Removal of dissolved humic acid from water by coagulation method using polyaluminium chloride (PAC) with calcium carbonate as neutralizer and coagulant aid

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Abstract

Coagulation experiments were performed to find out the optimum coagulant and alkaline chemical for the removal of humic acid (HA) from environmental water. This research clearly indicates the effectiveness of coagulation method using polyaluminium chloride (PAC) with calcium carbonate as neutralizer and coagulant aid to remove HA. The removal of HA was evaluated from absorbance at 260 nm and concentration of dissolved organic carbon (DOC). The highest removal ratio was found to be 96.6% for absorbance of HA and 91.6% for DOC concentration when 30 mg/L of PAC with calcium carbonate (CaCO_3) was used as alkaline reagent. In this method, the sludge volume (SV) was reduced about half compared with the PAC method using NaOH as neutralizer. Ca^{2+} which is derived from CaCO_3 makes HA colloid size bigger and easier to form flocks because of the compression in the electrical double layer (EDL) between HA colloids. The adsorption of HA onto porous CaCO_3 particles also plays an important role. The experiments conducted with sample water collected from Sebangau River, Indonesia consists of 33.4 mg/L of DOC and was found to have an removal efficiency of 86.5%, where by the final concentration of DOC was 4.5 mg/L. These results suggested that CaCO_3 requires a lesser amount of coagulants and also shortens the settling time. This proposed technique provides a more effective and conventional removal method for HA by coagulation-precipitation processes.

Keywords: Humic acid removal; Polyaluminium chloride (PAC); Calcium carbonate; Neutralizer; Coagulant aid

1. Introduction

Humic substances (HSs) are assemblage of high molecular weight natural polymers resulting from the decomposition of organic substances. HSs have reached a point of stability and resistant to microbial breakdown and hardly involves in microbial metabolism especially in anoxic habitats [1,2]. The presence of HSs in water introduces a yellowish to brown color. They also form a strong toxic disinfection byproducts (DBPs) such as chlorinated organic compounds which includes trihalomethanes (THMs). Some of DBPs exhibit mutagenic properties during the chlorination step in tap water production or water treatment [3,4]. The permissible values for DBPs in drinking water set by the World Health Organization should not exceed 100 µg/L [5]. DBPs are the probable cancer-causing agents and lead to dizziness, headaches, as well as problems associated with the central nervous system with short-term exposure [6]. The formation of DBPs is directly proportional to the concentration of total organic carbon [7]. Moreover, high affinity of HSs for complexation with various pollutants including [toxic metals](#) and hydrophobic organic matters causes contamination of ground and surface water. Since there are both hydrophilic and hydrophobic partitions in the molecule, HSs can easily associate with hydrophobic compounds via sorption. This brings HSs to increase the solubility of the non-ion organic compounds such as pesticides and PCBs [8,9]. There are also some reports on endemic diseases caused by HSs. Blackfoot disease which prevails in southwestern Taiwan is associated with the daily intake of high concentration of humic acid (HA) which is one of the fractions of HSs in artesian well water (approximately 200 mg/L) to be was the root cause of the disease [10-13]. It is believed that HA initiates growth arrest and apoptosis in fibroblasts. These changes is often associated with increased oxidative stress [14]. As a result of these potential threats to human health, the removal of HA from drinking water is crucial to maintain human health.

There are several methodologies which has proven to be very useful to remove HA from

water such as coagulation-flocculation, oxidation [15], electrocoagulation [16-20], photocatalysis [21], and membrane technology [22]. However, one of the disadvantages is the high operational cost, especially in the application of membrane technology. This is because of HA tendency to severely foul the membrane [22]. Therefore, none of the mentioned methods are considered to be commercially viable by industry standards because of economically reasons. Among of all the methods, adsorption has been considered as one of the most economically viable techniques for water and wastewater treatments and activated carbon is the most widely used adsorbents [23]. However, the main disadvantage of activated carbon is the high cost in manufacturing and treatment. Moreover it also requires regeneration to be performed after a certain period of time.

In water treatment, coagulation is an essential process for the removal of fine particulate matters [24]. Metal salt coagulant of polyaluminium chloride (PAC), aluminum sulfate (Alum) and ferric chloride (FC) are commonly used in this process. They are widely applied for water treatment due to their large coagulation activity. Coagulation could further reduce DBPs precursors in the raw water supply [25]. Many studies have reported that coagulation-precipitation process can be applied in removing HA. Unfortunately, they tend to overlook the effects of the metal ions associated with HA. At natural pH of water, HA is positively charged by the presence of metal ions such as Ca^{2+} and Mg^{2+} via ion exchange reaction between these cations and the hydrogen ions associated with the carboxyl and phenolic hydroxyl group in HA [26]. It is most likely that positively charged HA makes coagulation harder because the metal salt coagulants also are positively charged whereby the removal of HA become suppressed.

PAC pre-polymerized coagulant has been used in water treatment as an effective removal method for certain contaminants, turbidity and color, since 1980s throughout the world [27]. PAC have replaced a larger part of other traditional coagulants in the recent years and offers

advantages over simple salts including low dosage, wide pH range, low sensitivity to temperature and lower residual metal ion concentration [28,29].

This research aims to investigate the removal of HA from environmental water through coagulation method using PAC with CaCO_3 as neutralizer and coagulant aid. Studies was carried out to assess the ability of PAC to remove HSs from contaminated water and surface (river) water. The comparative efficiency of PAC and other coagulant reagents was also conducted. The sludge volume (SV) using CaCO_3 with different neutralizers was also investigated. Sample water collected from Sebangau River located in Central Kalimantan, Indonesia was used in this study.

2. Materials and methods

2.1. Materials and chemicals

PAC and HA was purchased from Taki Chemical Co. Ltd. (Hyogo, Japan) and Sigma-Aldrich (MO, USA), respectively. All other chemicals including $\text{FeCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, CaCO_3 , NaOH , Na_2CO_3 , $\text{Cu}(\text{OH})_2$ and bentonite were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). All reagents used in the research are of analytical grade. All solutions were prepared by distilled water.

A stock HA solution (1 g/L) was prepared by dissolving a measured amount of HA powder in 0.1 mol/L NaOH solution by high shear mixing under the nitrogen atmosphere for several hours until the HA powder dissolved completely. The solution pH was adjusted to 7.0 by 0.1 mol/L HCl . The working HA solution was prepared by diluting a calculated amount of stock solution with distilled water and the concentration of HA was 50 mg/L. In aggregation experiment, metal–HA complex solution was used. The metal–HA complex solution was prepared by mixing 1 mL of 150 mg/L CaCl_2 , 1 mL of 150 mg/L MgCl_2 and 5 mL of 1 g/L HA with 93 mL deionized water. The pH of this solution was adjusted to 7.0 with 0.1 mol/L

HCl or 0.1 mol/L NaOH and shook for 2 h at room temperature.

2.2. Experimental and analytical methods

Coagulation experiments were performed at room temperature with magnetic stirrer (REXIM RS-6DR, AS ONE, Japan). A hundred mL of the sample water was placed into a 300 mL glass beaker and each coagulant was added into the sample water under rapid stirring. The HA solution was stirred rapidly at 600 rpm for 2 min after coagulant dosing followed by slow stirring at 200 rpm for 10 min and then settled for 30 min. Then sludge volume (SV) was determined by direct reading as percentage of sludge/mL of water treated [30].

Adsorption experiments were conducted with reciprocate shaker (incubator personal Lt, TAI TEC, Japan). Various amounts of CaCO_3 (particle size of 0.1 mm) were added into HA solutions and shaken for 2 h. The solution pH was adjusted to 7.0 with 0.1 mol/L HCl. After the experiments, supernatants samples were withdrawn and filtered through 0.45 μm pore diameter membrane filter (mixed cellulose ester, ADVANTEC, Japan) and the UV absorbance at 260 nm was measured. The solution pH was measured with pH meter (TOA DKK., Japan).

The DOC measurements were carried out with a total organic carbon analyzer (TOC-5000A, Shimadzu, Japan). Ultraviolet (UV) absorbance was measured with a UV-VIS spectrophotometer (UV 2450PC, Shimadzu, Japan) at 260 nm using a quartz cell. [All the experiments were conducted in triplicate for reproducibility purpose.](#)

3. Results and discussion

3.1. Effect of coagulant types and dosages

Coagulation is a distinguished method for the removal of HA from water by its simplicity and efficiency compared to sorption process [31]. The treatment efficiency of coagulation can be improved through the proper selection of coagulants and optimization of the process parameters [32]. The removal of HA was evaluated for each coagulant dosage added to the

water sample by measuring their absorbance at 260 nm (A_{260}). The results shown in Fig. 1 describe the effectiveness of PAC with two other coagulants aluminum sulfate (AS) and ferric chloride (FC). It was found that PAC is an effective coagulant because the removal efficiency is higher than the two other coagulants used. PAC also showed comparatively higher removal efficiency even at a low dosage compared with FC. These results were obtained because PAC has large molecular weight and therefore it produces a huge amount of aluminum hydroxides which is the origin of the flocks. In addition, the alkali consumption of PAC was small compared with AS and FC. From these results, it can be said that PAC is a suitable coagulant for the removal of HA.

Taken into consideration of PAC as a proper coagulant, further investigation was carried out by removing HA through coagulation using PAC with CaCO_3 as neutralizer and coagulant agent. The comparison with the existing techniques are shown in Fig. 2 and it clearly indicates that PAC is even able to remove HA at low dosage. The removal ratio maintained more than 95% when the PAC dosage more than 20 mg/L. This removal ratio is higher than the case of using NaOH as an alkaline chemical. Since CaCO_3 behaves as a coagulant reagent, the sedimentation velocity was significantly high and the SV was reduced about half compared with the case of using NaOH as a neutralizer. Therefore, the utilization of CaCO_3 combination with coagulation method by PAC is efficient in removing HA because it is able to perform both as alkaline chemical and as a coagulant agent about the same time.

3.2. Effect of alkaline chemicals and particles

Four different types of alkaline chemicals consist of $\text{Ca}(\text{OH})_2$, NaOH, Na_2CO_3 and CaCO_3 were used to neutralize the solution pH after adding PAC. NaOH was added as 0.1 mol/L solution while others were powder. As it can be seen from Fig. 3 that CaCO_3 provided the highest removal of HA (96.6%) and DOC (91.6%) when compared to other alkaline chemicals. It seems that CaCO_3 particles were to be the flock core. Therefore, the flock

formation was promoted and the high removal efficiency was achieved. This effect is due to the remaining CaCO_3 acting as a coagulant aid by forming larger flocks which provide a relatively shorter settling time for the removal of DOC [33-35].

Bentonite was used as coagulant aid to investigate the effect of particles in order to clarify the role of CaCO_3 on coagulation of HA using PAC. PAC coagulated both positively charged CaCO_3 and negatively charged bentonite suspended in distilled water. CaCO_3 added into HA solution coagulated with PAC formed large flocks and precipitated rapidly. On the other hand, flocculation did not occur for bentonite in the existing HA and therefore no precipitation was found. From this experiment, it is clear that HA prevents coagulation with bentonite by PAC.

3.3. Effect of Ca^{2+} and CO_3^{2-} on HA removal

The effect of Ca^{2+} and CO_3^{2-} on HA removal was examined by the addition of CaCl_2 and NaHCO_3 solution and the results are described in Fig. 4. The presence of Ca^{2+} and bentonite as a coagulant aid has contributed towards the higher removal of HA and this trends can also be seen in the presence of Ca^{2+} , CO_3^{2-} and bentonite. On the other hand, the HA removal was lower than the control experiments, when CO_3^{2-} and bentonite were added to the HA solution. Other researchers have also reported on the similar results regarding the presence of turbidity-contributing materials (kaolin) and the interaction or association of HA with Mg^{2+} and Ca^{2+} ions which can enhance the removal of HA by PAC through coagulation process [28,36,37]. This is possible because Ca^{2+} ions is able to block the negatively charged groups of the surface molecules and also act as bridges between functional groups of the two adjacent molecules. It has also been reported that Ca^{2+} compresses the electrical double layer (EDL) of both the PAC surface and the HA colloid particles [38]. This reaction proceeds to compress the EDL of both HA and bentonite particles. Thus, the impact of electrostatic repulsion between the negatively charged bentonite particles and HA molecules may be reduced.

3.4. Humic acid adsorption onto CaCO_3 particles

CaCO_3 is porous and therefore it has the potential for HA adsorption onto CaCO_3 surface [39]. The experiment focused on examining the adsorption of HA in neutral pH solution and the results are shown in Fig. 5. As indicated, HA was removed based on the amount of CaCO_3 . The removal of HA reached the highest level of 56% with 2.0 g of CaCO_3 after which it remained as constant. The removal amount was found to be 1.4 mg of HA per gram of CaCO_3 . The amount of adsorption could be strongly influenced by the pH of solution and the electrostatic interactions play a role in controlling the amount of HA adsorption [39]. At neutral pH, the CaCO_3 particles are neutral or slightly positively charged. Thus, a high adsorption affinity of the negatively charged HA was observed. With increasing the pH, the CaCO_3 particles become negatively charged and electrostatic interactions between the CaCO_3 particles and HA were repulsive, and subsequently, adsorption was low. A study conducted by Petrovic et al. [40] also observed the decrease of HA adsorption onto CaCO_3 with increasing pH.

3.5. Application for real sample

In order to show the application in the environmental field, sample water taken from Sebangau River (Kalimantan, Indonesia) was chosen and examined. The physicochemical parameters including temperature, pH, oxidation reduction potential (ORP), electric conductivity (EC), dissolved oxygen (DO) and dissolved organic carbon (DOC) are shown in Table 1.

Figure 6 shows the removal of HA and DOC from the river water with each PAC dosage. This method displayed high removal even at 30 mg/L of PAC. Besides that, it also indicated little coagulation and low removal with NaOH. The higher the dosage of PAC, the higher was the removal ratio. The lowest residual DOC concentration of 4.5 mg-C/L, which is lower than the water quality standards for drinking water in Indonesia, was obtained with 70 mg/L of

PAC. The sedimentation velocity in this method was also high and achieved 92.7% of HA removal in 5 minutes. It indicated that CaCO_3 shortens the settling time after the coagulation process. The SV produced after 30 minutes settling time was nearly half of the one using NaOH. The results show that this method can be applied to river water treatment.

4. Conclusions

This study investigated on the effective coagulant and alkaline chemical for removing HA from water by coagulation experiments. The results obtained suggested that PAC is an effective coagulant for the removal of HA. In this study, it was found that CaCO_3 is a most suitable alkaline chemical not only due to the removal efficiency but also the sedimentation velocity and SV due to the CaCO_3 which played a role as a coagulant aid. Instead of using CaCO_3 , it might also be possible to replace it with egg or seashell powder. The enhanced removal of HA in the presence of CaCO_3 was caused by three processes; reducing the EDL of HA colloids by Ca^{2+} , adsorption onto CaCO_3 particles, and the formation of flocks with CaCO_3 . The proposed method is cost effective and fast to be used for HA removal in river water which consists of a high concentration of HA.

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Figure and Table captions

- Fig. 1** Removal of HA against dosage of Polyaluminum Chloride (PAC), Aluminum Sulfate (AS) and Ferric Chloride (FC). The removal was measured for each coagulant dosage added to sample water by measuring their absorbance at 260 nm (A_{260}).
- Fig. 2** Removal of HA and the sludge volume (SV) against Polyaluminum Chloride (PAC) dosage. The solution pH was adjusted with CaCO_3 (●) and NaOH (○). SV is described with bar graph: (■) CaCO_3 ; (▨) NaOH.
- Fig. 3** The removal efficiency of HA (■) and DOC (■) after addition of four different alkaline chemicals to adjust the pH at 7. NaOH was used as 0.1 M solution and others were as powder.
- Fig. 4** Effect of Ca^{2+} and CO_3^{2-} on the removal of HA. The effect was examined by adding CaCl_2 and NaHCO_3 solution. Bentonite (used as coagulant aid) was applied to investigate the effect of particles. Dosage of PAC was 30 mg/L.
- Fig. 5** The removal of HA by CaCO_3 adsorption at neutral pH condition. The pH of this solution was adjusted to 7 with 0.1 M HCl or 0.1 M NaOH and was shaking for 2 h at room temperature.
- Fig. 6** Removal of HA (●) and DOC (○) against PAC dosage using CaCO_3 (solid line) and NaOH (broken line).
- Table 1** The average value and the range of the physicochemical parameters of Sebangau River water (Kalimantan, Indonesia). Three replicates of each sample were prepared and their physicochemical parameters were analyzed simultaneously.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Parameters	Mean	Range
Temperature (°C)	30.3	29.6 - 31.0
Depth (m)	5.0	3.0 - 8.0
pH	4.14	4.11- 4.17
ORP (mV)	298	293 - 302
EC (μS/cm)	0.054	0.052 - 0.056
DO (mg/L)	3.69	2.07 - 4.95
DOC (mg/L)	33.4	30.9 - 35.3

Table 1