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Application of Chitosan as a Coagulant- A Preliminary Review

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ABSTRACT

One of the best water treatment methods is to use coagulants. Coagulation with metal salts e.g. aluminium or iron salt are commercially used in the treatment of turbid sea water today. However, this type of coagulant might leave toxic residues in the treated water since it is made up from metal or inorganic materials. Thus, it might affect the health if the water is used for drinking and such else. Several studies on synthetic and organic polymers have been carried out in order to identify which polymer can work as a coagulant to replace the use of metal salts. Chitosan is a natural polymer that can be used as a coagulant in the treatment of turbid sea water. Chitosan has been used as a water purification system for detoxifying water. This might be due to its ability to form bond or coagulate with other particles. It is able to absorb grease, oil and other potential toxins and also have relatively lowest toxicity or risk for human since it is organic. The contamination of water can affect both physical and chemical properties of water. Thus it is essential for the sea water to be treated to remove the turbidity so that the water can be used safely. There are many methods that can be used in the water treatment but may produce different properties of treated water. Some treated water may have poor microbiological quality which is unsafe to be used or consumed by human.

1. Introduction

Turbidity not just causes water to loose its transparency but also could be harmful to be used by human and even the sea ecosystem itself. This problem might occur when undesirable or toxic substances have contact or dissolve in a body of water. These foreign elements can be organic and inorganic particles in the body of water [1]. Common organic particles present in the water are known as algae, bacteria, viruses and protozoa while the inorganic particles are clay and silt. In the other word, the turbidity of water is actually caused by the presence of organic and inorganic particles in the water. Clay and silt are the familiar inorganic particles presence in the turbid sea water meanwhile the organic particles may be algae, bacteria, viruses, protozoa and other natural organic matter.

Coagulation is an effective way to remove turbidity of water and works great in the treatment of water. Synthetic chemical coagulant are the most commonly used in the coagulation process for

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water treatment. Not just may has the possibility to change the pH of the treated water, this synthetic chemical coagulant is also expensive and challenging to be accessed. However the coagulant agent that is used during water treatment may produce residue or large volume of sludge at the end of water treatment. Depending on the type of coagulant used, the deposition may be harmful especially for health. The harmful residue is usually from metal salts or any unnatural polymer coagulant. There is possibility that the coagulant used for the treatment can affect or alter the pH of the water.

Thus, organic or natural coagulant may be the better coagulant to be used in the treatment of turbid sea water. Chitosan is natural and bio degradable polymer derived from the outer shell of shrimps can act as coagulant very well. Chitosan cause the fine sediment particles to bind together so that it can be remove easily from the water. Several factors like pH or temperature of water might affect the coagulation process during the water treatment. Thus, the pH value of water might affect the coagulation process performed by chitosan if chitosan was used to treat turbid sea water.

2. Chitosan

Chitosan is a polysaccharide derived from chitin which is the skeletal substance of the shells of crustaceans such as crab, lobsters and shrimp. It is described as a high-nitrogen containing linear amino-polysaccharide polymer [2]. Chitosan contains no toxic, is biodegradable and widely available in nature [3]. Not just that, chitosan is also an indigestible element since it is a fibre. Chitosan is soluble when diluted in acidic solution but do not dissolve in water or even organic solvent [4]. Chitosan is known as a renewable polymer that is naturally available in large quantities and also carry unique characteristics in which it is a non-toxic polymer and bio-compatibility product [2].

In food industry, chitosan is used to produce weight loss supplements. The proper intake and dosage of chitosan can aid in weight loss because it is rich in dietary fibre which is the essential nutrient for weight loss. Not only that, it is also used in shrimp preservation as it has antimicrobial properties that can prevent food spoilage [2]. Chitosan also is used in the treatment of water as a coagulant to remove the turbidity of water [3]. In biomedical research, chitosan membrane can be used to make artificial kidney membrane due to its permeability and high tensile strength [2].

Coagulant can be described as a positive charge compound that works to neutralize the negative electrical charge on particles [5]. Due to the reaction, the particle will coagulate or bind together and form a more significant, heavy particle. Thus, coagulation is often used to describe the overall process of aggregation. Basically, coagulation is always regard as the process associated with destabilisation which mean process of overcoming the factors which contribute to the stability of suspension [6].

In previous study, [6] point out that coagulation is a necessary water treatment process in industrial wastewater treatment. Basically coagulation destabilizes the impurities and combine the small particles into a large particle which make it easier for filtration process. In other words, coagulation can be done by adding ions into dissolved particles whereby the ions must carry charge that oppose to the particle charge [7]. Thus, it will produce attractive force between the ions and the particle which cause them to bind together.

Coagulant is commonly used in water treatment to coagulate the dissolved unwanted particle in the water. The coagulation process was proven to be able to remove turbidity and impurities from water [8]. Not only that, coagulant was also used to remove dyes from aqueous solution [9].

Coagulant can be divided into two general groups namely metal coagulants and polymers. The most commonly used coagulant is known as metal coagulant which then was divided into two broad categories which are aluminium and iron-based coagulants [9]. The aluminium coagulants include aluminium sulphate, aluminium chloride, sodium aluminate, aluminium chlorohydrate and polyaluminum silicate chloride. The iron coagulant include ferric sulphate, ferrous sulphate, ferric chloride and ferric salts with organic polymer. Other chemical used as coagulants include hydrate lime and magnesium carbonate. The popularity of aluminium and iron coagulants arises not only from their effectiveness as coagulants, but also from their ready availability and relatively lower cost.

Meanwhile, polymers refer to a large variety of natural or synthetic, macromolecular compounds, which have the ability to coagulate or enhance flocculation of the constituent of a body of water. Polymer molecule can be described as a series of repeating chemical units held together by covalent bonds. Polymer that containing certain functional groups along the polymer backbone which may be ionize is known as polyelectrolyte. There are several types of polyelectrolytes currently used for water clarification which are activated silica and certain natural polyelectrolyte e.g. seeds from Moringa Oleifera tree, starches, guar gums, tannins and chitosan. In general, the advantages of natural polyelectrolytes are that they are virtually toxic free, biodegradable in environment and often available since it come from natural source [4].

Coagulation can be achieved in many ways, the mechanism depending on the type of coagulant, its concentration, the nature of colloids and the prevailing chemistry. The primary task was to overcome the effects of the energy barrier. There exist two principal routes for achieving this task, the first, coagulation contribute to destabilization which was promoted by reducing spatial extent of the double layer compression or by secondly reducing surface potential as a result of changes in the surface chemistry [10].

3. Chitosan as a Coagulant

Chitosan is known as a polymer that can be obtained from alkaline deacetylation of chitin. Chitosan can be used as a coagulant in the treatment of turbid sea water to replace the metal salts and other synthetic polymer coagulant. Chitosan is the better substitute since it is a natural coagulant and will not leave any harmful residue in the treated water like the other coagulant. Researchers from previous studies [3,4] point out some concern about the toxic residuals left in treated water when use aluminium salt as the coagulant. The residual aluminium can lead to Alzheimer's disease.

From previous study, [3] states that when chitosan alone was able to drop 85 % of water turbidity even when low concentration was used. As chitosan was added to water, the particle will start to bind together and settle down at the bottom of the flask. Chitosan also can be used in the treatment of drinking water since it has the lowest risks of organic release. Basically, chitosan is a favourable charge polymer that is produced from glucosamine residue [5]. Meanwhile, the dissolved organic and inorganic particles are commonly anion particles [7]. The difference charge between chitosan and dispended particles will produce attractive forces. Thus the particles and chitosan will bind or stick together and form a big particle or clump.

From previous study done by [11], it states that eventhough chitosan could be used as a coagulant in the treatment of drinking water since it can lead to the increase of total organic carbon (TOC) in solution that could cause the mechanism in a solution to coagulate. However, the effectiveness of chitosan as a coagulant is also relied on the initial turbidity and amount of chitosan used [12]. Other than water treatment, chitosan also can act as coagulant in leachate treatment in which it is able to eliminate the colour and turbidity from landfill leachate [13].

4. Turbid Sea Water

Turbid is known as the properties of a liquid which is synonym to being cloudy, murky, muddy and unclear while turbidity is the measure of liquid clarity. The turbidity of a liquid can affect the transmittance or penetration of light through the liquid medium. Thus the higher the turbidity, the higher the intensity of light scattered. Turbid sea water is a signal of the presence of dispersed and suspended solid such as organic matter, clay, algae, silt, microorganism and many others [3]. Turbidity of sea water can be measured in nephelometric turbidity units (NTU) or Jackson turbidity units (JTU) according to the measurement method used [14]. Beam transmissometer and nepherometer are several optical methods that can be used to measure turbidity of sea water [15].

The measurement of salt dissolved in water which is known as salinity, is also one of the significant factor that can affect the turbidity of water salt have the ability to resolve sediment which means it can reduce turbidity [16]. Thus, some of human activity like logging have the probability to affect the turbidity of sea water since it can disrupt the land salinity that connect to salinity of the sea. Turbid sea water usually contains humic acid which is a type of organic compound that can affect the coagulation process during water treatment [12,17].

The turbidity of water may affect the efficiency of chlorination [18] which is the process of adding chlorine to the treated sea water in order to eliminate the bacteria or microbes that are present in the water. The turbidity is a significant problem that can affect the quality matter of water [3]. Turbid sea water can give hazardous effect on marine life [15].

Treatment of turbid sea water can be described as a process of making the water become more acceptable for any specific uses such as to be used as drinking water. The treatment for water is essential since it will help to remove the turbidity and even the microorganisms in the water [4]. There are several methods that can be used in the treatment of turbid sea water. Different treatments might give different results and might even have specific purpose. One of the standard water treatment used is reverse osmosis (RO) system. RO water treatment system is actually the process that works to remove salt, mineral and dispended particles from the sea water through the semi-permeable membrane. RO water treatment system often is used in the production of drinking water [19,20]. Membrane of RO system has the ability to remove mostly all microorganism. Synthetic organic polymer like cellulose acetate is the material that is use to made up the RO membrane [20]. However, RO water treatment system is always considered as significantly costly.

Another method that can be used in the treatment of turbid sea water is sedimentation. Sedimentation can be described as the process to remove contaminants from turbid sea water under the gravity influence [21]. In this process, the velocity of water is slowed down so that the particles in the water will sediment in the bottom of the container used in the process and gravity will naturally settle it. This method is known as cheap technology that works well to remove settable solid and turbidity and maybe also the microorganism in the water.

Another easy and cheaper method that can be used in the treatment of turbid sea water is coagulation. Coagulation is known as the process of destabilizing the colloidal particle in water using coagulant so that the attraction forces between contaminant particles and coagulant increases [7]. Coagulation process can be done using coagulants such as metal salts e.g. aluminium salt and also synthetic polymers e.g. poly diallyl-dimethyl ammonium chloride. However, these types of coagulants has been claimed to leave harmful residues in the treated water which can lead to Alzheimer's disease [10]. Thus, the use of natural coagulants are invents for a better quality turbid sea water treatment. Chitosan and sesame seed are some of the natural coagulants that can aid the treatment of turbid water [7,22].

5. Characterization of Chitosan

5.1 Ultraviolet-visible (UV-Vis) Spectroscopy

All liquid samples underwent UV-Vis Spectroscopy test in Figure 1 to analyze the compounds in the Ultraviolet and Visible regions of electromagnetic spectrum. Ultraviolet-visible spectroscopy (UV-

Vis) or Ultraviolet-visible spectrometer is the reflectance or absorption spectroscopy in the ultraviolet visible region. UV-Vis can be used to measure spectral bandwidth, wavelength error, stray light and measurement uncertainty sources.

UV-Vis was used to analyze the intensity of light absorbed by the chitosan solution of different solvents and analyze the nanoparticles in the treated water. The liquid sample was almost fully-filled in the quartz cuvette. The transparent sides of the cuvette was cleanly wiped using tissue to ensure there was no dust on the surface of the cuvette that might affect the result. The cuvette was then placed between the light source and the photodetector. The sample was run at the wavelength range between 200 nm to 1000 nm. The intensity of light beam was measured before and after passing through the sample. Through this process, the intensity of light absorbed and scattered by the sample was measure.

Fig. 1. UV-1800 SHIMADZU UV Spectrophotometer

5.2 Field Emission Scanning Electron Microscope (FESEM)

FESEM in Figure 2 is a microscope that works with electrons (particles with a negative charge) instead of light. These electrons are liberated by a field emission source. The object is scanned by electrons according to a zig-zag pattern. A FESEM is used to visualize very small topographic details on the surface or entire or fractioned objects. For this test, samples of chitosan diluted in different solvents were chosen based on the UV-Vis results analysis. The solution that gave the highest absorbance from each solvent were chosen. This is to observe the morphology structure of chitosan in different solvents. Other three samples included the chitosan coagulation and flocculation that had been separated from the treated seawater. This study was performed to observe the structure of chitosan after being used in the treatment of turbid seawater and the coagulation structure that had been formed by chitosan with the particles in the seawater [23].

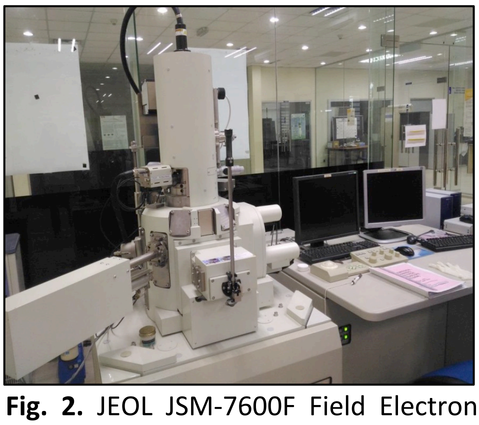

Fig. 2. JEOL JSM-7600F Field Electron Scanning Electron Microscopy (FESEM)

To prepare the samples for the test, the sample was dropped into glass slide and set to be dried. The glass slide was placed in the petri dish and covered with paper with some holes on it. It was then left in room temperature approximately for 1 day to let it completely dry. These dried samples were coated with gold (Au) for about 10nm thickness which takes about 15 minutes to be fully coated. The coating were done in order to enhance the conductivity of the samples. The results of each samples weas observed and discussed.

5.3 Scanning Electron Microscope-Electron Dispersion X-Ray (SEM-EDX)

The characterization process was performed in order to observe the morphology and to perform elemental analysis in certain samples. For this study, certain samples were chosen to be analyzed which the samples would be the sample of chitosan diluted in the most suitable solvent, sample of chitosan coagulation that is able to remove the greatest amount of turbidity, sample of turbid sea water and sample of treated sea water of the best pH value [24]. Scanning electron microscope is known as an electron microscope that works to produces topography images of a sample by directing beam of electrons toward the sample. Atoms of element in the sample interact with beam of electrons to produce various signals that contain image's information.

Samples that need to be characterized using SEM-EDX in Figure 3 were prepared. All the samples were dropped onto each clean glass slide that has been cleaned using acetone. The samples were placed in petri dish and let to dry at room temperature for one and half day until completely dry. The samples were then coated with gold for conventional imaging in the SEM. Coating help the samples to become more conductive and each samples must be electrically grounded using copper tape to prevent the accumulation of electrostatic charge at the surface of the image. The sample then were scanned and the morphology image was formed and the elemental analysis were conducted through EDX to obtain the elemental information of the samples.

Fig. 3. Hitachi Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray (EDX)

6. Example of Methodology for Chitosan as a Coagulant

6.1 Preparation of Sea Water Sample

Synthetic turbid sea water sample was prepared using water, salt, mud and soil. All the three was combined with ratio of 4:1:1. The salt was diluted into the water first before being added with soil and mud to create the turbidity to the water solution. The water sample then was distributed as 4 sets of water samples. For each set, the turbid water was divided into 3 beaker that was labelled as A, B and C respectively. The water then was divided equally into each beaker for all 4 sets of samples. The pH value of water in each beaker was adjusted using sodium hydroxide (NaOH) and hydrochloric acid, (HCL) of 0.1 $molL^{-1}$. So, pH of water sample in A, B and C was adjusted to 7, 6 and 8 respectively. This step was also used for the other 3 sets of turbid sea water samples. This step was carried out in order to study how the pH level of the water sample affects the chitosan to work as a coagulant. Two sets of water samples were then radiated with gamma ray in order to see whether radiation could affect coagulation or not.

6.2 Preparation of Coagulant

A beaker was filled with 100 ml of distilled water and about 30 gm of chitosan powder was added to it. The chitosan solution was stirred continuously for about 2 minutes to ensure the chitosan powder was dissolved. Another beaker was also filled with distilled water and 60 gm of chitosan powder dissolved in it.

6.3 Coagulation Test

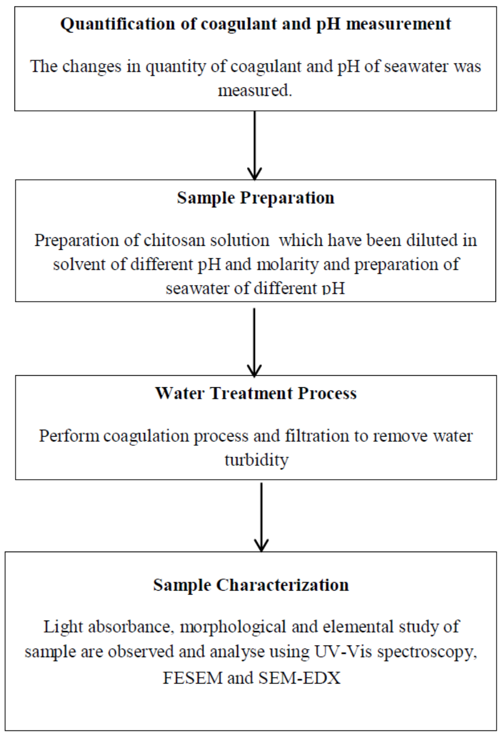

Fig. 4. Research methodology

Starting with sample water of set 1, each turbid sea water sample in beaker A, B and C was added with 100ml of 30gm chitosan solution. The mixture then was stirred vigorously for about 1 minute and slowly for 3 minutes. The same process goes to sample water of set 2 but the chitosan solution that was added to it was the solution that was added with 60gm chitosan powder. The different amount of chitosan used in solution could help to investigate whether the amount of coagulant can affect the efficiency of coagulant to remove turbidity. The same process was repeated on the two other water samples which was radiated turbid water. Then, third and fourth samples was further added with solution of 30 gm and 60 gm chitosan respectively. The mixtures were set aside for 30 minutes after being stirred. After ending the whole coagulation process, the mixtures was then filtered. The filtered water was collected into other clean beaker and was analyzed. All the filtered water samples were characterized with UV-Vis, FESEM and SEM-EDX.

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