each pH-adjusted solution was analysed using four different optical spectroscopy characterisation methods of (1) UV spectroscopy, (2) Fluorescence spectroscopy (i.e. excitation emission matrix, EEM), (3) Dynamic light scattering (DLS) particle size analysis and (4) Gel permeation chromatography equipped with UV detector.

UV Analysis

The stormwater samples adjusted to various pH conditions were analysed using UV spectrometer (Varian 50 Bio). The instrument was operated at bandwidth 1 nm, with quartz cell of 10 mm path length, wavelength of 190 to 400 nm and at a scanning speed of 190 nm/min (slow). In this instance, the photometric accuracy was 0.004 Abs at 1.0 Abs.

Fluorescence Analysis

Three-dimensional fluorescence spectra (EEM) were obtained using a spectrofluorometer (Perkin Elmer LS 55) with a wavelength range of 200 nm to 500 nm (for excitation); and 280 nm to 500 nm (for emission). The spectra were taken at an incremental wavelength of 5 nm in excitation; and 2 nm in emission. The EEM value of blank (MQ water) data was subtracted from the analysed samples for blank correction. The data obtained from EEM was analysed using Microsoft Excel.

Particle Size Distribution Analysis

Particle size distribution was measured by dynamic light scattering (DLS) method using Zetasizer NanoZS (Malvern). Humic and silica particles were selectively measured by selecting their refractive indices (humic refractive index 1.33; and silica refractive index 1.20) during analysis.

Size Exclusion Chromatography Analysis

Size exclusion analysis was carried out using HP-SEC (Shimadzu, Japan) that consisted of column (TSK Gel G3000SWxl) with UV detector (SPD M20A, Shimadzu, Japan). A flow rate of 1.0 mL/min was used for elution of 0.3 M NaCl in 0.05M phosphate buffer solution. The samples injection volumes of 100 µL were used.

RESULTS AND DISCUSSION

UV Analysis

UV absorption spectra (190-400 nm) provide information on both the nature and quantity of substances, their functionality composition change and alteration in colloidal particles (Korshin et al., 1997; Aryal et al., 2011). The method has also been used for inorganic analysis: Aspanut et al. (2008) used UV spectroscopy to quantify the silica colloidal size. They observed an increase in UV absorbance with silica particle sizes. Fardad and Massudi (2007) applied UV spectroscopy to understand the environmental effect on metal oxide nanoparticles. They observed similar spectra for analogous particles but a shift towards larger wavelength was evidenced at higher pH values.

Figure 1 shows the UV absorbance of colloidal particles in four stormwater samples (S1-S4) at pH 3, 7 and 11, respectively. All four samples had similar UV spectral intensity, as well as their trend under both acidic and neutral pH conditions. Under alkaline condition, the spectral intensity was almost two times higher at the lower wavelength range (190-205 nm). This result shows colloidal particles behave differently to a greater extent under alkaline conditions than the acidic condition.

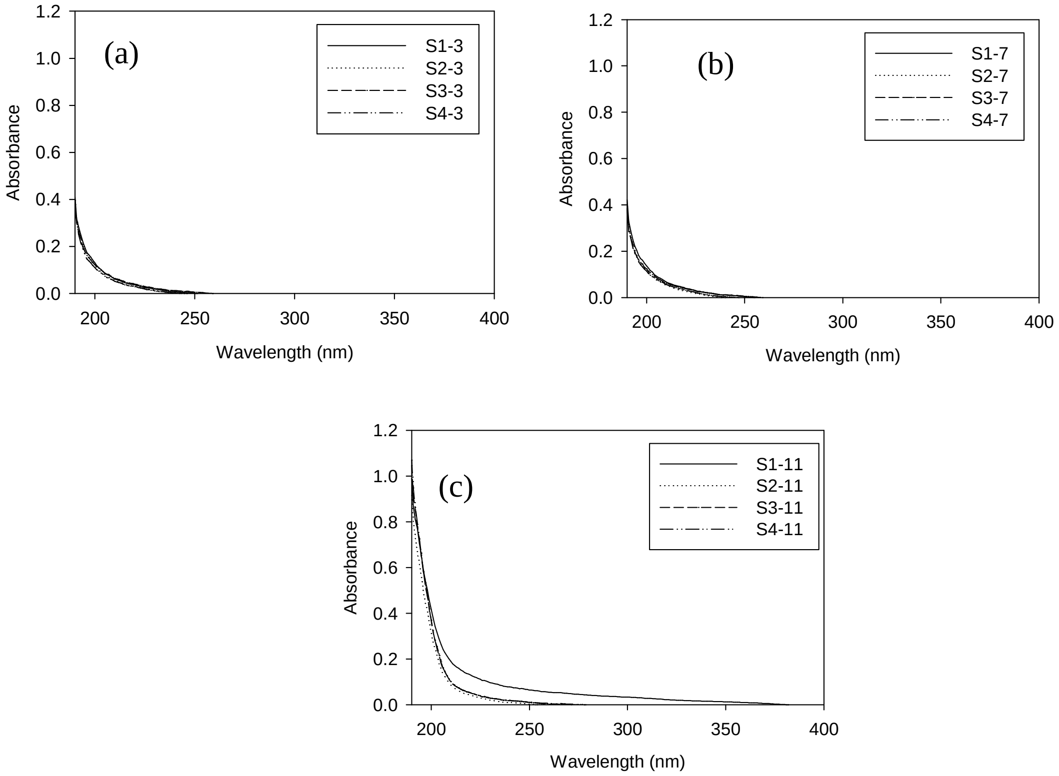

Fig. 1 - UV spectra of samples S1-S4 at different pH conditions. (a) pH 3; (b) pH 7 and (c) pH 11.

Fluorescence Analysis

Fluorescent spectroscopy is one of the most promising analytical tools to identify the nature of organics based on their properties. The spectra also known as excitation emission matrix (EEM), and has been widely used to identify the nature of organic substances found in water, stormwater and wastewater (Chen et al., 2003; Sheng et al., 2006; Aryal et al., 2009).

Figure 2 illustrates the fluorescence spectra of sample S1 under different simulated pH conditions. The spectra (Ex:Em 200-500nm:280-500nm) showed a significant pH influence on fluorescence intensity for colloid particles. Among the three spectra, pH3 spectra exhibited peak at a lower excitation and emission region (Ex 200-250nm and Em 280-330nm). At neutral pH, the spectral characteristics are similar, but the peak intensities are lower than the pH3 spectra. However, at alkaline pH, the peak intensity area was found to widen to a higher Ex and Em region (Ex 200-500nm: Em 330-500nm). When the fluorescence intensity of sample at neutral pH was made as the reference point, the lower pH samples (i.e. pH 3 and 5) was found to have 2.5 times higher intensity peak whereas the higher pH samples (i.e. pH 9 and 11) have only halve of the peak intensity at Ex:Em region 200-280nm: 280-380nm (e.g. amino acids, peptides and biopolymers). At excitation emission region of 280-500nm: 380-500nm (e.g. fulvic and humic substances), samples at lower and higher pH had 1.8 and 10 times higher intensity, respectively. Under acidic pH condition, the peak appeared at lower wavelength is possibly due to the amphoteric nature of proteins and their precursors in which case their existence have been verified. While at alkaline pH, both the proteins and its precursors, as well as the humics are soluble and this is why a broader spectrum of organics was observed.

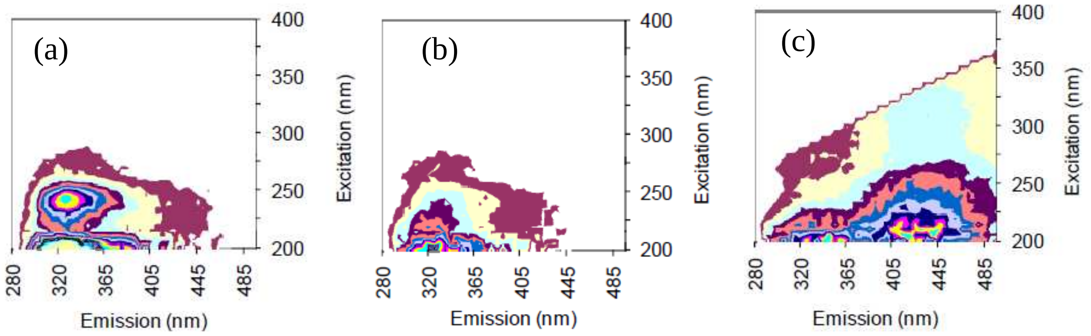

Fig. 2- Fluorescence spectra of colloids present in sample S1 under different simulated pH conditions (a) pH 3; (b) pH 7 and (c) pH 11.

Dynamic Light Scattering Analysis

Dynamic light scattering (DLS) is a technique used to measure the Brownian motion (diffusion) of the particle and its subsequent size distribution (number) within the solution. In this instance, the DLS was used to study the colloidal behaviour in stormwater. Particles were measured at two different refractive indices (1.33 for humic; 1.22 for silica). Figure 3 illustrates the size distribution of particles by volume (%) in sample S1 at three different pH conditions of pH 3, 7 and 11 respectively.

At neutral pH, the distribution exhibited a unimodal characteristic (50-200 nm) showing the continuum in particles size within the sample. Both acidic and alkaline pH shifted the unimodal to bimodal distribution charateristics. Results showed that acidic or alkaline pH favours the formation of smaller, as well as larger colloidal particles. At acidic pH, the abundance of smaller-size colloids was relatively low. This was consistent with the fluorescence result mentioned above. The result reflects that pH is an important factor in colloidal distribution within environmental stormwater samples.

Size Exclusion Analysis

Size exclusion chromatography (SEC) is a technique used to understand the particle sizes of organics and inorganics present within the samples. In this method, the colloidal particles in solution are separated according to their size. The media uses porous particles to separate molecules of different sizes. Separation is achieved when the particles passed through the pores of the packing material. The larger particles will elute prior to the smaller particles.

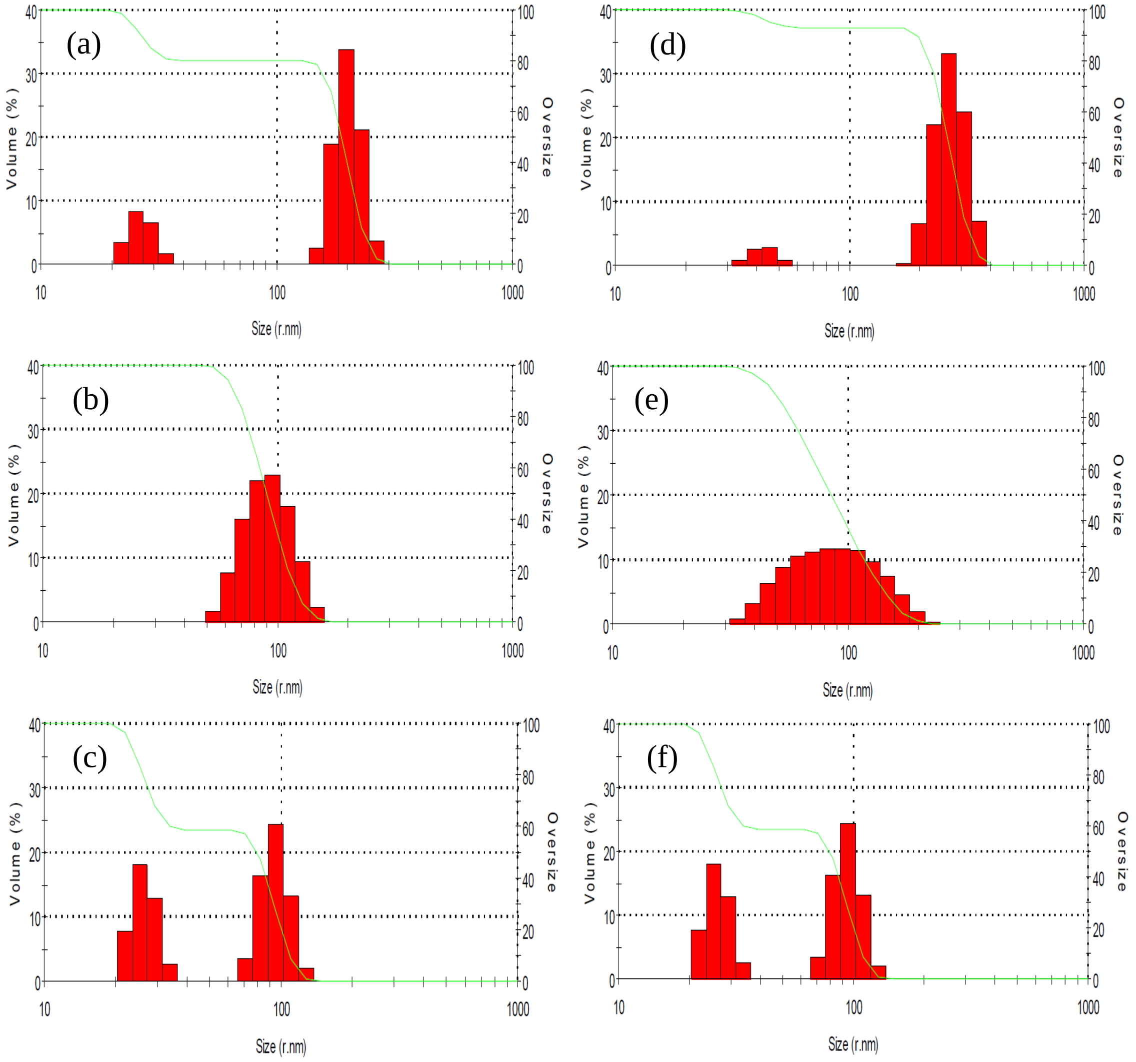

Fig. 3- Particle size distribution of humics (left) and silica (right) in sample S1 at pH 3 (a, d), 7 (b, e) and 11 (c, f).

Figure 4 illustrates the size distribution of colloidal particles in sample S1 at pH 3, 7 and 11, respectively. It should be noted that the intensity scale of Figure 4c is 5 times higher than that of Figure 4a and 4b. The dotted line represents the colloidal size present in the peak region. At neutral pH, the peak intensity and width were narrow. At acidic pH, ratio of smaller to larger particles was low and this ratio increased with pH. This is because most of the inorganic colloids and fulvic type organics are dissociated and/or dissolved at acidic pH while many inorganics such as metal ions are precipitated and some organics of high molecular weight are dissolved such as humics and biopolymers at higher pH. Precipitation of metal ions and dissolution of humic and biopolymers may increase volume/number of colloids. Broader and intense peaks around 5 to 9 minutes for (at) alkaline pH provide justification for this observation. In this instance, the earlier peaks at 5.5 min are biopolymers whereas later peaks around 8 min are humics and fulvics type substances.

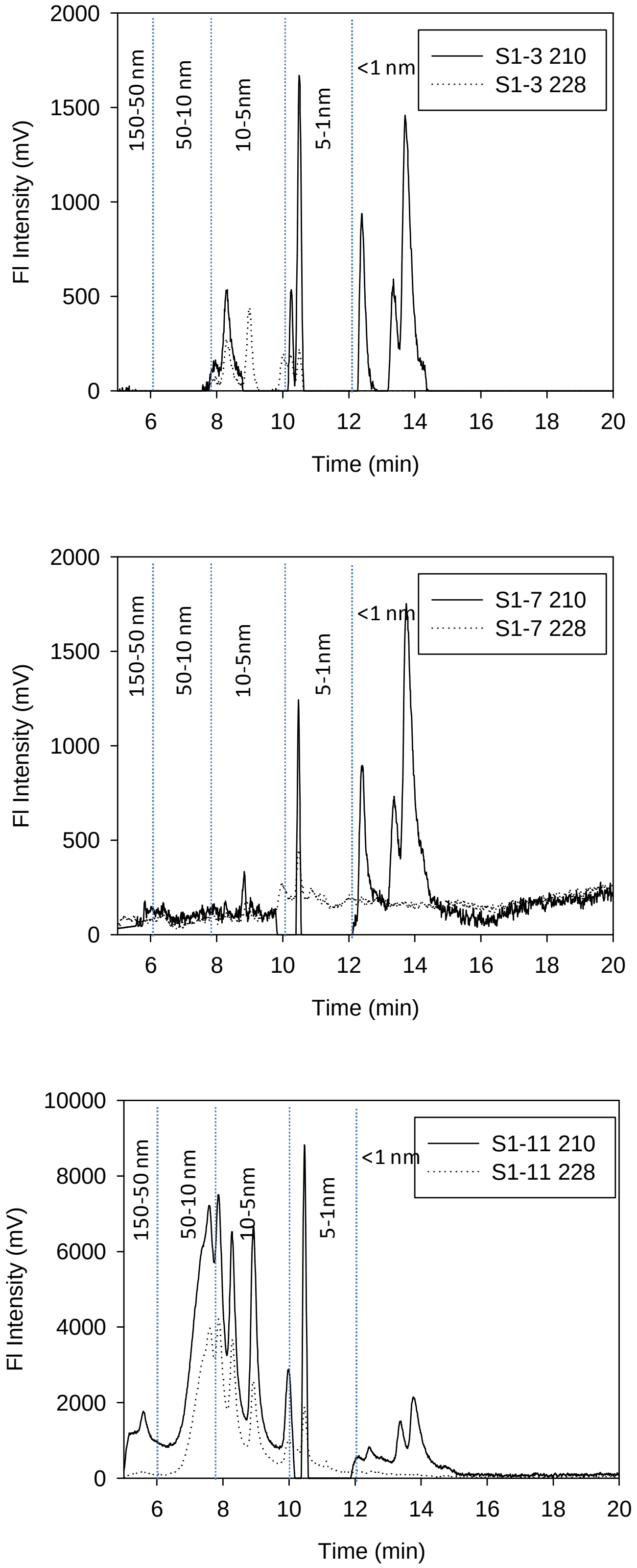

Fig. 4- Size distribution of colloidal particles in sample S1 at different pH conditions of pH 3, 7 and 11 and UV wavelengths of 210 and228 nm.

CONCLUSIONS

The influences of pH on colloidal particles found in stormwater was studied, by analysing the colloidal samples (<1.2 µm) using four different optical spectroscopy characterisation methods.

- UV spectra showed differences in absorbance intensity at different pH conditions. The differences in absorbance intensity were identified to be owing to the shift in colloidal particle sizes at higher pH in stormwater.
- The fluorescence spectra showed a significant influence of pH on the fluorescence intensity of colloids, as well as the peak appearance location. Almost 2.5 folds higher intensity was found at lower Ex:Em region for lower pH condition while, nearly halves of the intensity at higher pH condition. It was also examined that almost 1.8 and 10 times higher intensity at higher pH with respect to fluorescence at neutral pH, which indicates that both acidic and alkaline environment influences the physicochemical properties and behaviors of colloidal particles significantly.
- Particle size distribution analysis showed bimodal distribution of colloidal particles at acidic and alkaline condition, whereas continuum unimodal distribution characteristic was examined at neutral pH. The result reflected the presence of different types of contaminants in stormwater which might have drawn an electrostatic attraction charge towards the colloidal particles at different pH conditions.
- Size exclusion chromatography shows a strong growth of larger colloidal particles at higher pH condition, indicating the aggregation and/or dissolution of humics, fulvics as well as biopolymers and their precursors.

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REFERENCES

Aryal R.K., Furumai H., Nakajima F. and Boller M., (2006). Characteristics of particle-associated PAHs in first flush of highway runoff, *Water Sci Technol.*, **53**(2), 245-251.

Aryal R., Legegue J., Vigneswaran S., Knadasamy, J., Heran, M. and Grasmick A. (2009). Identification and characterisation of biofilm formed in membrane bioreactor, *Sep Purif Technol.*, **67**(1), 86-94.

Aryal R., Kandasamy J. and Vigneswaran, S., (2011). Application of Ultraviolet spectrophotometry in the assessment of membrane bioreactor performance, *Appl Spectrosc.*, **65**(2), 227-232.

Aspanut Z., Yamada T., Lim L. W. and Takeuchi, T. (2008). Light-scattering and turbidimetric detection of silica colloids in size-exclusion chromatography, *Anal Bioanal Chem.*, **391**, 353-359.

Awan M. A., Qazi I. A. and Khalid, I. (2003). Removal of heavy metals through adsorption using sand, *J Environ Sci.*, **15**(3), 413-416.

Badin A. L., Faure P., Bedall J. P. and Delolme, C. (2008). Distribution of organic pollutants and natural organic matter in urban stormwater sediment as a function of grain size, *Sci Total Environ*., **403**, 178-187.

Chen W., Westerhoff P., Leenheer J. and Booksh K., (2003). Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolvoed organic matter, *Environ. Sci. Technol*., **37**, 5701-5710.

Grolimund D., Borkovec M., Barmettler K. and Sticher H. (1996). Colloid-facilitated transport of strongly sorbing contaminants in natural porus media: A laboratory column study, *Environ Sci Technol*., **30**, 3118-3123.

Fardad S. and Massudi R. (2007). Environment effect on structure, size control and stability of ZnO and ZnO nanoparticles. Proceeding *of7th IEEE, Internantional Conference on Nanotechnology*, 2-5 Aug. Hong Kong.

Fletcher M. and Loeb G. I. (1979). Influence of substratum characteristics on the attachment of marine pseudomonad to solid surfaces, *Appl Environ Microbiol*., **37**, 67-72.

Grout H., Weisner M. R. and Bottero J. Y. (1999). Analysis of colloidal phases in urban stormwater, *Environ Sci Technol*., **33**, 831-839.

He Y. Y., and Wang X., (2011). Adsorption of a typical polycyclic aromatic hydrocarbon by humic substances in water and the effect of coexisting metal ions, *Colloids Surface A*., **379**, 93101.

Kang J. H., Li Y., Lau S. L., Kayhanian, M. and Stenstorn, M. K. (2007). Particle destabilisation in highway runoff to optimise pollutant removal, *J. Environ Eng*-ASCE., 133(4), 426-434.

Korshin G. V, Li C. W. and Benjamin M. M. (1997). Monitoring the properties of natural organic matter through UV spectroscopy: a consistent theory, *Wat. Res*., **31** (7), 1787-1795.

Richardson R. L., Mills A. L., Herman J. S. and Hornberger, G. M. (2000). Effect of humic material on interaction between bacterial cells and mineral surfaces, LEMCOL2001-01.

Schiff K, Bay S. and Diehl D. (2003). Stormwater toxicity in Chollas Creek and San\Diego Bay, California, *Environ Monit Assess*., **81**(1-3), 119-132.

Sharma M.M, Chang Y. I. and Yen T. F. (1985). Reversible and irreversible surface charge modification of bacteria for facilitating transport through porus media, *Colloids Surface*., **16**, 193-206.

Sheng G. P. and Yu H. Q. (2006). Characterisation of extracellular polymeric substances of aerobic and anaerobic sludge using three-dimensional excitation and emission spectroscopy, *Wat. Res*., **40**, 1233-1239.

Walsh C. J. (2004). Protection of in-stream biota from urban impacts: to minimize catchment imperviousness or to improve drainage design? *Mar Freshwater Res*., **55**(3), 317-326.

Zgheib S., Moilleron R., Saad M. and Chebbo, G. (2011). Partition of pollutants between dissolved and particulate phases. What about emerging substances in urban stormwater catchments? *Wat. Res*., **45**, 913-925.