Aluminum Rubbish as a Coagulant for Oily Wastewater Treatment

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ABSTRACT

In this study an experimental work was done to study the possibility of using aluminum rubbish material as a coagulant to remove the colloidal particles from oily wastewater by dissolving this rubbish in sodium hydroxide solution. The experiments were carried out on simulated oily wastewater that was prepared at different oil concentrations and hardness levels (50, 250, 500, and 1000) ppm oil for (2000, 2500, 3000, and 3500) ppm $CaCo_3$ respectively. The initial turbidity values were (203, 290, 770, and 1306) NTU, while the minimum values of turbidity that have been gained from the experiments in NTU units were (1.67, 1.95, 2.10, and 4.01) at best sodium aluminate dosages in milliliters (12, 20, 24, and 28) for oily wastewater of concentrations (50, 250, 500, and 1000) ppm of oil. Zeta potential and particle size measurements have been carried out to the samples of oily wastewater before treatment and during the coagulation- flocculation process at 2, and 22 minutes after the addition of the optimum coagulant doses in order to determine and investigate the operation conditions. The results were presented graphically in two dimensional co-ordinates showing particle size distribution and growth that have (greater intensity, largest volume, and greater surface area) as a function with time.

Key words: wastewater, emulsion, coagulation, zeta potential, particle size.

أستخدام نفايات الألمنيوم كمادة مخثرة لمعالجة المياه الملوثة بالزيوت

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الخلاصة

في هذه الدراسة تم إجراء عمل تجريبي لدراسة إمكانية استخدام مخلفات مادة الألومنيوم لإزالة الجسيمات الغروية من مياه الصرف الملوثة بالزيوت عن طريق إذابة هذه المخلفات في محلول هيدروكسيد الصوديوم. تم إجراء التجارب على مياه الصرف الملوثة بالزيوت الذي أعد في تراكيز مختلفة من الزيت ومستويات مختلفة من العسرة و هي (50، 250، 500، و 1000) جزء في المليون من الزيت ل(2000، 2500، 3000، و 3500) جزء في المليون من كربونات الكالسيوم $CaCO_3$ على التوالي. كانت قيم التعكر الأولية (203، 290، 770، و 1306) وحدة عكورة، بينما كانت أدنى قيم للعكورة التي تم الحصول عليها من التجارب في وحدات (1.67، 1.95، 2.10، و4.01) و لجرعات ألومينات الصوديوم المثلى (12، 20، 24، و 28) ملليلتر لمياه الصرف الملوثة بالزيوت بتراكيز (50، 250، 500، و 1000) جزء من المليون من الزيت على التوالي. تم قياس جهود زيتا المحتملة وحجم الجسيمات لعينات من مياه الصرف الملوثة بالزيوت قبل المعالجة وأثناء عملية التلبد- التخثر في زمن 2 و 22 دقيقة بعد إضافة جرعة المخثر المثلى من أجل تحديد و دراسة ظروف العملية. عرضت النتائج الثنائية الابعاد بيانيا والتي تبين توزيع حجم الجسيمات والنمو للجزيئات التي تمتلك (اعلى شدة، اعلى حجم ، واعلى مساحة سطحية) بوصفها متغيرة مع مرور الوقت.

الكلمات الرئيسية: مياه صناعية، مستحلب، تخثر، جهد زيتا، حجم الجسيمات.

1. INTRODUCTION

With industrial development, there is an increase in the amount of oil used, Oil polluted wastewater arises from diversity of sources like crude oil production, oil refinery, petrochemical industry, lubricant, metal processing, cooling agents, car washing, compressor condensates, and restaurants. Oily wastewater comprises toxic substances such as phenols, poly-aromatic hydrocarbons, petroleum hydrocarbons, which are inhibitory to plant and animal growth, equally, carcinogenic and mutagenic to human being. Likewise, oily wastewater comprises high oil content, chemical oxygen demand (COD) and color. Oil and grease is well-defined as a group of allied materials rather than a particular chemical composite extractable by certain solvents, like hexane. They are nonpolar and, as a result, are hydrophobic in nature, **Alade et al., 2011**. Oily wastewater pollution is mainly manifested in the following aspects:
(1) affecting drinking water and groundwater resources, endangering aquatic resources; (2) endangering human health; (3) atmospheric pollution; (4) affecting crop production; (5) destructing the natural landscape, **Yu et al., 2013**. Oil and grease in wastewater can exist in several forms: free, dispersed or emulsified. The differences are based primarily on size. In oil in water mixture, free oil is characterized with droplet sizes greater than 150 μm in size, dispersed oil has a size range of 20 to150 μm and emulsified oil has droplets typically less than 20 μm, **Cheryan and Rajagopalan, 1998**. Environmental limitations require that highest total oil and grease concentration in dispose waters to be 10–15 ppm for mineral and synthetic oils and 100–150 ppm for those of animal and vegetable origin, **The World Bank Group, 1999**.

Oily waters are commonly in the formula of oil-in-water (O/W) emulsions. Emulsions are heterogeneous systems in which the external phase (dispersion medium) is water, and the internal phase (dispersed phase) is oil. Therefore emulsion can be conveniently classified according to the distribution of oil and aqueous phases. Hence, a system which consists of oil droplets in an aqueous phase is called as oil-in-water or O/W emulsion and a system with water droplets dispersed in oil phase is termed as water-in-oil or W/O emulsion. The usage of emulsifiers, extreme heat, agitation and pumping in the milling process further assist the formation of these undesirable oil droplets, **Sethupathi, 2004**. Emulsifiers can be present as singular molecules in small amounts, or form poly-molecular aggregates which are called "micelles" **Fig.1**. The number of molecules per micelle can increase and concentrate at the interface. They may then become more water soluble or oil soluble and become soluble in one or the other phase. The function of the emulsifier is to migrate to the interface of the internal and external phase. It consists of a molecule with a hydrophilic portion and a hydrophobic portion. At the interface it forms a protective sheath (barrier) around the droplets of the dispersed phase (oil droplets). It does this in a manner that the hydrophobic end of the molecule migrates or partitions into the oil droplets and the hydrophilic end stays in the water. The stability that results from the addition of the emulsifier depends on its physical nature. When well dispersed it forms an interfacial film around the oil droplets, preventing oil droplets from approaching each other and coalescing. It accomplishes this by changing the interfacial tension of the internal and external phase. Emulsions form when the interfacial tensions between oil and water are reduced. When the interfacial tension value is reduced to zero, an emulsion spontaneously forms. This means that the surface area of the internal phase, (i.e. the oil droplets) has increased to its maximum. This means that very fine droplets have formed giving the emulsion a milky appearance and the oil particles are probably less than 1 micron in size, **Alther, 1997**. An important parameter of a surfactant is the hydrophilic-lipophilic balance (HLB), which correlates surfactant structures with their effectiveness as emulsifiers. The HLB value is given on an arbitrary scale of 0 to 18. An HLB = 0 corresponds to a completely hydrophobic molecule and

HLB = 18 would correspond to a molecule made up completely of hydrophilic components: the higher the HLB number the more hydrophilic is the surfactant. The type of emulsion formed depends on the type of emulsifier, o/w emulsions are produced with a hydrophilic surfactant (high HLB), and w/o emulsions are generated by a hydrophobic surfactant (low HLB). This rule states that, contrary to common sense, what makes an emulsion either o/w or w/o is not the relative percentages of oil or water, but the phase where the emulsifier is more soluble, **Coca et al., 2011**.

Currently the treatment of oily wastewater applies a primary treatment to separate the floatable oils from the water and emulsified oils. A secondary treatment phase is then required to break the oil–water emulsion and separate the remaining oil from the water. Several mechanical processes have been used to try to remove the oil, among which include filtration, and Flotation. The chemical processes have devised the addition of coagulating or flocculating agent that favors the formation of aggregates with drops of oil dispersed so that they can be removed mechanically **Rubi et al., 2009**. For the present work chemical destabilization (coagulation- flocculation processes) has been used, coagulation is an essential process in water and industrial wastewater treatment. It is one of the most important physicochemical processes. Coagulation has been defined as the addition of a positively charged ion of metal salt or catalytic polyelectrolyte that results in particle destabilization and charge neutralization . Coagulation targets the colloid particles of size 10^{-7} to 10^{-14} cm in diameter. Flocculation refers to the successful collision that occurs when destabilized particles are driven toward each other by the hydraulic shear force in the rapid mix and flocculation basin. It agglomerates of a few colloids then quickly bridge together to form micro flocs which is turned into visible floc masses. The process of coagulation separation comprises of four steps. The initial step is simple: the chemical is added to wastewater. This is followed by the second step, where the solution is mixed rapidly in order to make certain that the chemicals are evenly and homogeneously distributed throughout the wastewater. In the third step, the solution is mixed again, but this time in a slow fashion, to encourage the formation of insoluble solid precipitates. The final step is the removal of the coagulated particles by way of filtration or decantation. Coagulant chemicals come in two essential types' primary coagulants and coagulant aids. Primary coagulants neutralize the electrical charges of particles into the water which causes the particles to cluster together. Chemically, coagulants are either metallic salts (such as alum) or polymers. Polymers are human-made organic composites made up of a long chain of smaller molecules. Polymers can be either cationic (positively charged), anionic (negatively charged), or nonionic (neutrally charged). On the other hand, coagulant aid is an inorganic material, when used along with chief coagulant, increases or quickens the process of coagulation and flocculation by generating quick forming, thick and rapid-settling flocs, **Sahu and Chaudhari, 2013**.

1.1 Aluminum Rubbish as a Coagulant

The aluminum rubbish used in this study was dissolved in sodium hydroxide solution to produce 0.5 M from sodium aluminate according to the following equation:

$$2AL \quad + \quad 6NaOH \quad \longrightarrow \quad 2Na_3ALO_3 \quad + \quad 3H_2 \tag{1}$$
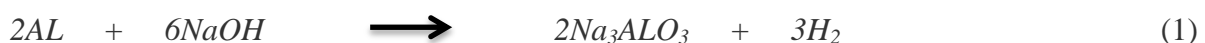
Sodium aluminate is a significant marketable inorganic chemical. It has been used as an active source of aluminum hydroxide for many applications. The commercial importance of sodium aluminate is due to the versatility of its technological applications. In water treatment methods it is used as an assistant to water softening systems, as a coagulant to eliminate

suspended solids and several metals (Cr, Ba, Cu), and for removing dissolved silica. In building technology, sodium aluminate is working to increase speed of the solidification of concrete, generally when working during cold episodes. It is also used in the paper industry, refractory brick production and alumina production, etc. Furthermore, it is used as a transitional in the production of zeolites for detergents, adsorbents molecular sieves, and catalysts. Sodium aluminate aids in the removal process, reacting with the precipitated hardness to form particles that can be removed more effectively, **Makki et al., 2010**. Sodium aluminate, which is alkaline, releases caustic soda and aluminum hydroxide as it dissolves in water.

$$Na_3ALO_3 \quad + \quad 3H_2O \quad \longrightarrow \quad AL(OH)_3 \quad + \quad 3NaOH \tag{2}$$

Aluminum hydroxide will produce a gelatinous precipitate of oil and impurities that presented in water. Also the Hydroxide ion will react with the Calcium bicarbonate and precipitate it as Carbonate ion which will react with the Calcium ion and precipitate it as salt in water. Likewise the Hydroxide ion will react with the Magnisium ion and precipitate it as Magnisium hydroxide, **Makki and Omran, 1995**.

$$2OH \quad + \quad Ca(HCO_3) \quad \longrightarrow \quad CaCO_3 \quad + \quad 2H_2O \tag{3}$$

$$2OH \quad + \quad MgSO_4 \quad \longrightarrow \quad Mg(OH)_2 \quad + \quad SO_4 \tag{4}$$

$$CO \quad + \quad CaSO_4 \quad \longrightarrow \quad CaCO_3 \quad + \quad SO_4 \tag{5}$$

1.2 Zeta Potential

Nearly all particulate or macroscopic materials in an interaction with a liquid obtain an electronic charge on their surfaces. Zeta potential is a significant and convenient pointer of this charge which can be used to expect and regulate the stability of colloidal suspensions or emulsions, **Ferhan, 2014**. Negatively charged particulates accumulate positive counter ions on and near the particle's surface to satisfy electro neutrality. A layer of cations will bind tightly to the surface of a negatively charged particle to form a fixed adsorption layer. This adsorbed layer of cations, bound to the particle surface by electrostatic and adsorption forces, is about 5 ˚A thick and is known as the Helmholtz layer (also known as the Stern layer after Stern, Beyond the Helmholtz layer, a net negative charge and electric field is present that attracts an excess of cations (over the bulk solution concentration) and repels anions, neither of which are in a fixed position. These cations and anions move about under the influence of diffusion (caused by collisions with solvent molecules), and the excess concentration of cations extends out into solution until all the surface charge and electric potential is eliminated and electro neutrality is satisfied, **Crittenden et al., 2012**, this potential is greatest at the surface and decreases to zero at the bulk of the solution. The potential at a distance from the surface at the location of the shear plane is called the zeta potential. Zeta potential meters are calibrated to read the value of this potential. The greater this potential, the greater is the force of repulsion and the more stable the colloid, **Sincero and Sincero, 2003**. Electrical double layer around a negatively charged oil droplet and the distribution of electrical potential around it has been presented in **Fig.2**.

In aqueous media, the pH of the sample is one of the most important factors that affect its zeta potential. A zeta potential value on its own without defining the solution conditions is a virtually meaningless number. Imagine a particle in suspension with a negative zeta potential. If

more alkali is added to this suspension then the particles tend to acquire more negative charge. If acid is added to this suspension then a point will be reached where the charge will be neutralized. Further addition of acid will cause a buildup of positive charge. Therefore a zeta potential versus pH curve will be positive at low pH and lower or negative at high pH, **Malvern Instruments Ltd, 2011**. Theories describing how the charge density around a particle varies with distance always use the concept of the diffuse double layer. In the simplest theory, the electrostatic potential decays exponentially with distance away from the shear plane. The inverse of the decay constant is a distance called the Debye double layer thickness. It is a function of free salt ion concentration (as embodied in the value of the ionic strength): the higher the concentration, the faster the decay, the smaller the double layer thickness. At high enough salt, the double layer collapses to the extent that the ever present attractive van der Waals forces overcome the charge repulsion. This is one example of the so-called "salting out" effect. Electrostatically stabilized colloidal suspensions will become unstable with the addition of enough salt, **Brookhaven Instruments, 2015**. The effect of the concentration of a formulation component on the zeta potential can give information to assist in formulating a product to give maximum stability. The influence of known contaminants on the zeta potential of a sample can be a powerful tool in formulating the product to resist flocculation for example**, Malvern Instruments Ltd, 2011**.

1.3 Particle Size and Distribution Application in Water Treatment

Physical properties of particles, such as size, shape, density, porosity, surface charge, and settling velocity, may influence their behavior in water and have some relationship to water treatment efficiency. As previously mentioned, particle size is the most significant property responsible for the stability of colloidal dispersion in water Analysis of sizes of flocs formed in the coagulation and flocculation processes are not routinely conducted. Particle size distribution (PSD) analysis can produce direct information about particulate material in water. Through measuring and analyzing the amount of different-sized particles in the raw water as well as in the effluent of each unit, we can evaluate water treatment process efficiency, assess operational problems, and design treatment processes in water and wastewater engineering **Geng, 2005**.

Dynamic light scattering (DLS) is an important experimental technique in science and industry. The principle behind dynamic light scattering is particles, emulsions and molecules in suspension undergo Brownian motion. This is the motion induced by the bombardment by solvent molecules that themselves are moving due to their thermal energy. If the particles or molecules are illuminated with a laser, the intensity of the scattered light fluctuates at a rate that is dependent upon the size of the particles as smaller particles are "kicked" further by the solvent molecules and move more rapidly. Analysis of these intensity fluctuations yields the velocity of the Brownian motion and hence the particle size using the Stokes-Einstein relationship. Note that the radius that is measured in DLS is a value that refers to how a particle diffuses within a fluid so it is referred to as a hydrodynamic diameter **Fig.2**. The radius that is obtained by this technique is the radius of a sphere that has the same translational diffusion coefficient as the particle, **Murarishetty, 2012**.

The Intensity Distribution defines how much light is scattered by the particles in different size bins. This distribution is the most truthful and dependable distribution, and is closely related to the raw measurements that the instrument takes. When understanding these data, it is imperative to save in mind that there is a very strong dependency of the intensity of light scattered, with respect to particle diameter. These two values have a sixth-power relationship, which incomes, for example, that a 100 nm particle will scatter one million times as much light as a 10nm particle The Volume Distribution measurement displays the entire volume

of particles in the different size bins. This distribution is calculated from the intensity distribution, the visual possessions of the material (specifically, Refractive Index and Absorption at 632 nm), and the formulation for the volume of a sphere: $V = (4/3) \pi r^3$. Note in the formulation, that particle diameter (or more definitely, radius) has a third power relationship with volume. This means that, alike to the intensity distribution, the volume distribution will be extra heavily weighted towards the larger, more voluminous particles in a distribution, **Nanocomposix Laboratory, 2015**. In any DLS measurement, the Surface Area standpoint is resulting from the Intensity (Volume) data; since it involve expectations about particle shape, this viewpoint is somewhat detached from the original data and may be less accurate for your measurement, **MNC, 2014**.

2. EXPERIMENTAL WORK
2.1 Materials
2.1.1 Hard water preparation

The hard water, its solutions, and reagents have been prepared according to the (**US EPA, 2013**).

2.1.1.1 Hard water solutions and reagents

A. Hard Water Solution 1
7.94 g $MgCl_2$ (anhydrous) or 16.94 g ($MgCl_2 \cdot 6H_2O$), and 18.50 g $CaCl_2$, have been dissolved in boiled de-ionized H_2O, and then brought to a volume of 250 mL volumetrically .
B. Hard Water Solution 2
14.01 g $NaHCO_3$, (Table 3.4) has been dissolved in boiled de-ionized H_2O; and then brought to a volume of 250 mL volumetrically.
The two solutions have been filtered and sterilized by using a 0.2 μm filter unit. These two solutions have been used for the preparation of hard water at various concentrations.

2.1.1.2 Hard water (as $CaCO_3$) preparation
1 mL of hard water solution 1 has been added for each 100 ppm of hardness desired. For example, for the preparation of 1 L of 400 ppm hard water, 4 mL hard water solution 1 and 4 mL hard water solution 2 have been added to a 1 L flask and bring to volume with sterile de-ionized water. The pH of the hard water sample has been determined. The pH should be between 7.6 and 8.0.

2.1.2 Mixed emulsifier preparation
A mixture of two emulsifiers has been used for the O/W emulsion preparation, where a mixture of 38% Span 85 and 62% Tween 80 has been used for the mixed emulsifier preparation .The calculation of how much of Span 85to blend with Tween 80 to attain a given HLB (hydrophilic- lipophilic balance) of X (oil HLB), the following equations have been used, **Croda Europe Ltd, 2010**:

$$A\% = \frac{X - HLB \ of \ B)}{(HLB \ of \ A - HLB \ of \ B)} \tag{6}$$

$$B\% = 1 - A\% \tag{7}$$

2.1.3 Oily wastewater (emulsion) preparation

Oil in water emulsion was prepared by mixing of oil, mixed emulsifier, and the prepared hard water. The emulsion was prepared by using homogenizer of 10000 rpm for 30 seconds. Gasoline and diesel fuel engine oil (Helix 15W-40) has been used in this preparation .The percent of the emulsifier has been taken as 10% of the oil (i.e. for 1000 ppm of oily water 0.9 g of oil and 0.1 g of the mixed emulsifier has been used per 1 liter volume).The emulsion has been prepared at different oil concentration and hardness levels. The oily wastewater has been prepared at four different hardness levels (2000, 2500, 3000, and 3500) ppm for (50, 250, 500, and   1000)   ppm   oil   concentrations   respectively.
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2.1.4 Coagulant preparation

Aluminum rubbish has been brought from aluminum factories waste. Sodium Hydroxide (NaOH) solution was prepared at a concentration of 1.5 M by dissolving 30g of NaOH in 500ml of deionized water. Sodium Aluminate was prepared at a concentration of 0.5 M by dissolving 6.75g of aluminum rubbish in NaOH solution. The reaction has been completed when all the aluminum dissolved in NaOH and Sodium Aluminate has been produced. The reaction container must not be covered during the reaction because of the hydrogen gas releasing.

2.2 Methods
1. For jar testing, a conventional unit capable of variable speeds from (50 – 250) rpm was used with six beakers, each 1000 ml in capacity.
2. System type Lovibond instrument has been used for turbidity measurement with a turbidity range from (0 to 800) NTU.
3. The pH values of the samples were measured by one device which is (Model 2906, Jenway Ltd, UK) with a pH range (0-14) pH.
4. The hardness of water was measured in parts per million (ppm), expressed in terms of Calcium as $CaCO_3$. Actually the hardness is due both to Calcium and Magnesium salts, but the two are determined together in the titration.
5. The measurements of the oil content in water samples have been done by a simple device TD500-D^{TM}Handheld Oil in water meter.
6. The zeta potential has been measured by Zeta-Meter System 4.0, Zeta-meter, Inc.
7. The particle size measurement have been done by Nano Brook zeta plus device (zeta potential and particle size analyzer), Brookhaven Instrument.

2.3 Procedure

Six dosages (4 ml, 12 ml, 20 ml, 24 ml, 28 ml, and 32 ml) of the chemical coagulant (Sodium Aluminate) have been added to the O/W emulsion. The jar tester has been worked at a high speed of 250 rpm for two minutes (Coagulation process), and then slow mixing at a speed of 50 rpm for 20 minutes (Flocculation process). After the slow mixing the tester has been stopped to allow the settling operation for 15 min, and after settling, samples of the clear part of water have been taken for farther analysis (i.e. turbidity, pH, hardness, and oil content measurements). From the turbidity measurements the optimum dose has been found for each concentration. The zeta potential measurements have been done to the optimum dose of chemical coagulant for each selected concentration of oil and hardness and to the oily wastewater before treatment. The measurement samples have been taken after the addition of the optimum dose and during jar testing at time of 2 min (after coagulation), at 22 min (after flocculation), and after the sedimentation. Likewise the particle size measurements have been done to the optimum dose of chemical coagulant for each selected concentration of oil and hardness. The particle size

measurements were done to the oily wastewater before the treatment and after the addition of the optimum dose, during jar testing samples of water have been taken at time of 2 min (after coagulation) and at 22 min (after flocculation). All the water samples have been filtrated with a whatman 44, $3\mu m$ pore size filter paper before measurement.

3. RESULTS AND DISCUSSION
3.1Optimum Coagulant Dosages

Figs.3 to 6 illustrate the results of the effect of different dosages of sodium aluminate as a coagulant on the residual turbidity through coagulation-flocculation and settling time. The residual turbidity has been decreased as the sodium aluminate dose increased until reaching the minimum value of turbidity at the optimum coagulant dose, then the turbidity has been increased with increasing sodium aluminate dosages. This may be explained as the particulates can be destabilized by adsorption of oppositely charged ions or polymer. Most particulates in natural waters are negatively charged (oils, clays, humic acids, and bacteria) in the neutral pH range (pH 6 to 8); consequently, hydrolyzed metal salts can be used to destabilize particles through charge neutralization. When the proper amount of coagulant has adsorbed, the charge is neutralized and the particle will flocculate. When too much coagulant has been added, the particles will attain a positive charge and become stable once again. For coagulant dosages up to optimum value, the electrophoretic mobility becomes more positive and the amount adsorbed increases. Higher dosage causes charge reversal, particle stability, and a higher residual turbidity. At the optimum dosage of coagulant, the particle charge is just neutralized and the collision efficiency reaches a maximum value and this agreed with **Makki et al., 2010**. The minimum values of turbidity that have been gained from the experiments in NTU units were (1.67, 1.95, 2.10, and 4.01) at optimum sodium aluminate dosages in milliliters (12, 20, 24, and 28) for oily wastewater of   concentrations(50, 250, 500, and 1000) ppm of oil respectively.

3.2 Effect of Coagulant Dosages on pH Value

Sodium aluminate is a very strong alkaline .The reasons for the addition of some form of alkali were to establish the optimum pH value at which coagulation can take place and to rise the final pH value after treatment to reduce corrosiveness. In coagulation, the pH value is important. Floc formed in any given water tends to be heaviest at specific pH value **Putros, 2001**. The effect of adding sodium aluminate on the pH value has been illustrated in **Fig.7**, where the increase of sodium aluminate dosages from 4 ml to 32 ml has been increased the pH value of the water of four different concentrations (50, 250, 500, and 1000) ppm with increasing rate of (46, 49, 52, and 52) % respectively.

3.3 Effect of Coagulant Dose on Hardness (CaCo₃) Removal

The oily wastewater has been prepared at four different hardness levels (2000, 2500, 3000, and 3500) ppm for (50, 250, 500, and 1000) ppm oil concentrations respectively. **Fig.8** illustrates the effect of sodium aluminate coagulant on the oily wastewater hardness, where the hardness has been decreased with the increase of the sodium aluminate dose, this can be explained as the Hydroxide ion will react with the Calcium bicarbonate and precipitate it as Carbonate ion which will react with the Calcium ion and precipitate it as salt in water. Likewise the Hydroxide ion will react with the Magnisium ion and precipitate it as Magnisium. The removal rates were (77, 90, 84, and 93) % for (2000, 2500, 3000, and 3500) ppm hardness levels of (50, 250, 500, and 1000) ppm respectively oily wastewater at the optimum coagulant dose.

3.4 Effect of Coagulant Dose on Oil Removal

Jar tests were performed using the prepared oily wastewater and the experimental results have been shown in **Fig.9.** The results suggest that the oil in water can be effectively removed by a suite coagulation, flocculation, and sedimentation processes, where the residual oil concentration has been decreased with the increase of the coagulant dose and this can be regarded that Oil droplets in an O/W emulsion exhibit a net charge the droplet surface. It is usually negative charge, if aluminum ions of positive electric charge are added, it neutralizes the electric negative charge, precipitate the oil particles and other presented pollutants in the wastewater, as hydroxides and facilitate their removal by physical separations through the sedimentation process**.** The oil removal rates were (100, 93, 96, and 97) % for oily wastewater of oil concentrations (50, 250, 500, and 1000) ppm respectively. The behavior observed in the oil removal denotes that the amount of sodium aluminate coagulant necessary to produce the destabilization of the emulsion is proportional to the oil concentration.

3.5 Zeta Potential Measurement

Fig.10 illustrates the effect of time of coagulation, flocculation and sedimentation on the value of zeta potential. Initially the zeta potential has been measured for the prepared oily wastewater (O/W emulsion) and the values were (-36, -35, -31, and -26) mv for oil concentrations of (50, 250, 500, and 1000) ppm respectively, so the prepared emulsions of concentrations of 50, 250, and 500 ppm oil are considered to be moderately stable because their zeta potential values were in the range of (-31 to 40), but for the emulsion of 1000 ppm oil concentration it considered to be plateau of slight stability because its zeta potential value was in the range of (-21 to -30). The time variation in the zeta potential that has presented in Figure 8 suggests that the addition of AL^{+3} ions neutralize the negative charges on the particle surfaces. The zeta potential that has been measured at pH=7 becomes positive when the emulsion is demulsified, and this can be explained as that initially, the negative colloid attraction effects some of the positive ions to form a definitely attached layer round the colloid surface, this layer of counter ions is identified as the stern layer, because of that the zeta potential will be a positive value**.** During flocculation the additional positive ions are still attracted by the negative colloid so the value of the zeta potential raises more until the colloids are repelled by the positive stern layer as well as by the other near-by positive ions that are trying to reach to the colloid. After sedimentation all the agglomerates have been settled out of the water, so the values of the zeta potential will be negative again due to the remained (OH-) ions in the water, except for 28 ml coagulant sample where the zeta potential value has been remained positive after sedimentation and this may be due to the remained positive charge flocs that didn't settle out and may need more sedimentation time.

3.6 Particle Size Measurements

Several experimental runs have been carried out to examine the particle size of oily wastewater before the clarification process (i.e. before treatment), after coagulation-filtration, and after coagulation-flocculation-filtration without the sedimentation step in order to study the effect of the coagulation and flocculation time on the effective diameter, volume, surface area, intensity (i.e. the fate of Nano particles and flocs), where the fate of the larger particles and flocs is well known during coagulation and flocculation process.

3.6.1 Effective diameter of the particles of highest intensity

DLS experiment first order result is the intensity distribution of particle sizes. According to the scattering intensity of each particle fraction or family the intensity distribution is logically weighted. **Fig. 11** illustrates the relation of the effective diameter of the particles that have the highest intensity and time. The effective diameter has been measured for oily wastewater and the results before treatment were (310.95, 543.13, and 575.88) nm for concentrations of (250, 500, and 1000) ppm oily wastewater respectively. The particle size is an indicator of the emulsion stability and the type of the oil in water, where smaller particle sizes and higher surface charge (zeta potential) will typically improve suspension and emulsion stability, and therefore the 250 ppm oily wastewater emulsion is more stable than the others, and since all the particle sizes are below 5 microns so the oil can be considered dissolved in water. After coagulation –filtration process, the effective diameter of the particles has been increased to (323.38, 587.26, and 577.63) nm for concentrations of (250, 500, and 1000) ppm oily wastewater respectively, and after coagulation – flocculation –filtration, the effective diameter has been more increased to (329.89, 668.87, and 762.05) nm for concentrations of (250, 500, and 1000) ppm oily wastewater respectively. This can be explained as that the effective diameter is the hard sphere diameter where this hard sphere diffuses at the identical speed as the molecule or particle being measured. The translational diffusion coefficient will not only depend on the particle size "core", but also on any surface structure, the concentration, and type of ions in the medium. The medium ions and the total ionic concentration may affect the diffusion speed of the particle by varying the electric double layer thickness during coagulation and flocculation. Any variation in the particle surface that affects the diffusion speed will correspondingly change the particle apparent size, where smaller particles are further "reflexed" by the molecules of the solvent and move more rapidly and vice versa.

3.6.2 Diameter of the particles of highest surface area

Before treatment the diameters of the particles and flocs that have the highest surface area were (455, 320.25, and 669) nm for oily wastewater of concentrations (250, 500, and 1000) ppm respectively. After coagulation –filtration step the results were (332, 332, and 790) nm for oily wastewater of (250, 500, and 1000) ppm oil respectively, so the diameters have been increased after this step except for 250 ppm oil concentration and this can be due to the high speed of mixing (250)rpm during this step. After the coagulation- flocculation- filtration step the results were (487.5, 660, and 410) nm for (250, 500, and 1000) oily wastewater respectively and there is an increase in the diameters except for the 1000 ppm oily wastewater, so for this concentration this step is not sufficient. **Fig.12** illustrates the relation between the time and the surface area that has been calculated depending on the assumption that the particles and flocs have the form of a spherical ball.

3.6.3 Diameter of particles of highest volume

Before treatment the results were (462, 850, and 1342.85) nm for oily wastewater of concentrations (250, 500, and 1000) ppm oil respectively. After coagulation-filtration step the results were (1002, 1690, and 860) nm for wastewater of (250, 500, and 1000)ppm respectively, so there is an increase in the diameters except for the 1000 ppm concentration sample and this may be explained as it need more time to achieve a larger diameter. After coagulation-flocculation –filtration step the diameters have been decreased to the values (782.5, and 1062) nm for the wastewater of concentrations of (250, and 500) ppm oil respectively, and increased for the 1000 ppm oil wastewater to (1524) nm, in spite of that there is an increment in the

diameter values after this step than the values before treatment. **Fig.13** illustrates the relation between the time and the volume that has been calculated depending on the assumption that the particles and flocs have the form of a spherical ball.

CONCLUSIONS

1. Successful in using aluminum rubbish as a coagulant for oily wastewater treatment with removing the bicarbonates, calcium, and magnesium ions that causing hardness and this coagulant can be used for treating the oily wastewater from different industries.

2. Within the range of the oil concentrations that have been studied, the optimum coagulant doses were (12, 20, 24, and 28) ml for oily wastewater of (50, 250, 500, and 1000)ppm oil and (2000, 2500, 3000, and 3500) ppm $CaCo_3$ respectively.

3. The pH values increases with increasing the coagulant dose, while the hardness level ($CaCo_3$ concentration), and the oil content decreases with increasing the coagulant dose.

4. Zeta potential values have been reversed from negative to positive charge values after the coagulation-flocculation process, where the initial values were (-36, -35, -31, and -26) mv, while the final values after coagulation-flocculation process were (20.2, 29.1, 24.56, and 27) mv for oily wastewater of initial concentrations (50, 250, 500, and 1000) ppm of oil respectively.

5. The results were presented graphically in two dimensional co-ordinates showing particle size distribution and growth that have (greater Intensity, largest volume, and greater surface area) as a function with time. For the particles and flocs that have the highest intensity the initial effective diameter values were (310.95, 543.13, and 575.88) nm, while the final values after coagulation-flocculation process were (329.89, 668.87, and 762.05) nm, but for the particles and flocs that have the highest surface area the initial diameter values were (455, 320.25, and 669) nm, while the final values after coagulation-flocculation process were (487.5, 660, and 410) nm, while for the particles and flocs that have the largest volume the initial diameter values were (462, 850, and 1342.85) nm, while the final values after coagulation-flocculation process were (782.5, 1062, and 1524) nm for oily wastewater of initial concentrations (250, 500, and 1000) ppm of oil respectively.

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NOMENCLATURE

A%= volume percent of Tween 80 emulsifier.

B%= volume percent of Span 85 emulsifier.

X= HLB number of oil has been used for emulsion preparation (HLB=10 for Helix oil).

HLB of A = hydrophilic- lipophilic balance of Tween 80 =15.

HLB of B = hydrophilic- lipophilic balance of Span 85 = 1.8.

Abbreviations

API	American Petroleum Institute
COD	Chemical Oxygen Demand
DAF	Dissolved Air Flotation
DLS	Dynamic Light Scattering
Dp	Particle Diameter
HLB	Hydrophilic Lipophilic Number
MF	Microfiltration
NF	Nanofiltration
NTU	Nephelometric Turbidity Unit
O/W	Oil in Water Emulsion
RO	Reverse Osmosis
UF	Ultrafiltration
W/O	Water in Oil Emulsion

Oil-in-water (O/W)   Water-in-oil (W/O)
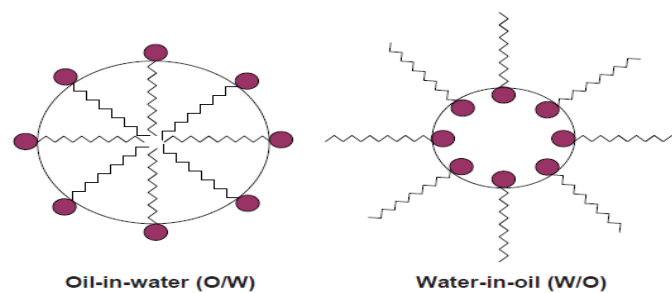
Figure 1. Surfactant stabilized micelles, **Sethupathi, 2004**.
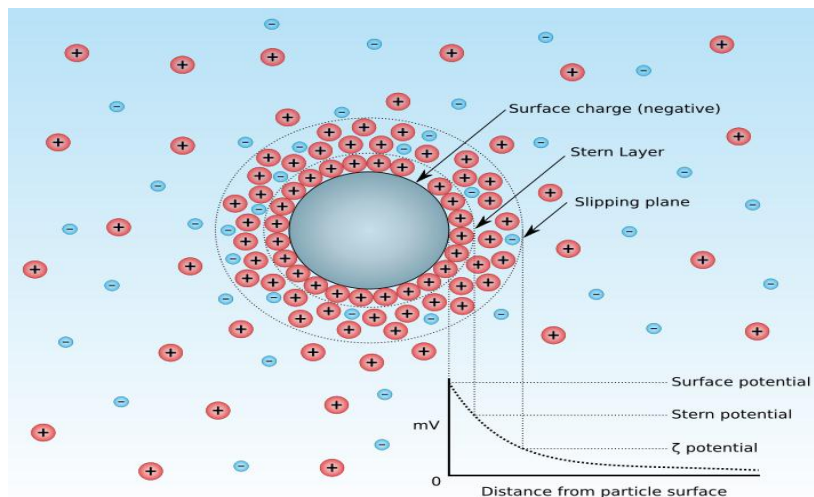
Figure 2. Electrical double layer surround a negatively charged oil droplet and the distribution of electrical potential around it, **Zghair, 2014**.
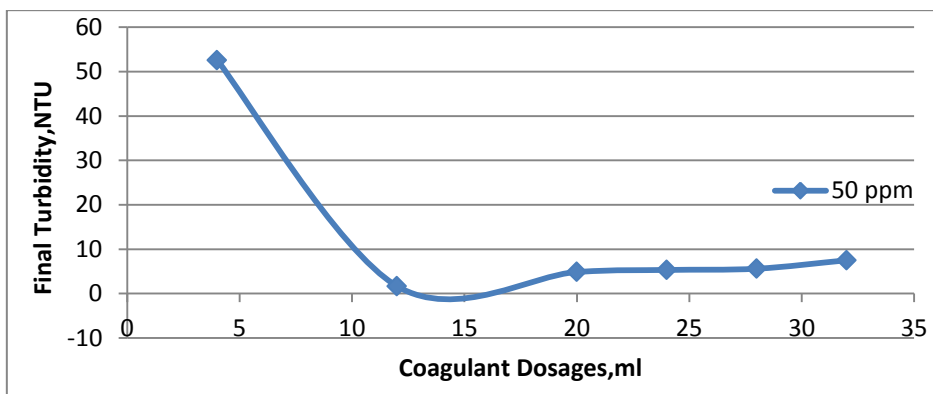
Figure 3. Final turbidity vs. coagulant dose for 50 ppm oily wastewater, initial turbidity=203 NTU.
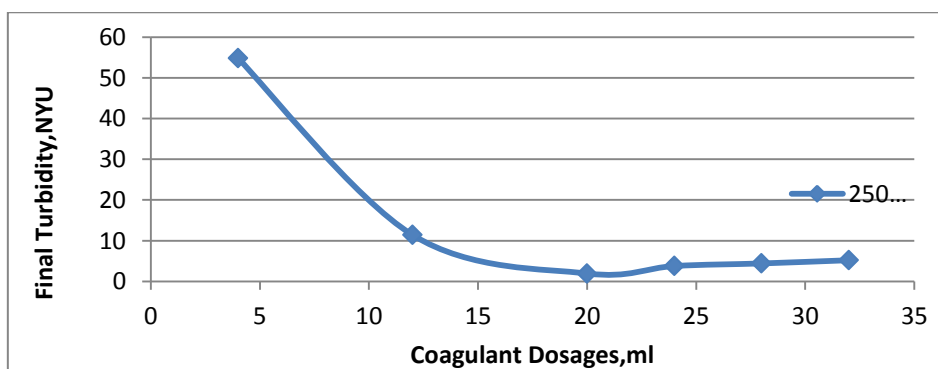
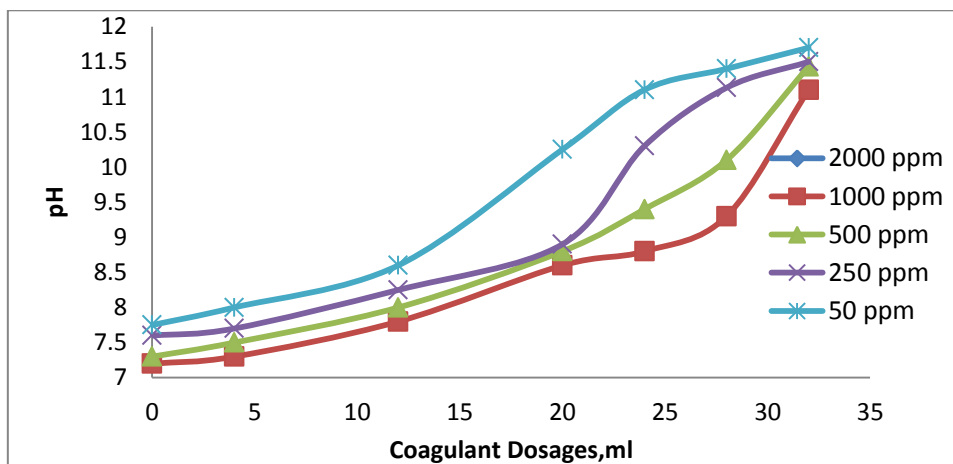**Figure 4.** Final turbidity vs. coagulant dose for 250 ppm oily wastewater, initial turbidity=290 NTU.
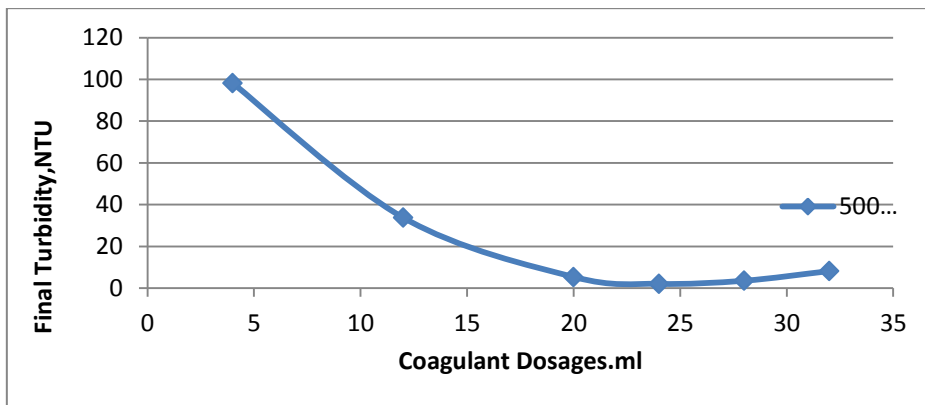
Figure 5. Final turbidity vs. coagulant dose for 500 ppm oily wastewater, initial turbidity=770 NTU.
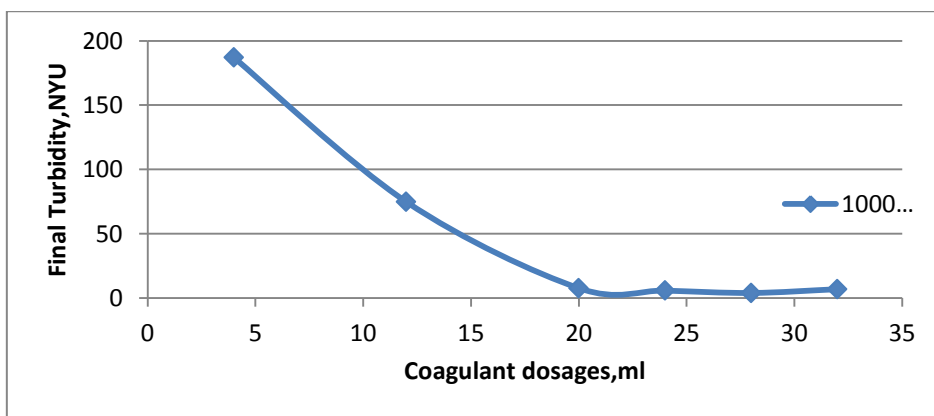
Figure 6. Final turbidity vs. coagulant dose for 1000 ppm oily wastewater, initial turbidity=1306 NTU.

Figure 7. pH vs. coagulant dose.
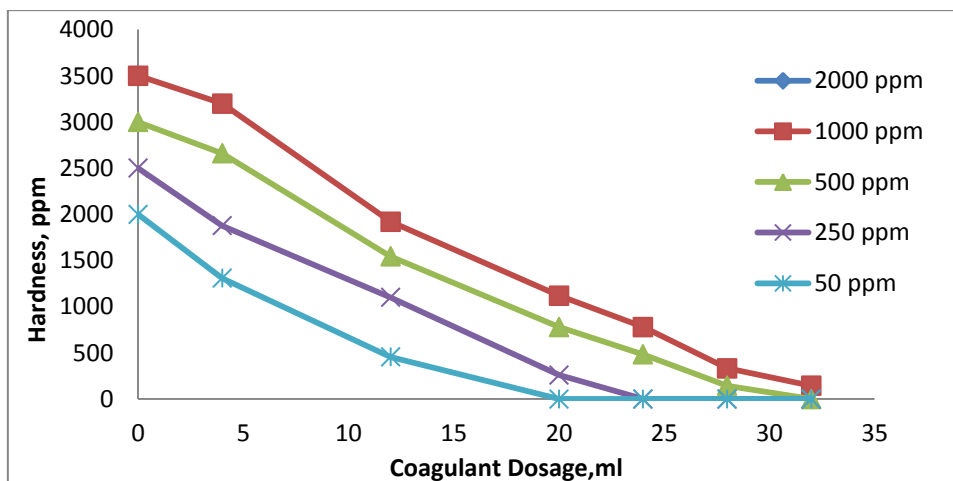
Figure 8. Oily wastewater hardness vs. coagulant dose.
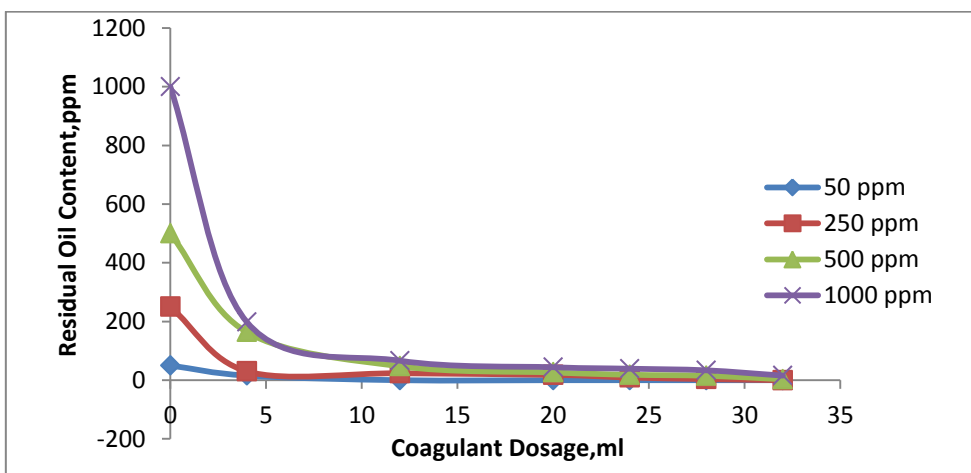
Figure 9. Residual oil content vs. coagulant dose.
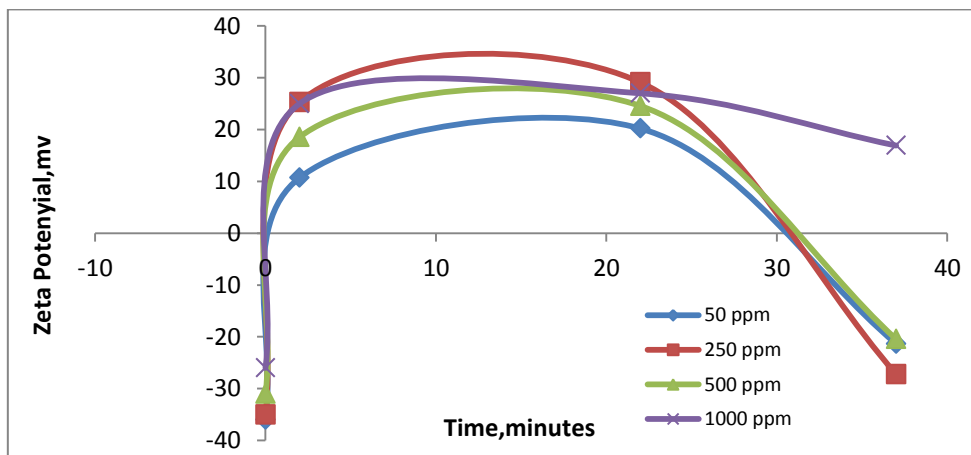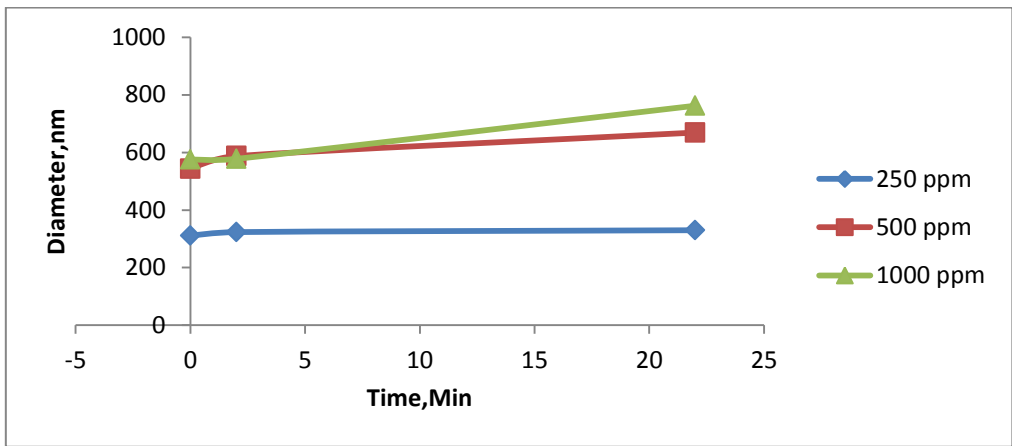

Figure 10. Zeta potential vs. time.

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Figure 11. Effective diameter of particles and flocs that have highest intensity vs. time.

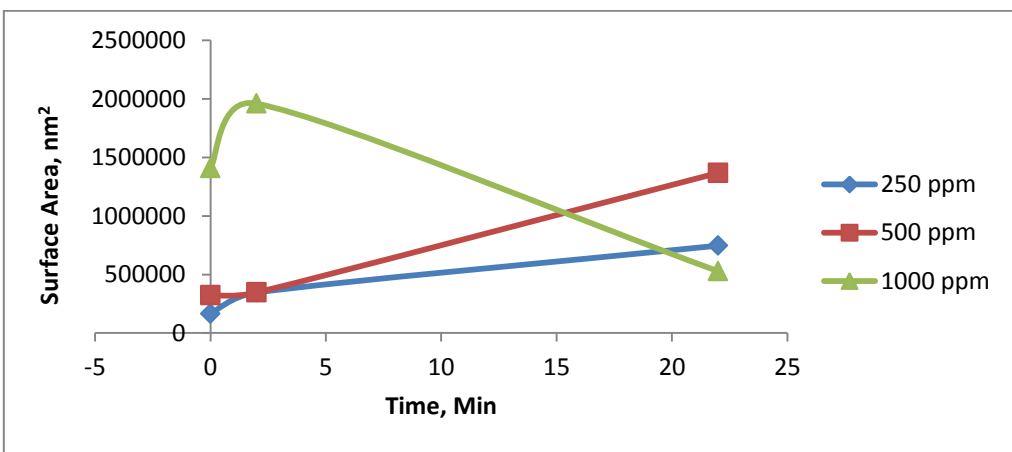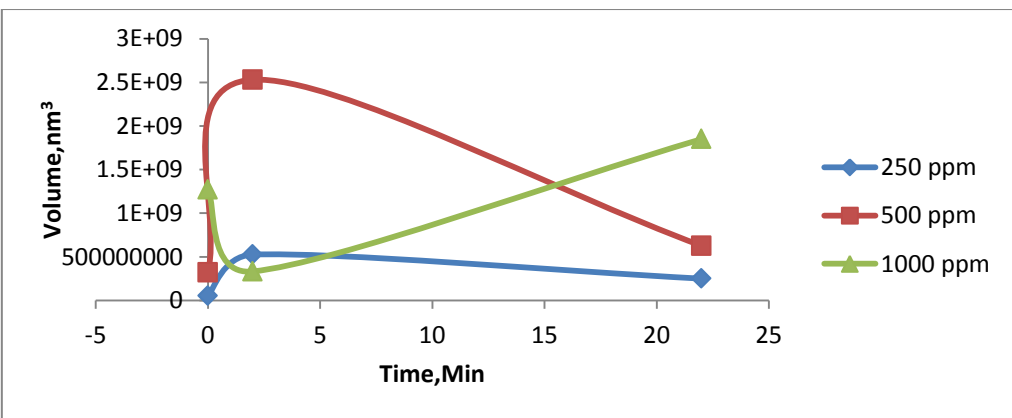**Figure 12.** Surface area vs. time.

Figure 13. Volume of particles and flocs vs. time.

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