Assessing the Role of Common Salt Valency and Concentration on Humic Acid and Alginate Removal from Synthetic Pond Water

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ARTICLE INFO	ABSTRACT
	Humic acid is a natural component of the aquatic environment that affects the water quality by colour, taste as well as enhances biological growth in the ecosystem. The present work demonstrated the feasibility of employing common salts for humic acid separation with the effect of salt valency and salt concentrations as the main investigation parameters. Three types of common salts, namely $NaCl$, $CaCl_2$, and $AlCl_3$, at the concentration of 0.005 M – 0.5 M were tested for their humic acid removal efficiencies via coagulation and natural sedimentation. Experimental results showed that mild amount of $AlCl_3$ (0.01 M) is sufficient to induce 82 % humic acid removal. On the other hand, the optimum humic acid removals were recorded as 77.4 % and 12.5 % when 0.1 M of $CaCl_2$ and 0.5 M NaCl were used, respectively. In fact, a comparison graph clearly showed that the humic acid removal efficiency increased following the salt valency (*i.e.* $Na^+ < Ca^{2+} < Al^{3+}$) at all tested concentrations. Nevertheless, a slight reduction in humic acid removal was recorded when the $AlCl_3$ concentration increased above it optimum value. The same salts were employed for alginate removal. Here, it was found that there is no separation detected when NaCl was used as the coagulant; while 0.5 M of $CaCl_2$ and $AlCl_3$ resulted in 62.5 % and 88.9 % alginate removal, respectively. Effectiveness of using common salts for both humic acid and alginate removal suggesting separation of dissolved organic matters can be done without the need to fully rely on synthetic materials such as membrane, activated carbon, synthetic flocculants, nanoparticles and etc.

1. Introduction

Humic acid and alginate are the common dissolved organic matters (DOMs) that can be found in the aquatic environment. Humic acid has been regarded as a macromolecular with molecular weight ranging from 2000 – 5000 Da and consist of multiple functional groups [1]. Alginate, on the other hand, is a natural polymeric acid composed of α-l-guluronic acid and β-d-mannuronic acid [2]. Although both humic acid and alginate appear naturally, their existence causes significant negative impacts to the water quality. In particular, the presence of humic acid affects the water quality by colour, taste as well as enhances biological growth in the ecosystem [3].

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Adsorption by activated carbon [4, 5] or nanoparticles [6, 7], and filtration by membrane technology [8-10] are the common approaches used for removal of DOMs from natural water. Nevertheless, all these methods required the fabrication of new materials as adsorbent or filter. In fact, the process of material synthesis can be rather energy and cost intensive. For instance, activated carbon from olive stones is produced via chemical activation with sulphuric acid followed up with multiple heat treatments (temperature up to 373 K) in order to achieve the desired porosity [11]. On the other hand, Sutrisno and Hidayat prepared activated carbon at 800 ºC activation temperature and 120 minutes activation time in order to obtain higher Brunauer–Emmett–Teller surface area and pore volume [12]. Meanwhile, in the application of membrane filtration for humic acid removal, Teow et al. [9] casted PVDF ultrafiltration membrane in N-N-dimethylacetamide together with TiO_2 nanoparticles for antifouling purpose. Colloidal stability of the TiO_2 nanoparticles was pre-strengthened through both chemical and mechanical treatments. This was achieved by adjusting pH of the TiO_2 suspension and further agglomerates breakdown by ultrasonication. Apparently, the whole material synthesis process itself has consume large amount of energy and create additional waste to the environment. Thus, it is important to develop a method that does not require new material synthesis for DOM removal.

Coagulation is a simple process involving ion interaction to precipitate dissolved matter from its solution. Alum and polyaluminum chloride are some of the common coagulants used for DOM removal [13-15]. DOMs, in particular, behave as important ligands for metal ions because of its ample complexing sites such as carboxyl, phenolic, amino, and sulphydryl functional groups [16]. Thus, ion interaction may occur between the DOM molecules and the metal ions of the coagulant. Despite of using alum and polyaluminium chloride, the present work aim to illustrate feasibility of using the easily obtained common salts, such as NaCl, $CaCl_2$, and $AlCl_3$ for the separation of humic acid and alginate from water via coagulation process. The addition of Na^+, Ca^{2+} and Al^{3+} into the solution would interact with the functional groups of DOMs and later on form complexes that would precipitate out. The effects of salt valency and concentration on the separation efficiency were systematically assessed in this study.

2. Experimental Materials and Methods

2.1 *Preparation of Salt Solution*

A known concentration of NaCl, $CaCl_2$ and $AlCl_3$ solutions were prepared as stock solution. Both NaCl and $CaCl_2$ solution were adjusted to pH 8 by using 1 M NaOH or 1M HCl. No pH adjustment for $AlCl_3$ solution due to the formation of white aluminium hydroxide precipitates when NaOH was added.

2.2 *Preparation of Humic Acid Solution*

500mg/L of humic acid stock solution was prepared by adding 0.125 g humic acid powder (Sigma Aldrich, Malaysia) to 250 ml of distilled water. The pH of the solution was adjusted to pH 10 in order to improve the dissolution process. The solution was then stirred for 3 hours under constant agitation 700 rpm [17]. Synthetic pond water mimicking natural condition (*i.e.* containing 50 mg/L humic substance) was prepared for the subsequent coagulation study [18, 19]. The pH of the humic acid was also adjusted to pH 8 as it is proven that at pH 8 will provide the highest aggregation rate between cations and humic acid [20, 21]. The as-prepared humic acid was shielded from direct sunlight to prevent decomposition.

2.3 *Preparation of Alginate Solution*

Sodium alginate powder was purchased from Sigma Aldrich, Malaysia. 500 mg/L of alginate stock solution is prepared by dissolving known amount of alginate powder in distilled water.

2.4 *Coagulation Study*

Experiment was started by mixing known amount of humic acid, salt solution and water into a plastic cuvette of 3 ml capacity. The cuvette was covered with lid and the mixture was well-mixed before placing it in a UV-visible spectrophotometer for determination of initial absorbance value at 350 nm wavelength. The sample was then allowed to stand in room temperature and its absorbance value was recorded from time to time. The same procedures were conducted at five different concentrations ranging from 0.005 M to 0.5 M for each type of salt solution.

The humic acid removal efficiency, η was evaluated by comparing the concentration of humic acid at time t to the initial concentration, using Eq. (1).

$$\eta = \frac{C_o - C}{C_o} \times 100\% \tag{1}$$

where C_o (mg/L) represents the initial concentration; C (mg/L) represents the concentration that remains in the solution at time t.

The same procedure was used to investigate the separation of alginate. The coagulated alginate was removed by filter paper and the remaining solution was sent for UV-visible spectrophometry measurement at 250 nm wavelength.

3. Results and Discussion

3.1 *Effect of Salt Valency and Concentration on Humic Acid Removal*

The effectiveness of humic acid removal from synthetic pond water using different concentrations of salt solution was conducted. The profile of the removal was evaluated over a period of 3 hours and plotted as Fig. 1. As shown in Fig.1, significant reduction in humic acid concentration were observed when $CaCl_2$ or $AlCl_3$ was used as the coagulant, whereby the $AlCl_3$ performed equivalent or even better than $CaCl_2$ at all concentrations. For instance, by using 0.005 M of $CaCl_2$, the humic acid concentration successfully reduced from 50 mg/L to 22 mg/L after 3 hours; while the same concentration of $AlCl_3$ further reduces the humic acid to 13.90 mg/L (see Fig. 1a). On the other hand, NaCl resulted in mild to almost no humic acid removal at all the tested concentrations. Such a coagulation efficiency follows the trend of the salt valency, whereby the efficiency increased by $Na^+ < Ca^{2+} < Al^{3+}$.

The correlation between salt valency and remaining humic acid concentration is interesting because it indicates the ability of the cations to interact with carboxylic group of the humic acid under a fixed period of time. The better coagulation performance induced by Al^{3+} as compared to Ca^{2+} and Na^+ can be ascribed to the higher cationic charge per ion that can neutralise more carboxylic groups of humic acid. As illustrated in Fig.2a, each sodium ion may neutralise one carboxylic group at one time and thus provided the poorest separation result among the three salt solutions. Meanwhile, each calcium ion may neutralise two carboxylic groups (Fig. 2b) and each aluminium ion may neutralise three carboxylic groups of the humic acid (Fig. 2c). Accordingly, under the same concentration, more carboxylic groups can be neutralised by Al^{3+} as compared to Ca^{2+} and Na^+. This answers the better coagulation efficiency induced by $AlCl_3$. Noteworthy that the interaction between the multivalent cations and the carboxylic group of humic acid induce aggregation of humic acid by reducing

negativity of the humic acid, which subsequently allows the formed complexes approach each other and coordinated with each other via weak hydrogen bonding [22]. The coagulated humic acid is heavier in mass and thus easily precipitated out from the solution.

To further evaluate the ultimate removal efficiency, the coagulation process was continued until both the coagulation and sedimentation has arrived its steady state. Accordingly, data was collected at 48 hours and plotted as Fig. 3. As shown in Fig. 3, 0.5 M of NaCl provided maximum 12.5 % removal efficiency. Meanwhile, both $CaCl_2$ and $AlCl_3$ showed a significant better in humic acid removal as compared to NaCl.
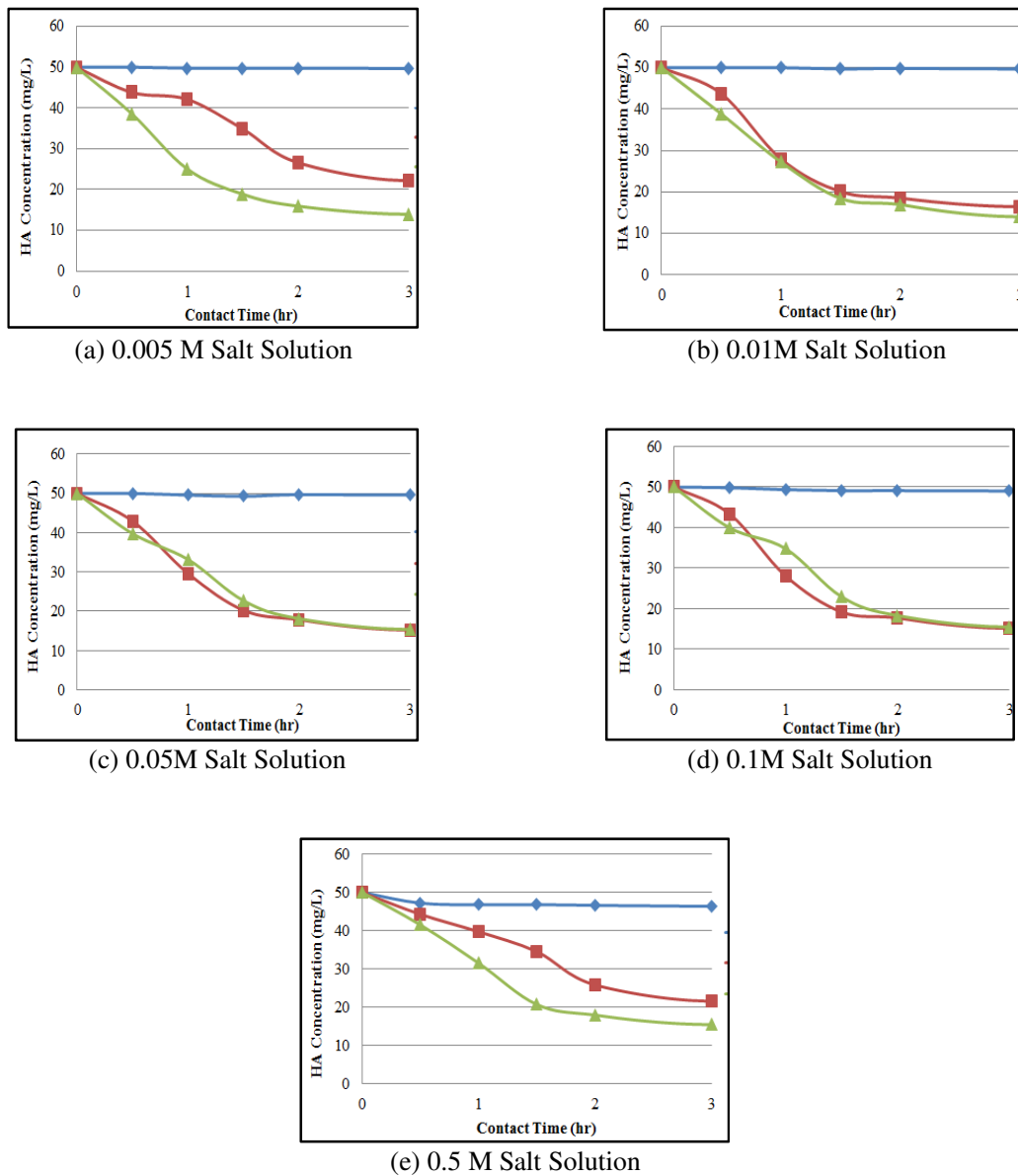

(a) 0.005 M Salt Solution

(b) 0.01M Salt Solution

(c) 0.05M Salt Solution

(d) 0.1M Salt Solution

(e) 0.5 M Salt Solution

Fig. 1. The reduction of humic acid concentration after coagulated with different concentrations of NaCl (*blue lines and markers*), $CaCl_2$ (*red lines and markers*) and $AlCl_3$ (*green lines and markers*)
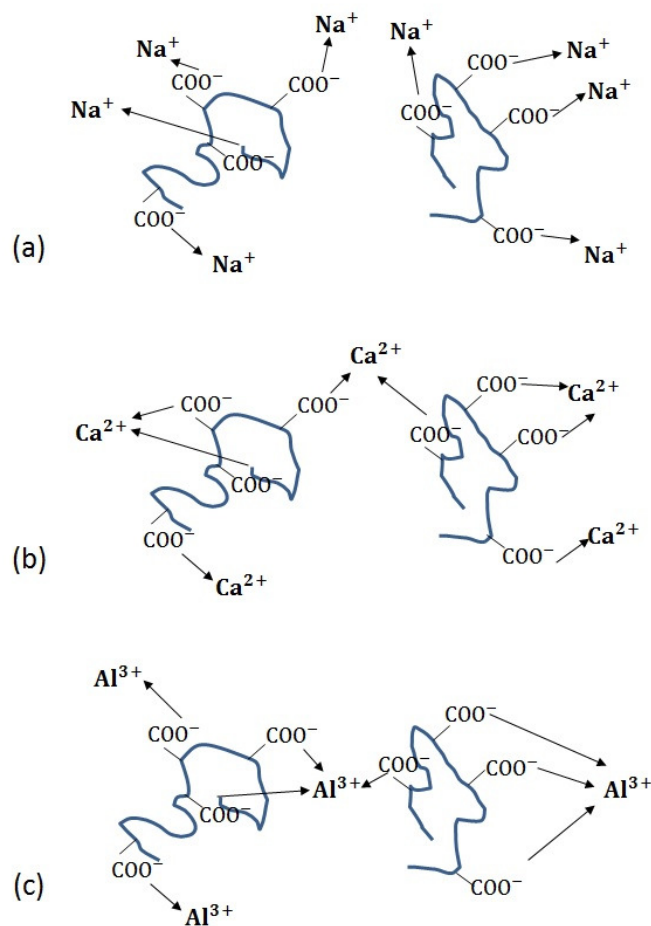
Fig.2. Coagulation of (a) Na^+, (b) Ca^{2+}, and (c) Al^{3+} with humic acid matrices

Fig. 3 shown that the humic acid removal efficiency by using $CaCl_2$ is rather effective whereby 72.5 % of removal was achieved even with low amount of $CaCl_2$ (*i.e.* 0.005 M). The highest removal efficiency was recorded as 77.4 % when 0.1 M of $CaCl_2$ was employed. In fact, a further increased in the $CaCl_2$ concentration does not induced much changes on the ultimate removal efficiency. Such observation indicated that the Ca^{2+} ions added in the present work was in excess compared to the amount needed to achieve optimum humic acid removal. Similar trend was observed when $AlCl_3$ was used as the coagulant, whereby 81.5 % of humic acid was successfully precipitated out with the use of 0.005 M $AlCl_3$. The highest removal efficiency was recorded as 82 % with 0.01 M $AlCl_3$. Fig. 4 shows the photos of the samples taken both before and after 48 hours of coagulation and sedimentation.

Interestingly, further increased in the $AlCl_3$ concentration lead to detrimental effect. Here, it was found that the removal efficiency dropped to 79.4%, 80.8%, and 76.1% when the $AlCl_3$ concentration was increased to 0.05 M, 0.1 M, and 0.5 M, respectively (see Fig.3). Such an outlier might be due to re-stabilization of the humic acid upon oversaturation with Al^{3+} ions. The same observation was reported by Zhang et al. who investigated the coagulation of an anionic TiO_2 nanoparticles by using alum [23]. It was found that the highest TiO_2 removal efficiency was achieved when 0.2 mmol/L of Al^{3+} was employed; however, further increase the Al^{3+} concentration to 0.4 mmol/L resulted in almost no removal due to over-charging of the TiO_2 nanoparticles by Al^{3+}. Such over-charging turned the TiO_2 nanoparticles into positive charge and thus being electrostatically re-stabilized.
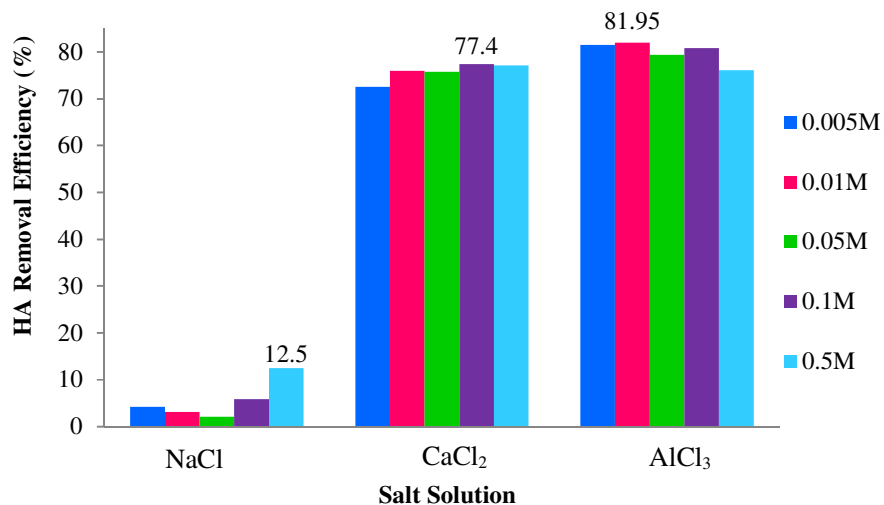
Fig.3. The ultimate humic acid removal efficiency after 2 days of coagulation

(a)   0.005M, 0.01M, 0.05M, 0.1M and 0.5M of NaCl *(from left to right cuvette)*

(b)   0.005M, 0.01M, 0.05M, 0.1M and 0.5M of CaCl₂ *(from left to right cuvette)*

(c)   0.005M, 0.01M, 0.05M, 0.1M and 0.5M of AlCl₃ *(from left to right cuvette)*
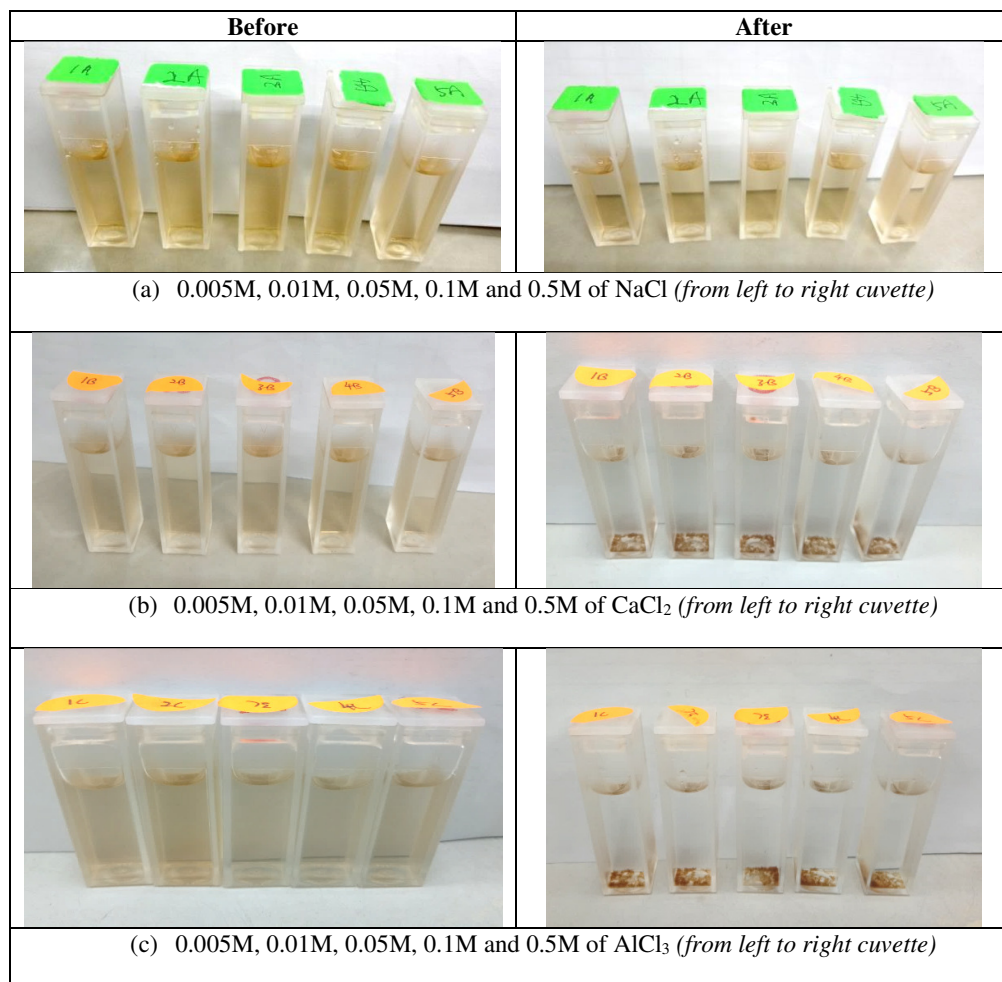
Fig. 4. Photos showing the sample at the initial condition and after 48 hours of coagulation and sedimentation

3.2 *Effect of Salt Valency and Concentration on Alginate Removal*

To study the role of salt valency and concentration on the separation of alginate from water samples, a series of experiments were conducted with a fixed initial alginate concentration (50 mg/L) mixed with NaCl, $CaCl_2$ or $AlCl_3$ solution. The experimental results are shown in Fig.5.
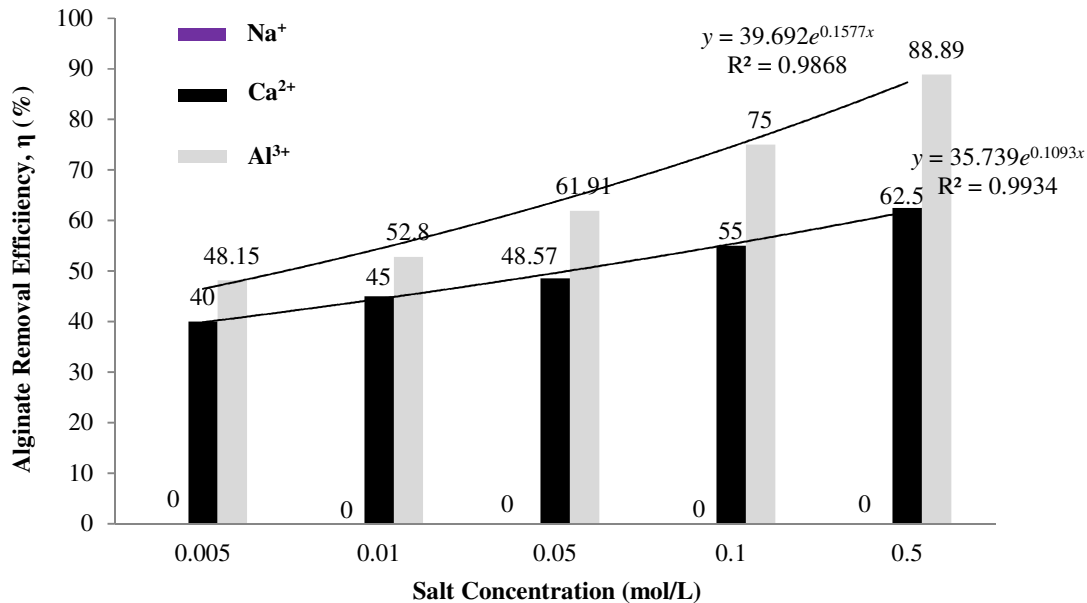

Fig.5. The separation efficiency of alginate with different concentration of $CaCl_2$ and $AlCl_3$

As shown in **Fig.5**, there was no separation recorded when NaCl was used as the coagulant. Meanwhile, the separation efficiency significantly improved when the concentration of $CaCl_2$ and $AlCl_3$ increased. The highest alginate removal efficiency was obtained from 0.5 M of calcium chloride and aluminium chloride solution at 62.5 % and 88.89 % respectively. Alginate is a polysaccharide consisting multiple carboxylic groups. These carboxylic groups can be cross-linked by polyvalent cations to form insoluble alginate gel [24]. The formed gel can then be filtered out from the solution.

Besides illustrating direct relationship between the alginate removal efficiency and the salt valency, it is interesting to note that the removal efficiency increased exponentially with the salt concentration. Here, the alginate removal efficiency with $CaCl_2$ or $AlCl_3$ nicely fitted in exponential curve with R^2 value 0.9934 and 0.9868, respectively. In addition, the difference of alginate removal efficiency between calcium chloride and aluminium chloride solution become larger as the concentration of salt solution increases as shown in Table 1. With 0.005 M salt solutions, the different in alginate removal efficiency between $CaCl_2$ and $AlCl_3$ is 8.15 %; meanwhile, with 0.5M salt solution, the percentage of difference increased to 26.39 %. This observation further confirms the prominent role of salt valency on alginate removal.

Table 1: Difference of alginate removal efficiency between $CaCl_2$ and $AlCl_3$ solutions.

Concentration of $CaCl_2$ & $AlCl_3$	0.005M	0.01M	0.05M	0.1M	0.5M
Percentage difference in Separation Efficiency	8.15	7.80	13.34	20.00	26.39

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4. Conclusion

Coagulation is a simple process that induce precipitation of a dissolved matter. The present work is set out to investigate the feasibility of employing common salts for the separation of humic acid and alginate from synthetic pond water via the coagulation process. Investigation was allocated on identifying the effects of the salt valency and concentration on the coagulation process. Ascribing to the higher cationic charge per ion that can bind to more carboxylic groups under the same concentration, $AlCl_3$ was found to perform best in both humic acid and alginate removal as compared to both $CaCl_2$ and $NaCl$. In particular, a mild amount of $AlCl_3$ (0.005 M) is sufficient to induce > 80% of humic acid removal; while both $CaCl_2$ and $NaCl$ at 100 times higher concentration resulted in ~ 77 % and only 12.5 % humic acid removal, respectively. Such a coagulation efficiency follows the trend of the salt valency, whereby the efficiency increased by $Na^+ < Ca^{2+} < Al^{3+}$. Nevertheless, separation of the formed complexes via natural sedimentation may take hours to days to complete. Alginate removal efficiency, on the other hand, was found to exponentially increase with the salt concentration. Such observation further confirms the prominent role of salt valency in promoting coagulation and thus separation of DOMs.

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