Analysis of water quality in Saigon River water and its treatment by traditional coagulation – flocculation

Bui Van Khanh1,2, Tran Thi My Duyen1,2, Lam Pham Thanh Hien1,2,*, Vo Nguyen Xuan Que1,2, Nguyen Nhat Huy1,2,*

1 Faculty of Environment and Natural Resources, Ho Chi Minh City University of Technology (HCMUT), 268 Ly Thuong Kiet St., Dist. 10, Ho Chi Minh City, Vietnam
2 Vietnam National University Ho Chi Minh City, Linh Trung Ward, Thu Duc District, Ho Chi Minh City, Vietnam
Email: lamhien87@hcmut.edu.vn, nnhuy@hcmut.edu.vn

Abstract. In natural water, colloidal particles play an important role in the transport of organic compounds, including pollutants. The analysis of colloidal particles creates more bases for the selection of river water treatment technology, making the treatment more efficient. In this study, the size and zeta potential of colloidal particles in Saigon river water were determined. Seven sampling sites were randomly selected along the river length in Ho Chi Minh City. One of the locations was selected to investigate colloidal properties at different times (i.e. 10 samples). The results showed that the colloidal particles have poor stability with Zeta potentials in the range from $-19 \text{ mV}$ to $-12 \text{ mV}$. Besides, statistical analysis showed that the zeta potential had an inverse correlation with the pH value and the permanganate index with the significant coefficients of $-0.67$ and $-0.73$, respectively. The size of colloidal particles in water is not uniform; however, due to poor stability, part of the particles join together and settle down. Coagulation- flocculation- sedimentation- rapid sand filtration experiments were also performed to remove colloidal particles from the water. The treated water has low turbidity with a removal efficiency of 97%. This shows that the colloidal particles presented in the Saigon River water could be easily removed by the traditional physicochemical method. However, the parameters of the permanganate index and Coliforms did not meet the standard of QCVN 01-1/2018/BYT for drinking purposes, which still require further treatment.

1. Introduction
The presence of colloidal particles (specifically natural organic substances - NOMs) in raw water supplies many drinking water quality challenges for water treatment systems. Therefore, there is a need to take a closer look at colloidal particles in water, and their removal should be of primary concern in supply water treatment systems. The surface charge of colloidal particles cannot be measured directly but can be roughly determined through the zeta potential ($\xi$). The zeta potential appears at the boundary between the adsorption layer and the diffusion layer or in the electric double layer of the colloidal surface. Colloidal ions and diffusers have a corresponding sliding motion. It is the sliding motion of two charged layers due to the molecular kinetics that give rise to the zeta potential. The electrodynamic potential is proportional to the surface charge density of the particle and
the diffuse layer thickness of the particle. The values of a zeta potential may be related to the stability of the colloidal dispersants. It indicates the degree of repulsion between adjacent, similarly charged molecules. For molecules and particles that are small enough, a high zeta potential will ensure stability, which means that the solution or dispersant inhibits the cohesive force. If the voltage is low, the attraction is greater than the repulsion when the dispersion will break and flocculate. Thus, colloids with high zeta potentials (negative and positive) are electrical stability, and colloids with low zeta potentials tend to coagulate or flocculate as shown in Table 1.

| Table 1. Zeta potential and stable properties of colloidal particles [1] |
|---------------------------------------------------------------|
| Zeta potential (mV) | Stable properties of colloidal particles |
| From 0 to ± 5 | Flocculation or rapid flocculation |
| From ± 10 to ± 30 | Stability begins |
| From ± 30 to ± 40 | Moderate stability |
| From ± 40 to ± 60 | Good stability |
| Higher ± 61 | Very good stability |

There have been some studies on the zeta potential of river water. The zeta potentials in water samples in the Ba River and Dong Nai River basins in the Central Highlands region was researched by Nguyen et al. [1]. The results showed that the colloidal properties in the Ba and Dong Nai river basins in the Central Highlands region are stable, and pH significantly affects the colloidal system while the suspended components did not. The pH value tended to be inversely proportional to the zeta potential at most of the sampling points, except at the upstream of the Dong Nai River. According to Diab et al. [2], sampling location and time (season) greatly affected colloidal properties when studying the physicochemical properties of colloidal sediments of the Litani River in Lebanon. In the research of Whitehouse et al. [3], the organic colloids in riverine, brackish, and oceanic waters are suitable for the size and distribution of organic particulate material. And the colloidal size in the Mackenzie River is in a range from 0.2 μm to low nm size. The association between organic carbon and nitrogen content to colloidal and suspended particles from the Mississippi River and some of its tributaries was reported by Rostad et al. [4]. The organic carbon content of colloids (15.2%) was much higher than the organic carbon content of granular materials (4.8%). The carbon/nitrogen ratio of the colloidal and seed phases was the ratio to the microorganism rather than the ratio to the soil, humic material, or plants.

Saigon River is a tributary of the Dong Nai River. It originates from Langbiang Plateau (Da Lat) and is confluent by many other rivers, such as La Nga and Be rivers. The Saigon River is the primary supply source of freshwater for Ho Chi Minh City with a flow rate of 15 billion m³ per year. Therefore, the water quality of the Saigon River almost directly affects the lives of people. However, the colloidal properties and its relationship with other water quality parameters of Saigon River water have not been reported.

In this study, the colloidal particles in the Saigon River water and its properties were extensively investigated. The effects of sampling location and time along the river length in Ho Chi Minh City were studied. Besides, several experiments were also carried out to find out the suitable conditions for the traditional flocculation method for the removal of colloids and other pollutants in water.

2. Experimental

2.1. Water sampling

Sampling purpose is essential for determining the method of sampling. This study determined the suitability of river water quality for specific uses in each basin. Above all, the Saigon River water samples were taken to examine the colloidal properties and some other water quality parameters. The analysis method followed the standards of Vietnam (TCVN 6663-6: 2018 Water quality - Sampling Part 6: Guidance on sampling of rivers and streams). Water samples were taken at seven locations along the Saigon River (Figure 1). Sampling time was in July 2020, during the rainy season period.
2.2. Determination of colloidal properties and other water quality properties

The zeta potential and size of colloidal particles are determined by the Phase Analysis Light Scattering (PALS) and Dynamic Light Scattering (DLS), respectively, using a Zeta potential Zeta Nano ZS machine (Malvern, USA). Other analytical methods of water quality properties followed the corresponding standard of Vietnam, such as pH (TCVN 6492:2011 (ISO 10523:2008) Water quality - Determination of pH), Pecmanganate index (TCVN 6186:1996 (SO 8467:1993 (E)) Water quality - Determination of permanganate index), Coliforms (TCVN 6186:1996 (ISO 9308-2: 1990 (E)) Water quality - Detection and enumeration of organisms thermotolerant coliform organisms and presumptive Escherichia coli. Part 2: Multiple tube (most probable number) method).

2.3. Coagulation and flocculation experiment

Coagulation and flocculation tests were experiments using a Jartest system (Daihan - Korea) with six beakers containing 500 mL of the water sample. 4 mL of 10% poly aluminium chloride (PAC) solution was added to each cup. The pH value was adjusted by a 0.1 N solution of H₂SO₄ or NaOH. The samples were stirred rapidly for 45 s (135 rpm), then slowly for 15 min (35 rpm). After 10 min of slow stirring, 2 - 3 drops of anionic polymer were added to each cup to aid in the flocculating and settling process. The samples were let stable for 30 min of sedimentation and filtered through a rapid sand filter column before water quality analysis. The rapid sand filtration column was made of acrylic resin with a diameter of 10 mm and a quartz sand layer height of 0.5 m. The chemicals used in this study were of high purity (98 - 99%) from China.

3. Result and Discussion

3.1. Properties of colloidal particles along the Saigon River

The results of zeta potential magnitude measurement simultaneously with pH determination, permanganate index of 7 samples taken along the Saigon River are shown in Figure 2. The sampling time was in July 2020, during the rainy season period. In general, the zeta potential distributes in the range from -12 to -19 mV, showing that the sustainability of the colloidal system in the Saigon River water was relatively stable. There is the phenomenon of combination in colloidal particles. However, it was not significantly. The results of zeta potential measurements obtained in the water samples had little difference but not notably, implying that the colloidal particles in the water samples were on the
same stream and had similar properties. It is possible that these colloidal particles have the same origin or are affected similarly during the migration from upstream to downstream.

Moreover, the Zeta potential, pH, and the permanganate index of the water samples were found to be positively correlated and had the same trend of fluctuation. Although there were still some samples that do not follow this trend, the effect was not significant. To have a more specific view, the correlation coefficient between these 3 factors has been determined. Statistical analysis showed that the zeta potential had an inverse correlation with the pH value and the permanganate index with significant coefficients of -0.67 and -0.73, respectively. The correlation coefficients show that these parameters were closely related to each other. The correlation coefficient between the zeta potential with pH and the Permanganate index was negative because the zeta potential value in water was negative; however, in terms of magnitude, they are positively correlated. It may be due to the presence of organic and inorganic substances, in colloidal forms with their Zeta potential or in other, determines the magnitude of the permanganate index and affects the pH value of water. However, there are still some water samples that tend to be inversely proportional due to the presence of many waterway vehicles (e.g., river buses and cargo ships), changing the properties of the colloidal system in river water.

![Figure 2. Properties of the colloids along the Saigon River](image)

Raw water samples were used to analyze the size and uniformity of colloidal particles (Figure 3). Most of the colloidal particles in the water had an average size ranging from 2000 to 3000 nm. However, there were water samples with larger particle sizes. The difference sizes of particles in samples can be attributed to different sampling locations and influence of waterway vehicles (e.g., in water Sample 1 and Sample 5). Especially in Sample 5, this sampling location is the port of container ships, where river water is regularly disturbed. The results showed that the dispersion index (PDI) of the water samples gradually increased to 1, proving that the colloidal particle size in the water was widely distributed and uneven.
3.2. Properties of colloidal particles at different times at the same location: Binh An port

The Binh An port was selected as a sampling point and ten samples at different times were determined to have the values of zeta potential, pH, and permanganate index. As shown in Figure 4, the obtained data shows that the pH values of water samples did not change significantly (ranging from about 6.92 to 7.25). Water samples at the test site had a permanganate index of between 8.16 and 9.80 mgO$_2$/L. Moreover, two water samples had quite different values, namely, on June 3, 2020 (12.40 mgO$_2$/L), and on July 2, 2020 (6.88 mgO$_2$/L). The water sample on June 3, 2020, was taken at the low tide time when the water level was shallow with a yellow-brown color and lots of suspended sediments. It is a location of the inner city of Ho Chi Minh City that is affected by the amount of domestic wastewater from nearby residential areas and scattered production factories. As for the water sample on July 2, 2020, it was taken at a time with nice weather, clear blue sky, lots of sunshine, high tides, less sediment, and lighter water color.

The influence of pH and the permanganate index on the zeta potential value in river water samples is described in Figure 4. The pH values and the Permanganate index of all ten water samples at Binh An port with different sampling times tend to be proportional to the magnitude of the Zeta potential. For example, the water sample was taken on May 26, 2020, with a pH of 7.07 and permanganate index of 8.40 mgO$_2$/L had a zeta potential of -12.05 mV. On the other hand, the water sample was taken on July 30, 2020, with a pH of 7.09 and permanganate index of 9.52 mgO$_2$/L had a zeta potential of -14.10 mV. Statistical analysis also showed similar results on the correlation between zeta potential, pH value, and permanganate index with the significant coefficients of -0.53 and -0.52, respectively.
3.3. The change of colloid size in Saigon river water during sedimentation

The results from the measurement of colloidal particle size with different settling time are displayed in Figure 5. The average particle size of colloidal particles decreased gradually with the settling time. The initial water sample had a large particle size of 3258 nm, and it dropped to 1025 nm after 35 min of sedimentation. Moreover, when the large-sized colloidal particles settled down, the dispersion index reduced with the settling time. The particle size of the colloids became more uniform in the water sample.
3.4. Isoelectric point of Saigon River water

The isoelectric point (pH_{zpc}) is the pH value of the medium in which the charge of the colloidal surface is zero. Analysis results and calculation for pH_{zpc} of Saigon River water are shown in Figure 6. First, the zeta potential of the water sample was a negative value of -18.3 mV. The pH was adjusted downward to determine the pH_{zpc}. The zeta potential was measured at each pH value. At values of zeta potentials from -5 to 5 mV, the pH was too low and it was too hard to measure the zeta potential with the instrument. Therefore, the FORECAST function in Excel was used to predict the pH_{zpc} value. At low pH (approximately 2), colloidal particles in water lost their stability, and the zeta potential approached zero. When colloidal particles are unstable, they can combine to form larger particles. These particles are easy to settle to the bottom, which facilitates the removal of colloidal particles from the water environment. However, if this pH adjustment is applied to remove colloidal particles, it would be quite expensive and unsafe. Also, it cannot remove the smaller colloidal particles or the particles that do not agglomerate with other particles in the water environment. One simple and effective traditional colloidal removal method is flocculation using conventional coagulants.
3.5. Coagulation and flocculation test
To test the ability to remove colloidal particles from water, the Jartest was performed using a 10% PAC solution as a coagulant. From experimental results, pH 6 and alum dosage of 800 mg/L were determined to be the suitable conditions for Saigon River water treatment. The analysis results of some river water quality parameters before and after treatment are shown in Table 2. The coagulation with PAC generates micro flocs, which are then transformed into macro flocs by the flocculation process. The macro flocs are easily removed by the sedimentation process. The micro flocs and small suspended particles are subsequently removed by the rapid sand filtration. Table 2 indicates that the water quality parameters after treatment almost met the permitted standards according to the drinking water quality of Vietnam (QCVN 01-1: 2018 National technical regulation on Domestic Water Quality). The most visible result of colloidal removal is proven via turbidity treatment. The turbidity index after treatment reached up to 97% removal efficiency. This very high efficiency means that the colloidal particles were almost completely treated. However, the treated water still has some parameters such as Coliforms and permanganate index (i.e. natural organic matters) that were also higher than the standard. Therefore, it is necessary to have other treatment methods for disinfection and further treatment of organic compounds in the water.

| No. | Criteria         | Unit     | QCVN 01-1:2018/BYT Raw water | After settling | After filtration |
|-----|------------------|----------|-----------------------------|----------------|-----------------|
| 1   | pH               |          | 6.0 - 8.5                   | 7.08           | 6.64            | 6.73            |
| 2   | Coliforms        | CFU/100mL| < 3                         | 15000          | 7500            | **1500**        |
| 3   | Turbidity        | NTU      | 2                           | 33.16          | 3.95            | 1.05            |
| 4   | Permanganate index | mg O₂/L | 2                           | 8.24           | 3.92            | **3.60**        |
| 5   | Total hardness   | mgCaCO₃/L| 300                         | 284            | 264             | 232             |
| 6   | Chloride         | mg/L     | 250 (or 300)               | 9.40           | 7.10            | 5.60            |
| 7   | Total iron       | mg/L     | 0.3                         | 0.57           | 0.33            | 0.07            |
| 8   | Nitrite          | mg/L     | 0.05                        | 0.15           | 0.08            | 0.04            |
| 9   | Sulphate         | mg/L     | 250                         | 30.41          | 21.63           | 15.97           |
| 10  | Ammonia          | mg/L     | 0.3                         | 9.20           | 1.26            | 0.27            |

4. Conclusion
The zeta potential of colloidal particles in Sai Gon river water was determined to be in the range from -19 mV to -12 mV, and the pHzpc was estimated to be at pH 2. The pH, permanganate index, and Zeta potential magnitude of colloidal particles in river water have a positive correlation with each other. Besides, statistical analysis showed that the zeta potential had an inverse correlation with the significant coefficients of -0.67 and -0.73, respectively, with the pH value and the permanganate index. The size of colloidal particles was not uniform, with average particle size in the range from 2000 to 3000 nm. It may be influenced by environmental factors affecting the water source. When leaving the water sample to stand for a long time, large particles with sizes of > 1100 nm settled quickly while the smaller ones were very stable in the water. Traditional treatment systems have very high efficiency in treating colloidal particles. Specifically, the flocculation, sedimentation, and rapid sand filtration process remove up to 97% of colloidal particles through turbidity. However, the
Coliforms and organic compounds in the treated water did not meet the standard, which needs further treatment in the future.

Acknowledgements
This research is funded by Vietnam National University Ho Chi Minh City (VNU-HCM) under grant number C2020-20-45. We acknowledge the support of time and facilities from Ho Chi Minh City University of Technology (HCMUT), VNU-HCM for this study.

References
[1] Minh N T, Hung D D, Thang C S and Duc T M 2015 Zeta study of water samples on Ba and Dong Nai river basins Vietnam Journal of Earth Sciences 37 6
[2] Diab W, Villieras F, Koubayssi B, Mortada H, Lakis H and Hamieh T 2014 Study of physicochemical properties of colloidal sediments of Litani River in Lebanon Physics procedia 55 251-8
[3] Whitehouse B G, Macdonald R W, Iseki K, Yunker M B and McLaughlin F A 1989 Organic carbon and colloids in the Mackenzie River and Beaufort Sea Mar. Chem. 26 371-8
[4] Rostad C E, Leenheer J A and Daniel S R 1997 Organic carbon and nitrogen content associated with colloids and suspended particulates from the Mississippi River and some of its tributaries Environ. Sci. Technol. 31 3218-25