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Coagulation of turbid waters using extraction of long bean

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ABSTRACT Coagulation is an important process in water treatment. The common chemical coagulant used in the water treatment is alum (aluminium sulphate). However, since the publicity of *Moringa Oleifera* seed as natural coagulant, researchers have tried to exploit the possible usage of natural coagulants as well as developing new natural coagulants from other plants. The potential of a locally available vegetable, long bean, to act as natural coagulant was studied using jar test. Synthetic turbid water used was prepared by adding kaolin to distilled water. It was discovered that long bean extract alone could not remove the turbidity. However, the coagulation activity was remarkable only when bivalence cation such as Ca^{2+} and Mn^{2+} were added. In this study, the active component of long bean was extracted using sodium chloride solution. The long bean extract achieved an average turbidity removal efficiency of 80 %.

ABSTRAK Koagulasi merupakan satu proses yang penting rawatan air. Bahan koagulasi kimia yang biasa digunakan dalam rawatan air adalah alum (alumina sulfat). Walau bagaimanapun, semenjak pengenalan benih *Moringa Oleifera* sebagai bahan koagulasi yang semulajadi, para penyelidik telah mengeksploitasikan pelbagai bahan koagulasi secara semulajadi dan juga memperkembangkan dalam penyelidikan dalam menghasilkan bahan koagulasi dari tumbuhan. Potensi menggunakan sayuran seperti kacang panjang untuk dijadikan bahan koagulasi telah dikaji dengan menggunakan ujian bikar. Air keruh secara sintetik telah disediakan dengan mencampurkan kaolin ke dalam air suling. Adalah didapati bahawa ekstrak sayur kacang panjang tidak dapat menjernihkan air keruh dengan sendirinya tetapi proses koagulasi hanya terjadi apabila kation bivalen seperti Ca^{2+} dan Mn^{2+} dimasukkan. Dalam kajian ini juga, komponen aktif daripada sayur kajang panjang telah diekstrakkan menggunakan larutan natrium klorida dan mencapai purata kecekapan penyingkiran kekeruhan sebanyak 80%.

(Coagulation, turbidity, NaCl extraction, jar test, long bean)

INTRODUCTION

The tap water that we used everyday is treated using coagulation, flocculation, sedimentation, filtration and disinfection processes before it reaches our water tap. Since the quality of tap water affects our health either direct or indirectly, the water treatment process becomes a very worthy subject for research, and coagulation is one of it. The main concern in the study of coagulation process is the coagulants. Alum (aluminium sulphate) is by far the most widely used coagulant in water and wastewater treatment. However, alum in water treatment can cause Alzheimer's disease. Its residual in water also triggers similar health related problems [1]. The coagulation effect of *Moringa Oleifera* seeds receives a great deal of attention. Among others were on coagulation active agents, mechanism of coagulation [2,3] and improve method to extract coagulation active component [4,5,6].

Cowpea, often called long bean in eastern countries, is a potential natural coagulant. Long bean has a shape of smooth pale green pods. It is frequently used in oriental cooking. Long bean can grow up to 40cm. Some varieties such as yard-long beans can even grow longer. It is a cheap priced vegetable that grows in Malaysia and ready to harvest in just around 50-60 days.

The purpose of this study is hence to examine the quality of the turbid water treated by coagulation process using long bean to explore its potentiality and compare it with that of the alum treated water.

MATERIALS AND METHODS

Model Turbid Water

For the purpose of this study, a synthetic turbid water was prepared by adding kaolin of laboratory grade into distilled water. Coagulation study was conducted based on this turbid water. Two grams of kaolin were added into a beaker containing 800ml distilled water. The suspension was stirred at 100rpm for 30 minutes using jar test apparatus for uniform dispersion of the particles. The suspension was then allowed to stand for at least 20 hours to allow for complete hydration of the kaolin. This was used as the stock solution for the preparation of water samples for the coagulation tests. From the stock solution, turbidity of 100 NTU was prepared by serial dilution of the stock solution. Turbidity was measured with a Hach turbidimeter Model 2100N. Four types of bivalence cationic salts i.e. $FeSO_4.7H_20$, $MnSO_4.H_20$, $CaCl_2.2H_2O$ and $Ca(OH)_2$ were also added into the diluted turbid water accordingly.

Preparation Of Long Bean suspension

Long bean used for this study was procured from local market. First, it was sun-dried for two weeks and heated for half an hour in an oven at 55°C before ground into powder using ordinary food blender. Active coagulation component of long bean was extracted using 1 mol/L sodium chloride (NaCl) solution. One gram ground *long* bean and 5.85g NaCl salt were added into 100ml distilled water and stirred at 100rpm for 30 minutes using jar test apparatus to extract the active ingredient. Then the residual was filtered using a Whatman filter paper. The filtered green coloured stock solution was used as coagulant. The stock solution was prepared fresh for use and when needed since deterioration sets after extended period of storage.

Preparation Of Alum

Alum $[Al_2(SO_4)_3.18H_2O]$ was used to compare the performance of the long bean as a potential coagulant. The alum solution used for the comparison test was prepared by adding 10 gram of alum into 1 litre distilled water.

Coagulation Test

Coagulation tests were conducted using jar test apparatus of Phipps & Bird using 400ml capacity jars. First, a rapid mix at 100rpm for two minutes at which during this time, the required coagulant dosage was quickly added into all beakers using pipette. Then followed by a slow mix of 30 minutes at 40rpm. After that, followed by 30 minutes of sedimentation. Comparative coagulation tests were run under the same conditions as described above but using alum solution instead of long bean extraction.

RESULTS AND DISCUSSION

Moringa Oleifera seed can dissolve in water as well as in NaCl solution contained 1 mol/L NaCl. The NaCl extracted *Moringa Oleifera* coagulant showed a remarkable coagulation activity when the turbid water contained strong bivalence cation such as Mg^{2+}, Ca^{2+}, or Ba^{2+}. These bivalence cations might electrically absorb to the negatively charged *Moringa Oleifera* active component to form insoluble net-like structure to capture the suspended kaolin particle. On the other hand, the univalent cation cannot form nets because one valence cannot connect to two active components together. A mechanism called "enmeshment" mechanism has therefore been suggested [2,3].

Earlier study on long bean indicated that it did not dissolved completely in water and hence did not contain water soluble coagulation active component. When 1 mol/L NaCl extracted long bean suspension was used, it showed coagulating characteristics when the turbid water contains sufficient dosage of $CaCl_2$ salt. This can be seen in Figure 1.

The calcium chloride used in the study was calcium dihydrate $[CaCl_2.2H_2O]$. Figure 1 shows that the optimum dosage of $CaCl_2.2H_2O$ was found to be at 75mg/L. A minimum dosage around 25~50 mg/L of $CaCl_2.2H_2O$ was needed for coagulation. This is equivalent to 0.23~0.45 mmol/L $CaCl_2.2H_2O$. This finding was comparable with results obtained by Okuda that at least 0.2 mmol/L Ca^{2+} was necessary for coagulation using salt extracted *Moringa Oleifera* coagulant [3].

Bivalence cation, such as Ca^{2+} by itself can react as coagulant agent at a sufficient dosage because it can destabilize negatively charged colloid. However, the possibility of that, flocs formed due to $CaCl_2$ instead of long bean was not true. Jar test was conducted using.

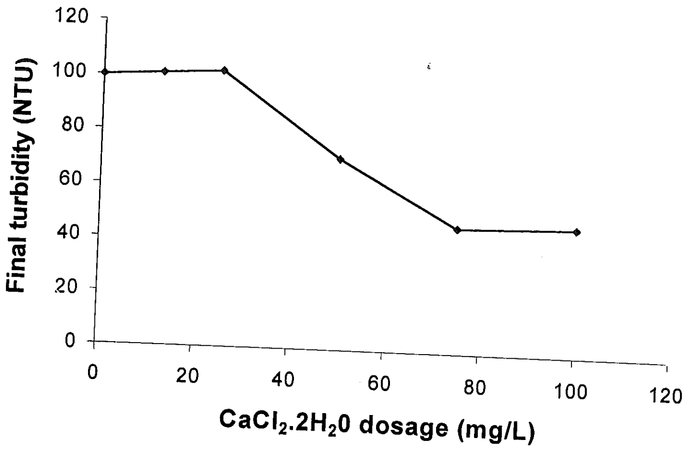

Figure 1. Effect of $CaCl_2.2H_2O$ with 40 mg/L long bean suspensions on turbid water with initial turbidity of 100 NTU.

$CaCl_2.2H_2O$ as coagulant without long bean to justify this hypothesis. The results have shown that at least 125 mg/L $CaCl_2.2H_2O$ was needed to form the flocs

However, in this study using long bean extract, it showed that 75 mg/L $CaCl_2.2H_2O$ was enough for coagulation purposes. Thus, long bean extract has coagulation effect up to a certain degree. Long bean extract was then further studied by varying its dosage at 75mg/L of $CaCl_2.2H_2O$ to obtain its optimum coagulation condition as shown in Figure2

Unfortunately, the turbidity removal efficiency of long bean extract was far behind of that compared to alum. At optimum dosage, long bean extract achieved an average turbidity removal efficiency of 80% whereas alum achieved a higher percentage of 97.2%.

Observation has showed that the flocs formed faster as the long bean extract dosage was increased. However, the trend line of long bean extract suggested that the optimum long bean extract dosage was around 100 mg/L. There was no significance improvement with the increase

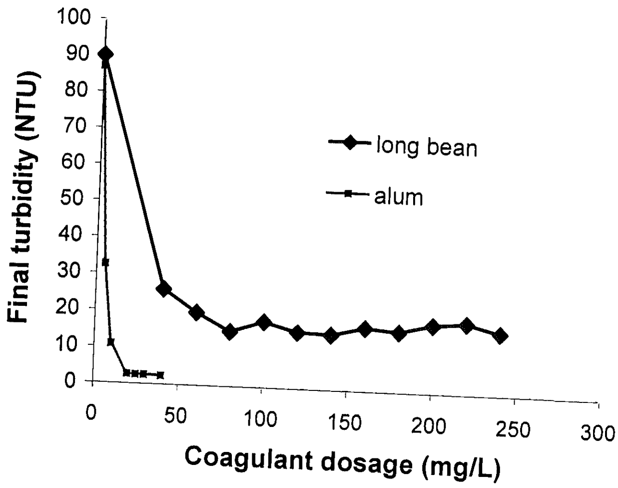

Figure 2. Coagulating activity of (a) long bean with 75mg/L calcium chloride [$CaCl_2.2H_2O$], and (b) alum with 10mg/L hydrated lime [$Ca(OH)_2$]

of long bean extract dosages after this. This was mainly because of the coagulation activity depended on both long bean extract dosages and $CaCl_2.2H_2O$ dosages. For long bean extract dosages of 100 mg/L or above, the 75 mg/L $CaCl_2.2H_2O$ was fully utilized to achieve final turbidity of around 16 NTU. Similarly, at $CaCl_2.2H_2O$ dosage of 80 mg/L or above, the 40 mg/L long bean extract was fully utilized to achieve final turbidity of 46.6 NTU (Figure 1). Hence, the turbidity removal efficiency using long bean extract as shown in Figure 2 will be improved by increasing the calcium chloride dosages. On the other hand, the turbidity removal efficiency will be improved as well by increasing the long bean extract dosages (as shown in Figure 1).

It must be noted that the flocs formation using long bean extract do not settled completely within 30 minutes. The complete sedimentation process took approximately one and half hours. It was not due to the flocs size because the flocs sizes were comparable to those at optimum alum dosage. It may be possible that the flocs using long bean extract is lighter in weight as compared those using alum.

The study of long bean extract was repeated using hydrated lime [$Ca(OH)_2$] to replace $CaCl_2$. Interesting result was obtained as can be shown in Figure 3. Although lime is not a true coagulant, it is known as coagulant aid and has certain turbidity removal ability. However, in spite of coagulation effect of lime, it showed a similar turbidity removal trend line when compared with $CaCl_2$ at the same molar dosage. Its difference only became significant when $Ca(OH)_2$ dosage was above 0.5 mmol/L. This suggested that long bean extract depended on bivalence cation Ca^{2+} to form the flocs but not anion Cl^- or OH^-. It was very similar to the criteria for their "enmeshment" coagulation mechanism for *Moringa Oleifera* seed coagulation [3]. Thus, it suggested that long bean extract may have the same "enmeshment" mechanism.

Besides Ca^{2+}, Ba^{2+} and Mg^{2+}also showed a remarkable coagulating activity. For this study, attention was mainly paid to bivalence cations that contained in raw water. If there are suitable bivalence cations existing in raw water, this means that long bean extract can be used in raw water treatment directly, without necessity to add extra bivalence cations into the raw water. The bivalence cations that matched this purpose were Ca^{2+}, Mg^{2+}, Fe^{2+} and Mn^{2+}. However, ferrous and manganese are two major parameters need to be removed from raw water for the purpose of water treatment. Their presence in raw water is often

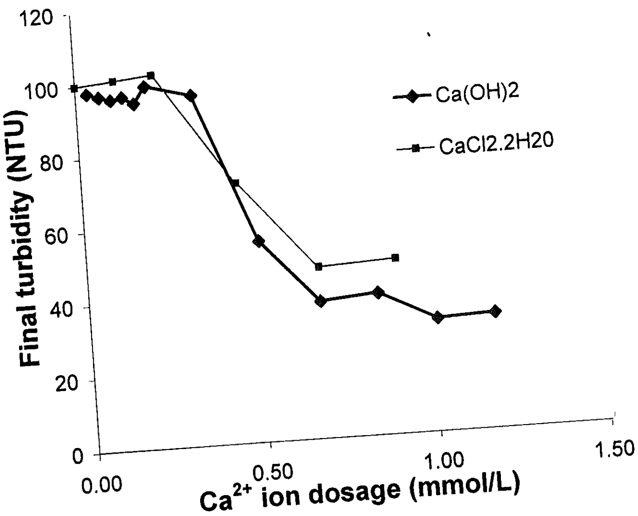

Figure 3. Comparison of the turbidity removal by 40 mg/L long bean coagulant, with Ca^{2+} ion from two different salts: (a) hydrated lime [$Ca(OH)_2$] and (b) calcium chloride [$CaCl_2.2H_2O$].

significant. For Ca^{2+} and Mg^{2+}, WHO Water Quality Standard stated that the maximum allowable concentration of calcium ion is 200mg/L and magnesium ion is 150mg/L [7]. According to Ndabigengesere and Narasiah, Sherbrooke tap water contained 48.0mg/L Ca^{2+} and 21.0mg/L Mg^{2+} [1]. This concentration may not true for Malaysia scenario but it is true that raw water contained Ca^{2+} and Mg^{2+} [8]. Even if the concentration of these ions is low in Malaysian raw water, the total concentration of these four ions might be still sufficient for coagulation using long bean extract. Since Okuda already justified that Ca^{2+} and Mg^{2+} can caused remarkable coagulation activity [3], the study will also examined on other bivalence cations such as Fe^{2+} and Mn^{2+}. Ferrous sulphate [$FeSO_4.7H_2O$] and manganese (II) sulphate [$MnSO_4.H_2O$] were chosen in this study. This was because these two salts are easily dissolved in water. Study showed that long bean extract formed flocs with Mn^{2+} but not Fe^{2+} as seen in Figure 4.

Overall Figure 4 showed that manganese (II) sulphate [$MnSO_4.H_2O$] has surprisingly coagulation effect when used with long bean extract. On the other hand, ferrous sulphate [$FeSO_4.7H_2O$], a well-known chemical coagulant other than alum, showed low coagulation effect. Small flocs were formed at the dosage of 0.67mmol/L $FeSO_4.7H_2O$. Ferrous salt performed the charge neutralization coagulation mechanism. This mechanism needs alkalinity in the water. So it was possible that the coagulation activity was low because there was insufficient alkalinity. At this stage, it was deduced that ferrous salt will not help coagulation using long bean extract, whereas manganese (II) ion and calcium ion tested were being able to formed flocs when long bean extract was used. These two cations may have concentration lower than expected in Malaysian raw water, or it may not be in free cation condition (may be in complex structure) that can react with long bean extract. Figure 4 also showed that the coagulation using long bean

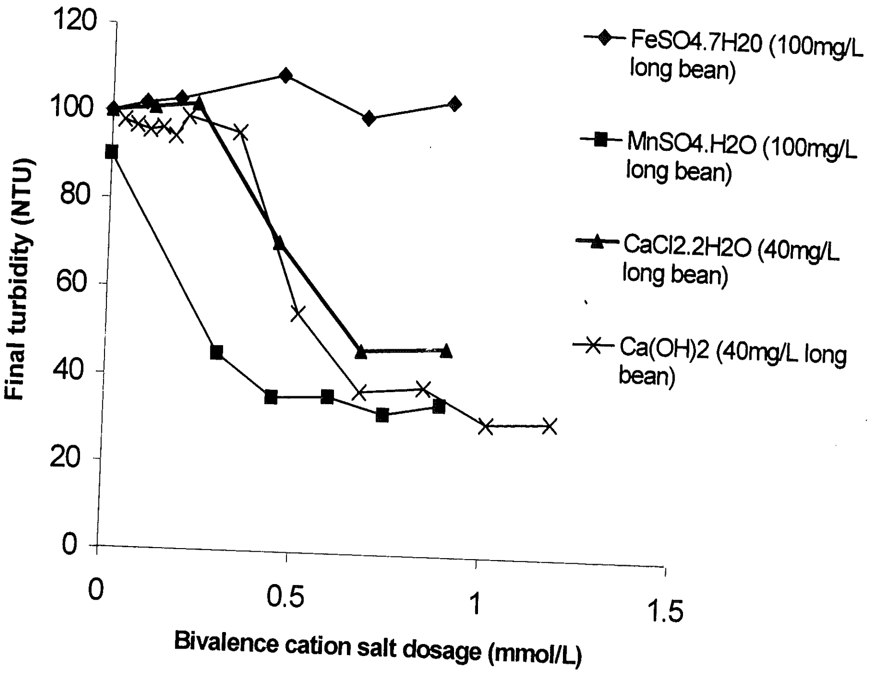

Figure 4. The effect of different bivalence cation salts on turbidity removal using long bean: (a) ferrous sulphate [$FeSO_4.7H_2O$] with 100 mg/L long bean extract, (b) manganese (II) sulphate [$MnSO_4.H_2O$] with 100 mg/L long bean extract, (c) calcium chloride [$CaCl_2.2H_2O$] with 40 mg/L long bean extract, and (d) hydrated lime [$Ca(OH)_2$] with 40 mg/L long bean extract

extract does not depend on pH. It is clear in this study that flocs were formed when calcium chloride, manganese sulphate or hydrated lime was added. Turbid water was acidic when Cl^- or SO_4^{2-} is added, but it became alkaline when OH^- was added. Since flocs formed in both acidic and alkaline cases, it indicated that coagulation using long bean extract did not depend on pH. Also, final pH of treated water was in the range of 6.88~7.01. It suggested that coagulation using long bean extract do not significantly affect the pH value.

Effect of NaCl

The long bean active component was extracted using NaCl, and Na^+ is a univalent cation. Thus, NaCl would have certain coagulating effect. In fact, in the study of colloid science, the coagulation power of NaCl is been tested long ago. It showed that univalent cation such as NaCl has coagulation power 20~80 times weaker than bivalence cation salt such as $CaCl_2$. However, the coagulation effect of cations mixture was additive [9]. It means that if NaCl has coagulation power of 0.1 unit, and $CaCl_2$ has coagulation power of 1.0 unit, the mixture of NaCl and $CaCl_2$ will have total coagulation power of 1.1 unit. Hence the NaCl contained in *long bean* will enhance the charge neutralization coagulation effect of Ca^{2+}. However, the coagulating power of NaCl was not high. It would not enhance the coagulation power of $CaCl_2$ to a significance degree. Hence, if mixture of NaCl and $CaCl_2$ were to cause the charge neutralization mechanism in the study, it would not be dominant mechanism in the coagulation process. The dominant mechanism still was the reaction between long bean extract and $CaCl_2$.

Although NaCl did not help much in coagulation, it can extract the active coagulation agent in long bean. The NaCl increases the affinity of the distilled water, causing it possible to extract the ionic active coagulation component contained in long bean.

CONCLUSIONS

NaCl extracted long bean coagulant is proved to have coagulation effect when bivalence cation Ca^{2+} or Mn^{2+} is contained in turbid water. Since raw water contained these bivalence ions, it is an advantage to utilize these ions, other than to remove it. These ions will settle together with the flocs. Besides that, long bean extract coagulation does not depend on pH. Long bean extract also has advantage as non-toxic coagulant. Unlike chemical coagulant such as alum, long bean extract is an organic material.

The most important one is that its turbidity removal efficiency is lower than alum. The second disadvantage is that complete sedimentation of flocs using long bean extract takes more than 30 minutes. Third disadvantage is that it used NaCl salt to extract the active coagulation component.

Turbidity removal efficiency depends on both long bean extract dosage and total concentration of bivalence cations contained in raw water. The coagulation efficiency dropped when either one is insufficient. Raw water does not have a constant turbidity and bivalence cations concentration.

In short, One mol/L NaCl salt solution is used to extract active component of long bean in this study.

1. Long bean extract only removes turbidity when sufficient bivalence cations contained in turbid water such as Ca^{2+} and Mn^{2+} cations. The coagulation activity does not depend on anions such as Cl^-, OH^-, and SO_4^{2-}
2. Long bean extract coagulant is not pH dependent.
3. At the tested dosage range, optimal dosage found for long bean extract is 100 mg/L, with addition of 75 mg/L calcium chloride [$CaCl_2.2H_20$]. It removes 80% of turbidity and hence long bean extract turbidity removal efficiency is lower as compared to alum.

At this moment, long bean extract still has many weaknesses and further research still needed in the future.

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