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Effects of Concentration and Molecular Weight of Polycation on the Precipitation of SiO₂ Particles and Humic Acid

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ABSTRACT

There are various substances in our water resources that could cause to harmful effects upon human consumption. Suspended solids (e.g. SiO₂ particles) and dissolved organic matters (e.g. humic acid) are two of the common contaminants that significantly affect the water quality. The present work aims to investigate the feasibility of using poly (diallyldimethylammonium chloride) (PDDA), a cationic flocculant, to purify water contaminated with SiO₂ particles and humic acid via flocculation and precipitation process. Various concentrations (0.1 ppm – 1000 ppm) and molecular weights of PDDA were tested for their contaminant removal efficiency. Results showed that a mild amount of PDDA (0.1 ppm) is sufficient to completely separate 300 mg/L of SiO₂ particles from its suspension (100 % removal). At this optimum concentration, the effect of PDDA molecular weight on the removal efficiency is rather insignificant. However, excess amount of PDDA reduced the removal efficiency as the PDDA may re-stabilize the SiO₂ particles. The same PDDAs were tested for humic acid removal. In this case, it was found that 10 ppm of PDDA is needed to achieve effective removal of humic acid. Similarly, adding excess amount of PDDA (i.e. > 10 ppm) reduced the humic acid removal efficiency. Worth to highlight that the removal kinetic profiles appear to be vastly different for both SiO₂ and humic acid, owing to the different physical natures of these two contaminants.

Keywords:

Water purification, Suspended solid, Humic acid, Polycation, Flocculation

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1. Introduction

Natural water purification has been the focus of research and development considering most natural water resources are contaminated. In specific, the presence of small particulates (suspended solids) and dissolved organic matters (DOMs) reduce the clarity, and thus quality of the water [1-4]. Besides increase the water turbidity, the suspended solids also increase the water treatment costs, reduce the navigability of channels when the solids are deposited, as well as reduce the fisheries resources [3, 5]. Humic acid, one of the most abundant DOMs found in soil and water [6], induces biological growth besides affect the colour of water at concentration above 5 mg/L [7, 8]. More importantly, humic substances were reported to produce carcinogenic trihalomethanes, haloacetic acids, as well as

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disinfection by products (DBPs) upon interacted with chlorine in the water [9]. Owing to the aforementioned adverse effects, the removal of both suspended solids and dissolved organic matters is thus necessary in order to supply safe and clean water for community usage.

Silicon dioxide (SiO_2) or silica is a common fine suspended solid that can be found in most natural waters [10, 11]. This finely dispersed solid can be separated from water via various strategies such as electrocoagulation [12, 13], coagulation and flocculation [14, 15], membrane filtration [16, 17] and etc. On the other hand, in the attempt to remove humic acid, adsorption [18, 19], photocatalytic degradation [20, 21], and ion exchange [22] methods have been widely researched besides applying the same strategies applied to remove SiO_2 particles [23-26]. Of all the aforementioned methods, coagulation and flocculation is one of the favorable methods considering its simplicity and ease of implementation. In fact, the application of flocculation is not new in natural water and wastewater remediation industries. Various types of polycation, polyanion, as well as natural flocculants are now commercially available for this purpose. Organic polymers are preferable than inorganic coagulants in industrial wastewater treatment considering the former is efficient in removing solid from liquid, requires lower dosage, smaller volume of sludge formed, does not impart high ionic load to the water, as well as saving cost up to 25 % - 30% [27].

Nevertheless, the efficacy of flocculation process is strongly depending on several key parameters, such as the flocculant concentration, flocculant molecular weight, stirring speed, medium pH and etc. All these parameters will determine the time needed for the formed flocs to settle down. Thus, process optimization study is needed prior to large-scale implementations [28]. With this in mind, the present work aims to investigate the role of flocculant molecular weight and concentration on the removal of SiO_2 and humic acid from water. Here, poly(diallyldimethylammonium chloride) (PDDA), a commercialized polycation, was used as the flocculant. Four different molecular weights of PDDA (namely very low MW, low MW, medium MW, and high MW) were prepared at different concentrations for this study. Noteworthy that the studied contaminants are of different natures, whereby SiO_2 is particulate; while humic acid is macromolecule. Hence, the effectiveness of PDDA (as a macromolecule type of flocculant) in the removal of particulate and macromolecule contaminants can be compared.

2. Methodology and Experimental Setup

2.1 Preparation of Flocculant, Suspended Solid, and Humic Acid Stock Solution

Poly(diallyldimethylammonium chloride) (PDDA) of various molecular weights (MW) were purchased from Sigma Aldrich and were used without further purification. The MW of PDDA are very low MW PDDA (less than 100 kg/mol), low MW PDDA (100 – 200 kg/mol), medium MW PDDA (200 – 350 kg/mol) and high MW PDDA (400 – 500 kg/mol). Stock solution of all these PDDA were prepared at 10000 mg/L by dissolving known amount of the PDDA into distilled water.

Powdered silica (SiO_2) was used as suspended solid. It was purchased from R&M Chemicals. Similarly, 10000 mg/L of SiO_2 stock solution was prepared by dispersing known amount of SiO_2 powder in distilled water. Meanwhile, 500 mg/L of humic acid was prepared as stock solution by dissolving 125 mg of humic acid powder (Sigma Aldrich, Malaysia) in 250 mL distilled water. To assist the dissolution, the solution was adjusted to pH 10 using concentrated NaOH solution.

2.2 SiO_2 Particles and Humic Acid Removal Study

The removal of SiO_2 particles and humic acid via flocculation and precipitation was conducted in a 3 mL cuvette. In brief, the SiO_2 and PDDA stock solutions were well mixed and diluted with distilled water to produce a final suspension containing 300 mg/L of SiO_2 particles, and different concentrations (i.e. 0.1 mg/L, 1 mg/L, 10 mg/L, 100 mg/L, and 1000 mg/L) of PDDA. Absorbance reading of the

mixture was collected at wavelength 290 nm [29] over 24 hours. This is to trace the sedimentation profile. The same procedure was repeated using PDDA of different MWs as the flocculant.

Meanwhile, in humic acid flocculation study, the same procedure was followed but by fixing the humic acid concentration at 50 mg/L and the time-lapse absorbance reading was collected at wavelength 350 nm [30] for a period of 24 hours. Calibration curve has been developed for both SiO₂ and humic acid at their respective wavelengths and was found to follow a linear trendline with R² > 0.98.

The percentage of SiO₂ and humic acid removal were then determined by using Eq. (1):

$$\% \text{ removal} = \frac{\text{abs}_0 - \text{abs}_t}{\text{abs}_0} \times 100 \% \quad (1)$$

where abs_t and abs_0 refer to the absorbance value collected at time t and during the initial mixing, respectively. The removal kinetic profile was plotted for comparison purpose.

3. Results and Discussions

3.1 Role of PDDA MW and Concentration on SiO₂ Removal

A series of experiments was conducted to reveal the role of PDDA MW and concentration on SiO₂ removal efficiency. The experimental data are shown in Fig.1. Results showed that for all the MWs of PDDA, 100 % removal efficiency can be achieved with 0.1 ppm of PDDA. Further increase in the concentration resulted in detrimental effect. For instance, the removal efficiency reduced to 83.1 %, 77.1 %, 35.8 %, and 32.8 % when the concentration of very low MW PDDA increased to 1 ppm, 10 ppm, 100 ppm and 1000 ppm, respectively (see Fig.1a). This inverse relationship was observed for others MW PDDA.

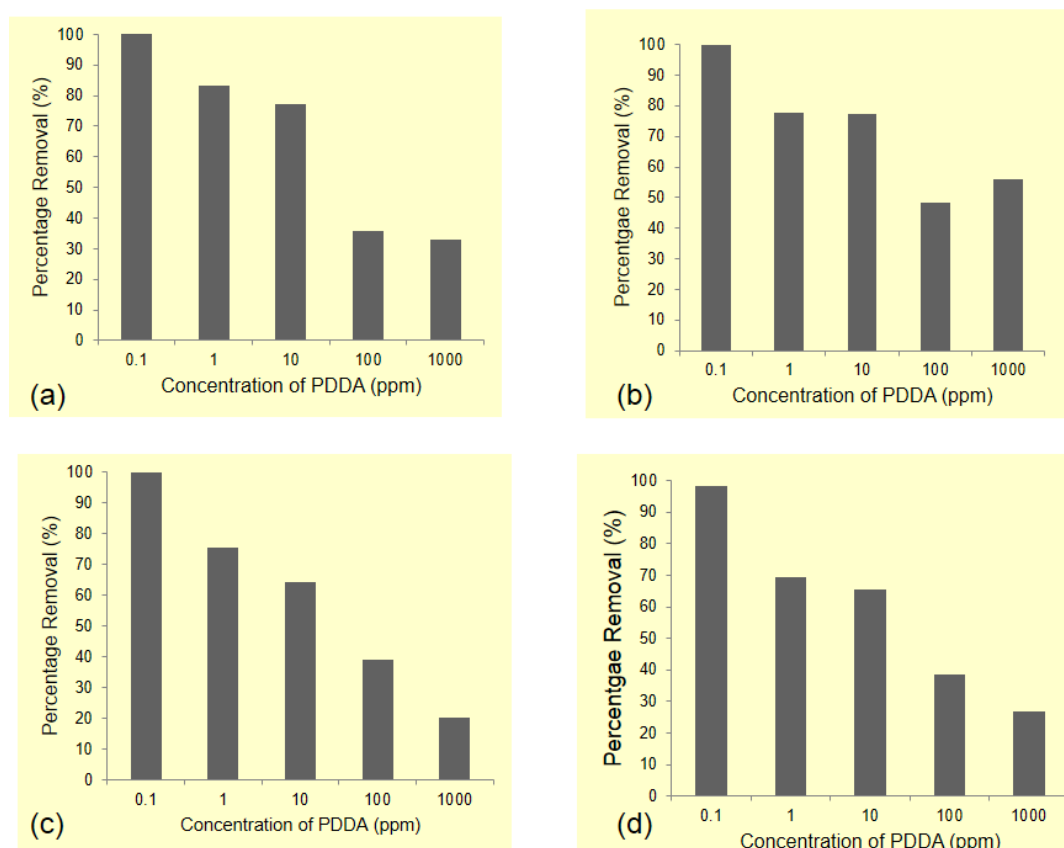


Fig. 1. SiO₂ removal efficiency by using different concentrations of (a) very low MW PDDA, (b) low MW PDDA, (c) medium MW PDDA, and (d) high MW PDDA as flocculant.

Fig. 2 shows the associated SiO₂ removal kinetic profile. All the PDDAs exhibited similar pattern in the removal process, whereby 0.1 ppm of PDDA induced the fastest initial precipitation rate; while 1000 ppm of PDDA lead to slowest initial precipitation rate. For all PDDA at the optimal concentration (*i.e.* 0.1 ppm), steady state of precipitation was achieved after 5 hours. **Fig. 3** shows the photo of the samples after extending the precipitation duration to 24 hours. Here, a white cloud can be seen at the bottom of all the sample cuvettes. This white cloud is SiO₂ precipitates. The appearance of this white cloud is particularly obvious for 0.1 ppm PDDA because SiO₂ precipitation efficiency was highest (100 %) at this concentration. Meanwhile, for 1000 ppm PDDA, the formation of white cloud is rather insignificant as most of the SiO₂ particles remain suspended. The same observation is applicable for all MW of PDDA.

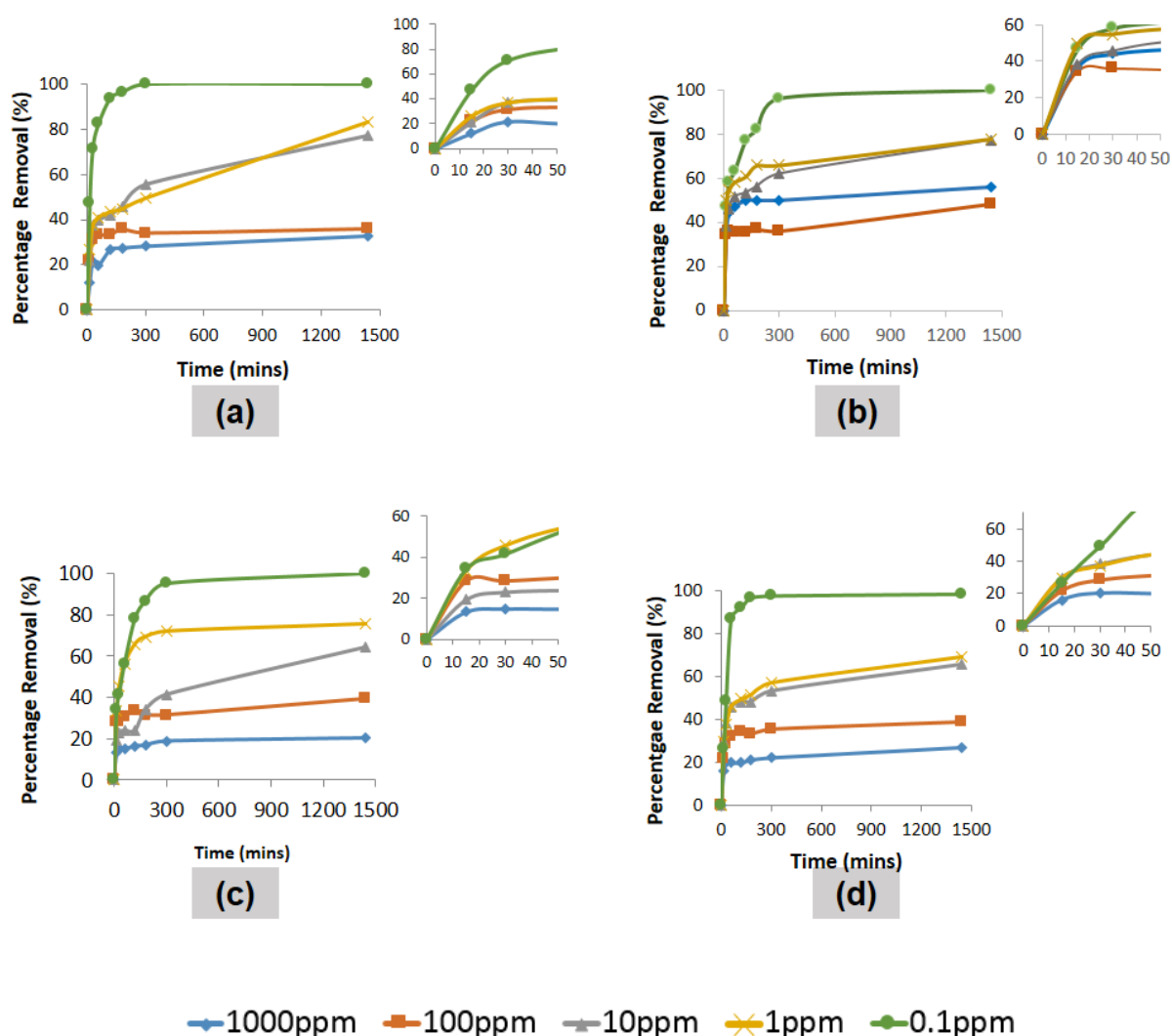


Fig. 2. The SiO₂ removal kinetic profile using different concentrations of (a) very low MW PDDA, (b) low MW PDDA, (c) medium MW PDDA, and (d) high MW PDDA as flocculant.

The flocculation of SiO_2 particles by PDDA involved a bridging effect whereby the negatively charged SiO_2 particles will adsorb onto the positively charged PDDA. Charge neutralization occurred upon the adsorption. A large and loose floc will form when the added PDDA provide sufficient positive sites to neutralise the SiO_2 particles [31]. In the present work, 0.1 ppm of PDDA was found sufficient to induce such effective flocculation and precipitation. The adsorption may continue beyond the neutralization point which later on lead to overcharging [32-34]. Such overcharging causes the flocs to be electrosterically stabilized. Thus, the phenomenon whereby higher concentrations of PDDA could not achieve higher percentage removal is due to the fact that re-stabilization region developed among the colloidal particulates with the increase of PDDA concentration [35]. Yan et al. [36] reported the same observation whereby re-suspension of their alumina particles was found to happen when the flocculant concentration is above the optimum dosage (*i.e.* overdose).

In addition, another plausible reason for the phenomenon seen at higher concentration of PDDA is due to the effect of drag force. It is generally known that a particle that undergo natural sedimentation will experience gravitation force and an opposing drag force. The magnitude of drag force is directly proportional to the suspension viscosity in accordance to Stokes' law [37], thus, considering viscosity of the suspension will increase with the increase in polymer MW [38, 39] and concentration [40], it is reasonable to ascribe the poor removal efficiency obtained at higher PDDA MW and concentration to the domination of drag force.

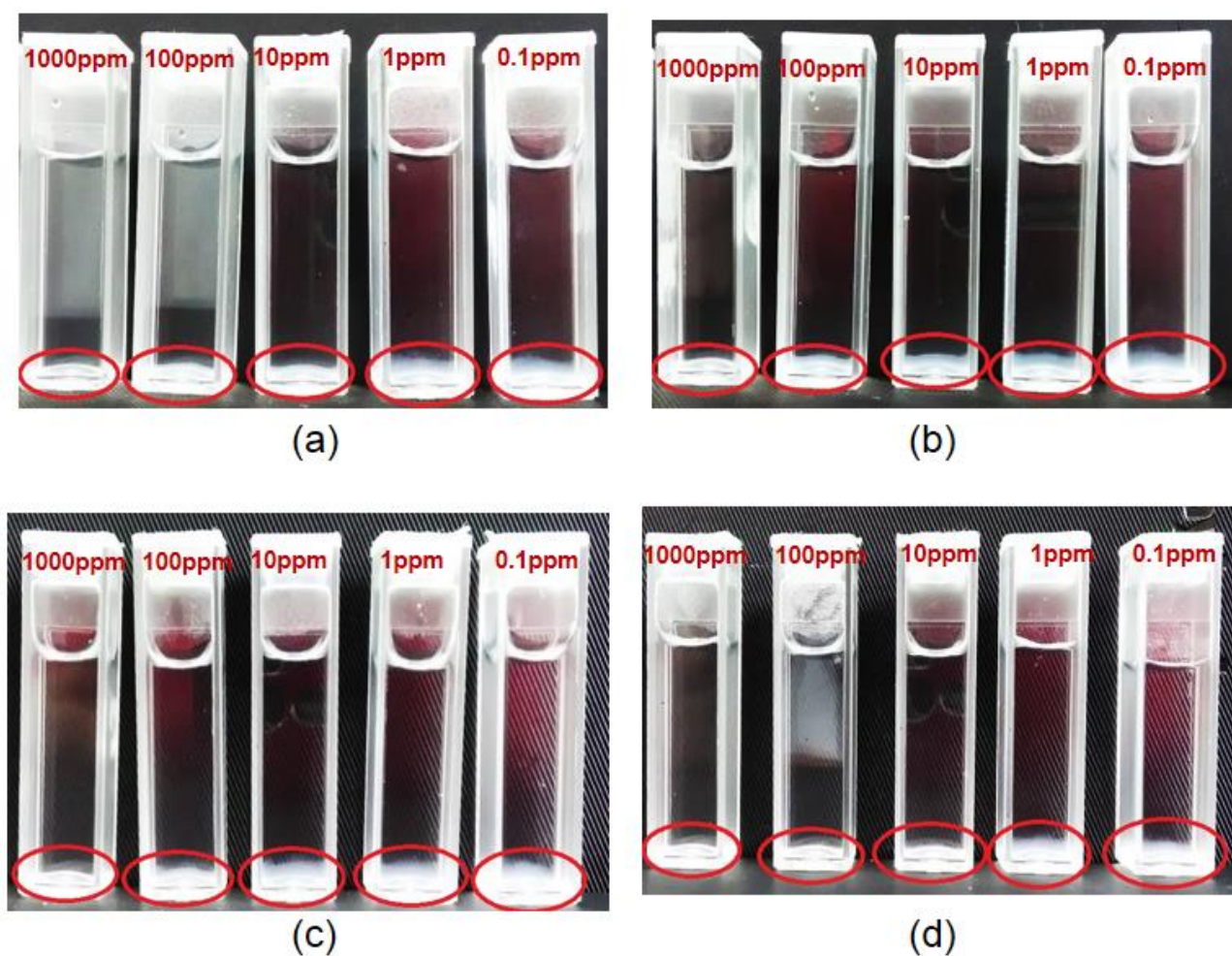


Fig. 3. Photos of the SiO_2 samples after 24 hours precipitation using different concentrations of (a) very low MW PDDA, (b) low MW PDDA, (c) medium MW PDDA, and (d) high MW PDDA as flocculant.

3.2 Role of PDDA MW and Concentration on Humic Acid Removal

The same range of polymer MW and concentration were tested on humic acid removal. Fig.4 depicts the experiment result obtained from the humic acid removal study; while Fig. 5 delineates the photo of the samples after 24 hours of precipitation. As shown in Fig.4, it was found that the very low MW PDDA at concentration lower than 10 ppm presented removal percentage of around 2 - 3 % only. However, increase the concentration to 10 ppm successfully induced the highest removal percentage, which was 62.4 %. Similarly, for low MW PDDA (Fig. 4b), at concentration lesser than 10 ppm, the maximum removal percentage achieved was between 2 - 4 %, whereas at 10 ppm, the removal efficiency improved to 57.2 %. For medium MW PDDA (Fig.4c), concentration of 1 ppm and 10 ppm resulted in 81.3 % and 72.6 % removal efficiency, respectively. Meanwhile, for high MW PDDA (Fig. 4d), 74.9 % of humic acid removal was recorded when 10 ppm concentration was employed. Interesting to note the removal percentage is almost negligible when the concentration of all types of PDDA being increased to 100 ppm and 1000 ppm.

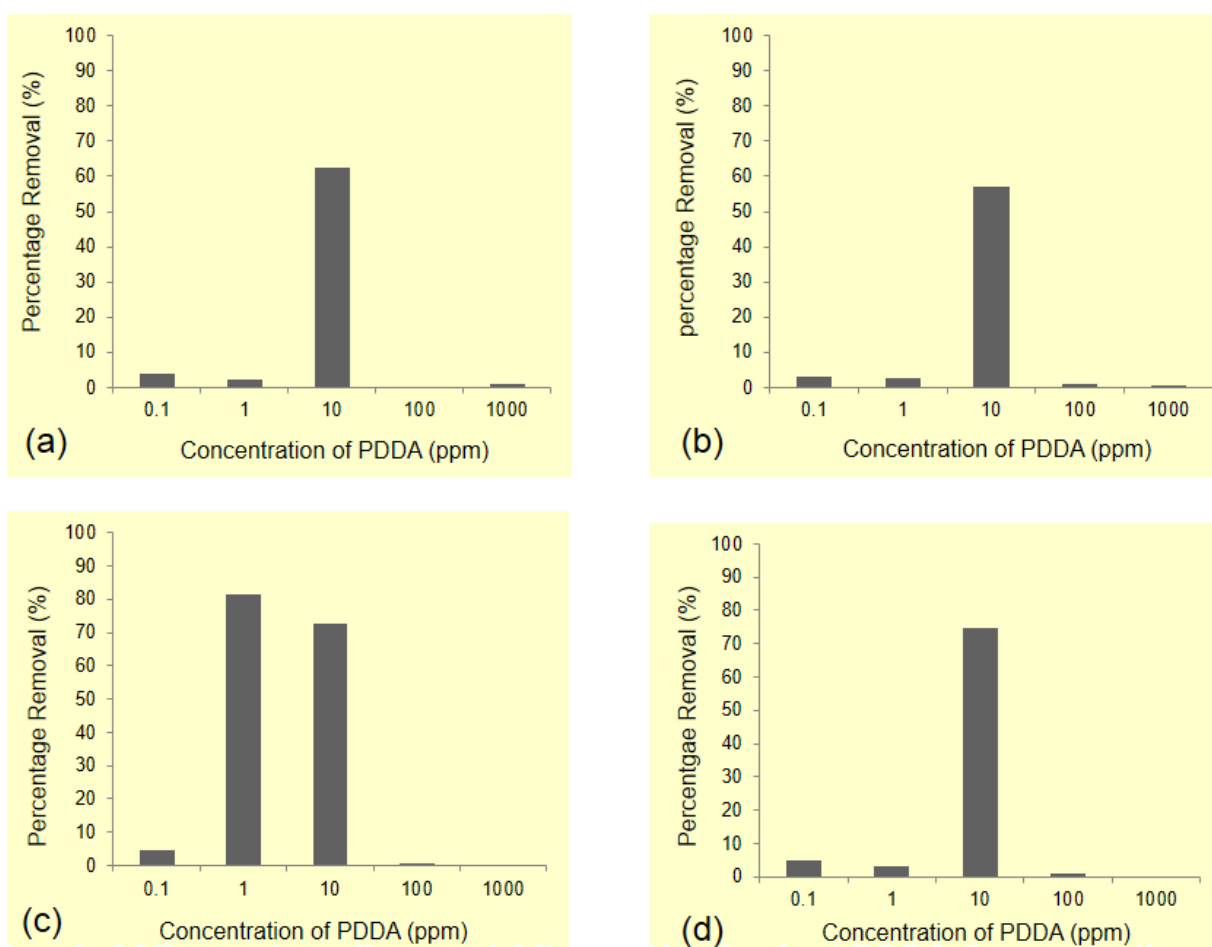


Figure 4. Humic acid removal efficiency by using different concentrations of (a) very low MW PDDA, (b) low MW PDDA, (c) medium MW PDDA, and (d) high MW PDDA as flocculant.

The limited removal efficiency attained at low concentration range can be ascribed to insufficient amount of PDDA to induce effective flocculation of humic acid. Thus, increase the PDDA concentration to 10 ppm increase the humic acid removal efficiency. Nevertheless, further increase the PDDA concentration to ≥ 100 ppm decrease the removal efficiency. This phenomenon may due to excess amount of PDDA, which re-stabilize the formed complexes. Dautzenberg and Karibyants (1999) reported that polyelectrolyte complexes that are formed by mixing polycation and polyanion

consist of a core of neutralized polymers, and an outer shell formed by the polymer in excess. The outer shell serves as the source of electrostatic stabilization [41]. Thus, less precipitation is expected when one of the polymer was in excess [41, 42]. The same observation was reported by Yu et al. [43] whereby more humic acid was found to retain in the supernatant when the flocculant concentration is above the optimum range.

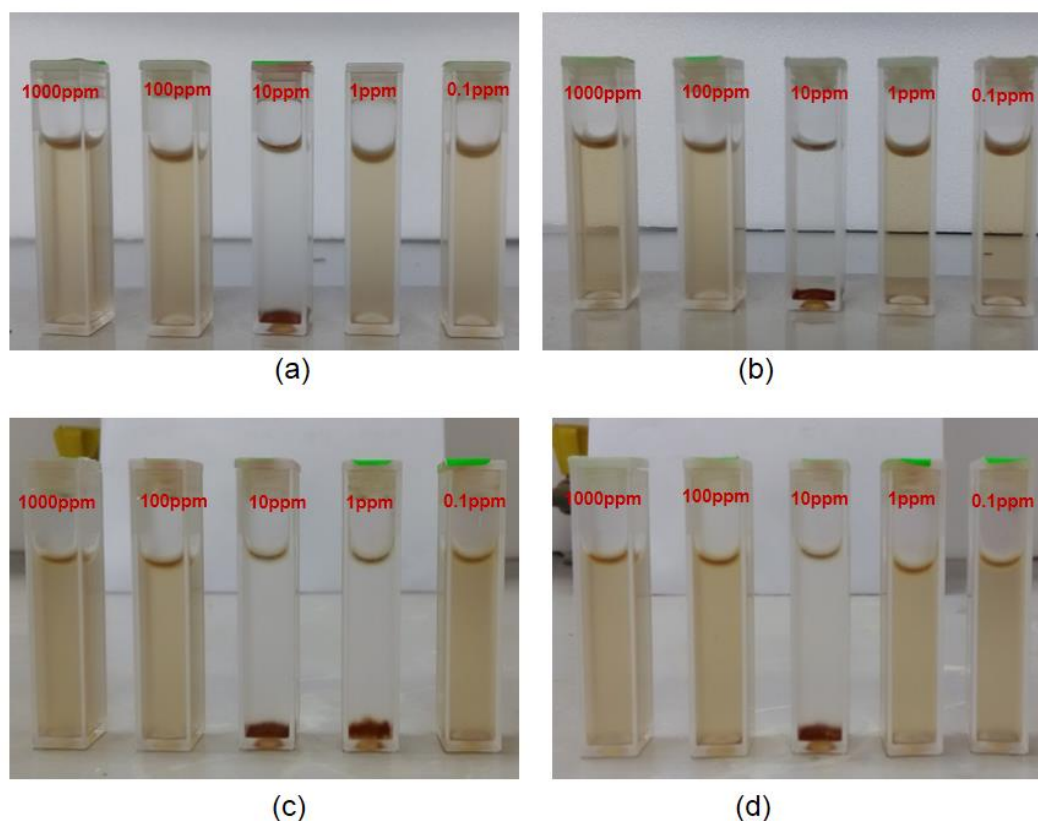


Fig. 5. Photos of the humic acid samples after 24 hours precipitation using different concentrations of (a) very low MW PDDA, (b) low MW PDDA, (c) medium MW PDDA, and (d) high MW PDDA as flocculant.

Fig. 6 shows the kinetic profile for the removal of humic acid from water using different MWs of PDDA as flocculant. We observed a peculiar phenomenon during the first few hours flocculation of humic acid, whereby ‘negative’ removal percentage was recorded (see the enlarged inset figures in Fig. 6). This particularly obvious when 10 ppm of PDDA (*i.e.* at optimal concentration) was used as flocculant. Such negative removal percentage was due to higher solution absorbance at time t (abs_t) as compared to the initial absorbance value (abs_0). The higher abs_t indicated that the humic acid solution became more turbid after mixed with PDDA. Upon the mixing, the anionic humic acid molecules immediately interacted with the cationic PDDA chain forming polyelectrolyte complexes. These polyelectrolyte complexes increased the solution turbidity, and thus the absorbance value detected by spectrophotometer [42, 44]. Accordingly, a negative removal percentage was recorded. The turbidity of the solution reduced when the formed flocs start to settle down.

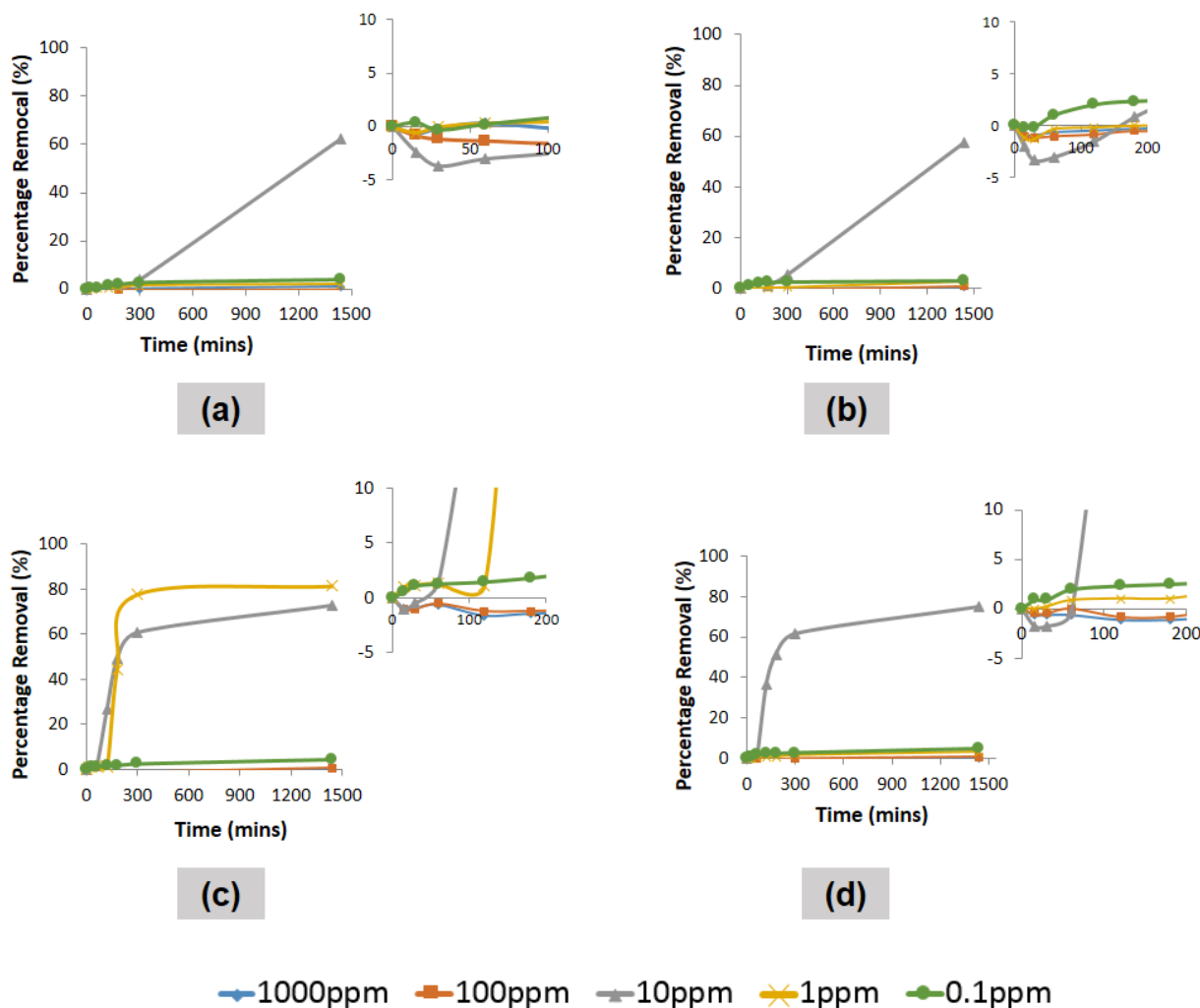


Fig. 6. The humic acid removal kinetic profile using different concentrations of (a) very low MW PDDA, (b) low MW PDDA, (c) medium MW PDDA, and (d) high MW PDDA as flocculant.

4. Conclusion

The present work investigated the effectiveness of using cationic polymer, *i.e.* PDDA, for the removal of SiO_2 particles and humic acid from water by taking consideration on the impact induced by the concentration and MW of PDDA. Despite using the same range of PDDA concentration and MW, the separation profiles of both SiO_2 particles and humic acid appear to be dissimilar owing to their different natures, whereby the former is a particulate; while the latter is a dissolved macromolecule. In specific, PDDA is more effective in removing SiO_2 particles than humic acid. Here, it was found that all the MW of PDDA able to remove SiO_2 particles with the best removal efficiency ($\sim 100\%$) achieved at 0.1 ppm PDDA. Such result is encouraging as it indicated a mild concentration of PDDA is sufficient to remove 300 mg/L of SiO_2 particles. PDDA MW does not showed much influence on the removal efficiency at this optimum concentration. However, excess amount of PDDA lead to re-stabilization of the SiO_2 particles and thus rendered to a poorer removal. In the removal of humic acid, higher concentration of PDDA is needed for an effective removal. In general, the optimum PDDA concentration for humic acid removal was 10 ppm for all the MWs of PDDA. Concentration lesser than that was not effective mostly due to insufficient amount of cationic sites to neutralize the anionic sites of humic acid. Meanwhile, further increase the PDDA concentration to ≥ 100 ppm

resulted in poorer humic acid removal. This was ascribed to the excess amount of PDDA which stabilize the polymer complexes. A more detail work has to be done, in particular, to reveal the compactness of the formed flocs which closely related to the precipitation rate.

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