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Water Treatment Improvement by Ultrasonic Approach

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Abstract Water as the most prominent substance on the earth, needs treatment to use. On the other hand, different impurities with different physical or chemical specifications should be purified by specific additive materials and methods. Recently, Nanomaterials as additives instead of common materials have been used to eliminate water impurities what made water treatment more efficient because of Nano size extraordinary physical potentials, but they also can pollute water that their elimination would be more difficult and needs specific methods. Then, Nanoparticles are one of the most important impurities what needs precise treatment. There are some different common processes to demolish Nano impurities, but ultrasound as mechanical wave in aqueous area not only is capable to eliminate them from water but also it is the most powerful and efficient method to effect on nanoparticles.

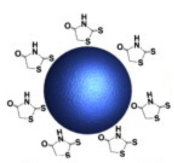
Keywords Nanoparticles, Ultrasound, Water Purification, Ultra sonification

1. Introduction

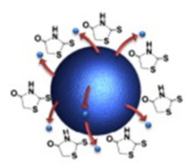
Water is the most important enablers of life on the earth. Recently, water quality has been associated with the development index of society. Realizing the molecular nature of contamination in drinking water, significant progress has been made to utilize the chemistry of nanomaterials for water purification [1, 2].

Nanotechnology, the engineering and art of manipulating matter at the nanoscale (1-100 nm), offers the potential of novel nanomaterials for treatment of surface water, groundwater and wastewater contaminated by toxic metal ions, organic and inorganic solutes, and microorganisms. Due to their unique activity toward recalcitrant contaminants and application flexibility, many nanomaterials (nanostructured catalytic membranes, Nano sorbents, Nano catalysts and bioactive nanoparticles) are under active research and development.

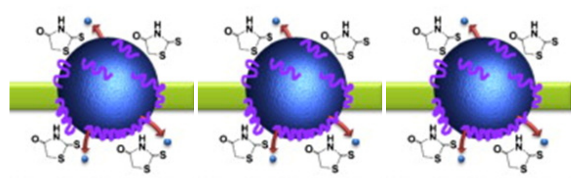
Among all nanoparticles available at the market, a few of them show the tremendous role in water purification, such as Au, Ag, zero-valent iron, Fe_3O_4, and TiO_2 nanoparticles. Ag nanoparticles have generally been used for the removal of pathogens from water and heavy metals from many years. Recently, nZVI nanoparticles have been used mainly for the degrading toxic organic pollutants and removal of heavy metals. They have been found to be useful for the removal of As (III) and As (V) from water, which is a significant work in water purification. Fe_3O_4 nanoparticles have been used as non-absorbent for the removal of pollutants, and these nanoparticles have been easily removed by applying magnetic field (Fig. 1). Further, TiO_2 nanoparticles have effectively been used for the degradation of pesticides present in water, and due to their catalytic property, they have been used for the inactivation of bacteria present in water. Hence, nanoparticles have tremendous application in water purifications [3].



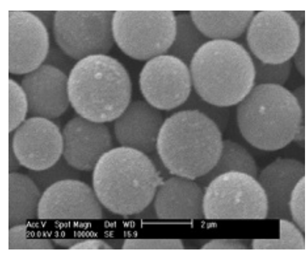
Magnetic nanoparticle surrounded by cluster



Magnetic cation is going from the surface rhodamine



Polymerization on the surface of the magnetic nanoparticles



Electron microphotography of magnetic particles

Figure 1. Scheme of usage of magnetic nanoparticles for water cleaning

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At the same time the risk assessment of nanoparticles and nanomaterials is of key importance for the continuous development in the already striving new field of nanotechnology. Humans are increasingly being exposed to nanoparticles and nanomaterials, placing stress on the development and validation of reproducible toxicity tests. Tests currently used include genotoxicity and cytotoxicity tests, and in vivo toxicity models [4, 5].

Accordingly, the task of cleaning water from nanoparticles (natural and injected) is also standing as the significant question. Nanoparticles physical properties make high potentials for materials with extraordinary strengths but the extra small size of nanoparticles makes their treatment process more difficult than routine processes and different special methods usage is inevitable then. One of the possible utilization of nanoparticles should be done in liquid environment. High power ultrasound is often the only method to affect nanoparticles effectively and it is the only efficient tool to achieve the desired milling and dispersing results of nanoparticles [6].

2. Method of Ultrasonic Treatment

Ultrasonic waves as useful instrument for water purification is well known [7, 8]. Effective application of the ultrasonic purification process requires consideration of a number of parameters, while time, temperature and chemical nature of the particle remain important in ultrasonic as they are in other purification technologies, there are other factors which must be considered to maximize the effectiveness of the process. Especially important are those variables which affect the intensity of ultrasonic cavitation in the liquid. For maximizing the cavitation very important is to precisely manage the temperature which is the most important single parameter to be considered in maximizing cavitation intensity. Changes in temperature result in changes in viscosity, the solubility of gas in the liquid, the diffusion rate of dissolved gasses in the liquid, and vapour pressure, all of which affect cavitation intensity. In pure water, the cavitation effect is maximized at approximately 70°C. For most effective purification, the cleaning liquid must contain as little dissolved gas as possible. Gas dissolved in the liquid is released during the bubble growth phase of cavitation and prevents its violent imploding, which is required for the desired ultrasonic effect. In water at a temperature about 70°C, optimum cleaning is often seen at higher or lower temperatures which depends on concentration of impurity particles in the specific volume of the water. During the negative pressure portion of the sound wave, the liquid is torn apart and cavitation bubbles start to form. As a negative pressure develops within the bubble, gasses dissolved in the cavitating liquid start to diffuse across the boundary into the bubble. As negative pressure is reduced due to the passing of the rarefaction portion of the sound wave and atmospheric pressure is reached, the cavitation bubble starts to collapse due to its own surface tension. During the compression portion of the sound wave, any gas which diffused into the bubble is compressed and finally starts to diffuse across the boundary again to re-enter the liquid. This process, however, is never complete as long as the bubble contains gas since the diffusion out of the bubble does not start until the bubble is compressed. In addition, once the bubble is compressed, the boundary surface available for diffusion is reduced. As a result, cavitation bubbles formed in liquids containing gas do not collapse all the way to implosion but rather well in a small pocket of compressed gas in the liquid. This phenomenon can be useful in degassing liquids. The small gas bubbles group together until they finally become sufficiently buoyant to come to the surface of the liquid. At slower pulse rates, more rapid degassing of liquids occurs as coalescing bubbles of air are given an opportunity to rise to the surface of the liquid during the time the ultrasonic energy is off. At more rapid pulse rates the cleaning process may be enhanced as repeated high energy "bursts" of ultrasonic energy occur each time the energy source is turned on.

In sweep operation which is very dependent on the ultrasonic amplitude, the frequency of the output of the ultrasonic generator is modulated around a central frequency which may itself be adjustable.

In order to well understand the process of degassing, the liquid (water) it is useful to go through the process of condensation of water vapour onto aerosol particles, which is happening during the ultrasonic cavitation. The ambient atmosphere often becomes slightly water supersaturated [9]. This typically occurs as air masses become elevated when crossing higher orographic obstacles, for example accessing a mountain from the direction of the sea. Other mechanisms include convective cooling during changes in daylight. A supersaturated air mass exceeding 100% relative humidity will hold a few percent more water in the gaseous state for a period of time than expected in the equilibrium state. Usually there are two main routes for the return to equilibrium conditions. The first is dilution by dry air masses – in this case no condensation of water will be observed. The second mechanism is condensation on ultrafine water-soluble particles. Simply put, water vapour forms brine at the particle surface (e.g. NaCl). Because of the water vapour, pressure above such droplet surfaces becomes depleted (according to Raoul's law). As described by Fick's law water diffusion remains active in the direction of the "sink" (the brine), as long as there is a vapour pressure gradient between the particle acting as the condensation nuclei and the surrounding supersaturated air mass. This process comes to a halt after some time because of increasing dilution of the brine vapour pressure gradient no longer exists to stimulate further water vapour condensation. Because of the release of condensation heat during diffusion to and from condensing nucleus the whole process might become very complex. Qualitatively, well dissolvable particle cores will serve as very efficient condensation nuclei. In essence, the particles will become incorporated into the water cycle and have a chance to become precipitated.

For the assessment of the role of dispersed nano-engineered particles within the water cycle, we have to identify those which can be involved in such water condensation processes. As already mentioned above, dissolvable material would fit perfectly. In contrast, hydrophobic particles as individuals can only act as condensation nuclei when a certain water supersaturation is present. The well-known Kelvin equation describes such a situation of condensing water vapour without any dissolution process [10, 11]. Originally set only for pure water droplets this equation at least qualitatively gives an estimate for the ruling principle:

$$Sr = 4\,\gamma VmRT/ \ln Peq \qquad (1)$$

Where as:
Sr: is the size of the droplet
γ: the surface tension
Vm: molar volume of the water
R: universal gas constant
T: temperature
Peq: the equilibrium vapour pressure (Equilibrium vapour pressure depends on droplet size)

If we cool the vapour, then T decreases. This means that Peq increases as the liquid is cooling. The further a vapor is supercooled, the smaller critical radius becomes. Ultimately it gets as small as a few molecules, and the liquid undergoes homogeneous nucleation and growth. The change in vapor pressure can be attributed to changes in the Laplace pressure. When the Laplace pressure rises in a droplet, the droplet tends to evaporate more easily.

When applying the Kelvin equation, two cases must be distinguished: A drop of liquid in its own vapor will result in a positively curved liquid surface, and a bubble of vapor in a liquid will result in a negatively curved liquid surface.

This would mean that nanoparticles with very low probability would be incorporated into condensing water, since the required water supersaturation for acting as condensation nuclei would be tremendously high (by far exceeding the available 1 or 2% within a cloud or fog situation). Hence, any change of particle surfaces, either by a chemical reaction or agglomeration with ionisable material, will lead to an actively participating condensation nucleus. If there is a change of wettability of such a particle system for example by agglomeration with other small particles during residence time in air, lower supersaturation is needed to trigger condensation. This is due to dissolution and diameter increase.

For purification of water from nanoparticles of different origin as well their compexes with organic and inorganic compounds the minimum amount of energy needed to achieve cavitation at ambient temperature was estimated to be 0.3 to 0.5 watts per square centimeter for the transducer-radiating surface operating at 40 KHz. What this means is we must supply adequate power to the transducer to initiate cavitation. There are two general types of ultrasonic transducers in use today: Magnetostrictive and piezoelectric. Both accomplish the same task of converting alternating electrical energy to vibratory mechanical energy but do it through the use of different means [12].

The magnetostrictive type transducers contain ferromagnetic nickel laminations surrounded by electrical coils. During operation a varying magnetic field causes the laminations to alternately expand and contract generating a sound wave or pressure wave that is driven into the liquid of an ultrasonic tank. Magnetrostrictive transducers at this time are low frequency devices and cannot operate practically at frequencies higher than approximately 20 KHz. Magnetostrictive transducers can lose up to 50% of their applied energy in the form of heat making it difficult to maintain a low temperature in the ultrasonic bath. Magnetostrictive transducers are a low voltage, high current device that requires polarization. Due to the low operating frequency sub harmonics from the fundamental frequency are at high amplitude in the human hearing range and usually will require ear protection by operating personal or other precautions will have to be taken (Fig.2).

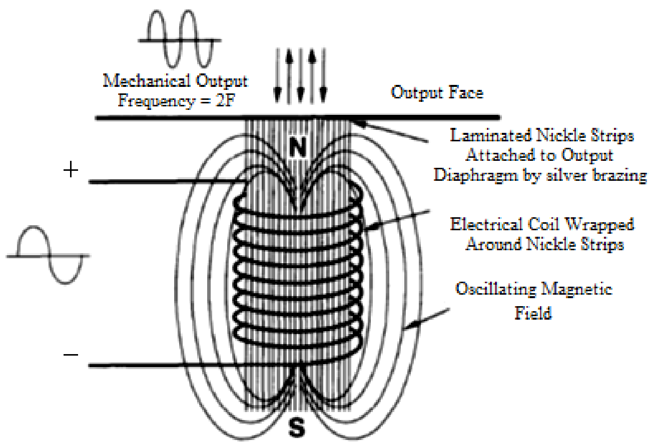

Figure 2. Scheme of magnetostrictive transducer

Electrostrictive (piezoelectric) transducers have ceramic crystals, which similarly expand, and contract (vibrate) in a varying electrical field. First quartz was used, then barium titanate. The draw back with the quartz was the high cost. The draw back with the barium titanate was the low operating temperature of 160 degrees Fahrenheit (70 Celsius) maximum, or the transducer would become de polarized and destroyed. The new lead zerconate titanate ceramic transducer element can withstand temperatures in excess of 250 degrees Fahrenheit (120 Celsius). These piezoelectric transducers are a high voltage low current device and are far more efficient in energy conversion (in excess of 90%). The piezoelectric ceramic can be manufactured to virtually any operating frequency making in the most widely used material used for ultrasonic applications. The transducer ceramic crystal is compressed into a “sandwich” consisting of a steel back plate and a steel or aluminum face plate for protecting the fragile ceramics. Piezoelectric transducers convert alternating electrical energy directly to mechanical energy through use of the piezoelectric effect in which certain materials change dimension when an electrical charge is applied to them. Electrical energy at the piezoelectric transducers, on the other hand, can easily operate well into the megahertz range. Electrical energy at the ultrasonic frequency is supplied to the transducer by the ultrasonic generator. This electrical energy is applied to piezoelectric element(s) in the transducer which vibrate. These vibrations are amplified by the resonant masses of the transducer and directed into the liquid through the radiating plate (Fig.3).

There is a routine method for surface water treatment that based on screening, coagulation, flocculation, filtration and disinfection. On the other hand, the methods speed and efficiency is the basic feasible parameter for treatment. Ultrasound can improve coagulation, flocculation then sedimentation that as the most important water treatment process step is efficiency and fixed price determinant.

A high frequency sound wave effects on substances that refer to quantity and quality, this property can be used in different fields. One of the most interesting applications is thermo dynamical property change of fluids by ultrasonic cavitation, which is possible to use for water purification of different unpleasant nanoscale particles.

Refer to investigations, this method not only make smaller construction and cheaper plant price but also decreases coagulant consumption that should be important in sludge management.

Dispersion and DE agglomeration by ultra-sonication are a result of ultrasonic cavitation. The sound waves that propagate into the liquid result in alternating high-pressure and low-pressure cycles that apply mechanical stress on the attracting forces between the individual particles. Ultrasonic cavitation in liquids causes high-speed liquid jets of up to 1000km/hr (approx. 600mph). Such jets press liquid at high pressure between the particles and separate them from each other. Smaller particles are accelerated with the liquid jets and collide at high speeds. This makes ultrasound an effective means for the dispersing but also for the milling of micron-size and submicron-size particles [14-17].

Effective means of DE agglomerating and dispersing are needed to overcome the bonding forces after wetting the powder. The ultrasonic breakup of the agglomerate structures in aqueous and non-aqueous suspensions allows utilizing the full potential of Nano size materials. Investigations at various dispersions of Nano particulate agglomerates with a variable solid content have demonstrated the considerable advantage of ultrasound when compared with other technologies, such as rotor stator mixers piston homogenizers or wet milling methods.

Meanwhile, because of dependence of rhythm of longitudinal wave and fluid vibration rhythm, cavitation speed (bubbles generation and collapse) is controlled by longitudinal wave frequency. Therefore, higher frequency makes faster cavitation that clear ultrasonic role in this process but stable cavitation is commonly observed at frequencies more than 200 kHz.

3. Drinking Water Treatment

Drinking water treatment in most municipalities is performing by a huge treatment plant based on screening, coagulation, flocculation, filtration and disinfection [19].

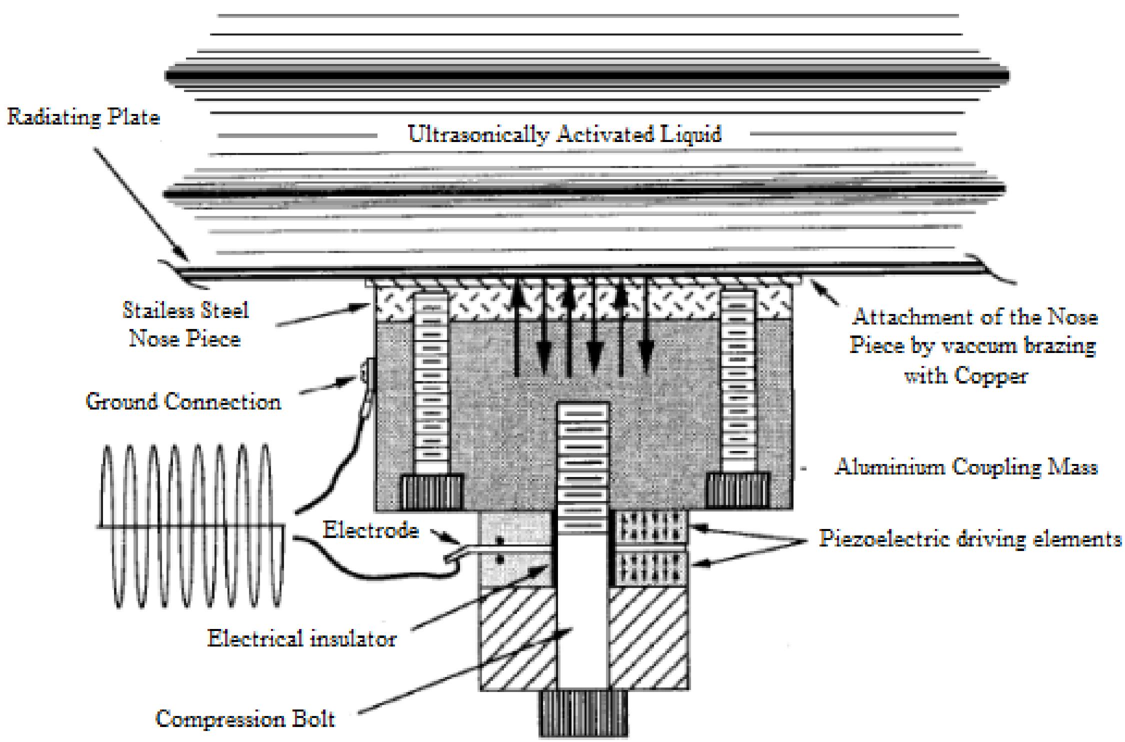

Figure 3. Scheme of piezoelectric transducer

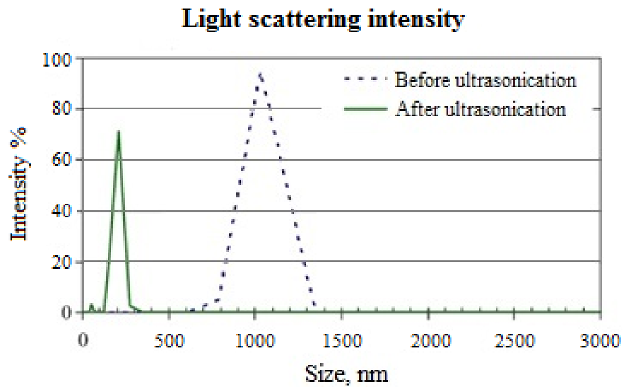

Figure 4. Improvement of ultra-sonication [18]

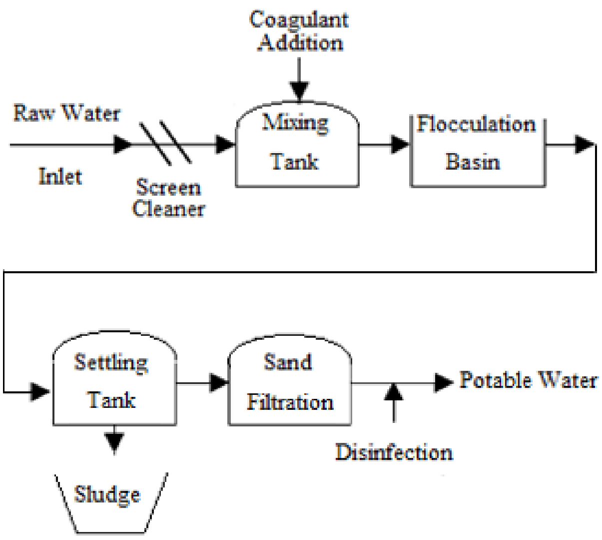

Figure 5. Basic model of water treatment

Basically, coagulation and flocculation are used to separate the suspended solids portion from the water. Suspended solids in water have a negative charge and since they have the same type of surface charge, they repel each other when they come close together then suspended solids will remain in suspension. Therefore, they will not clump together and settle out of the water, unless proper coagulation and flocculation is used. Coagulation and flocculation occurs in successive steps, allowing particles collision and growth to floc and then followed by sedimentation. To release suspended solids negative charges, coagulant with charges opposite those of the suspended solids are added to the water to be neutralized then the small suspended particles are capable of sticking together. Then, coagulant makes submicroscopic microflocs that in flocculation they collide together and make bonds to produce larger visible pinflocs. Flocs size continues to build larger and once they reach optimum size, strength and weight then it will be ready for sedimentation.

As a matter of fact, there are different flocculation process according to different rate that depend on collision frequency induce by the relative motion. Relative motion caused by Brownian movement is called perikinetic flocculation and if it is caused by velocity gradient is called orthokinetic that flocculation by external forces categorized in the second one [20].

Generally, coagulation and flocculation remove turbidity, colour, pathogens, algae, phosphates, bad smell and bad taste factors and some others then it is an important step of water treatment that its improvement means more efficient treatment.

Hence, coagulants should be added to water in flash mixer for flocculation in flocculation basin. Flocculation improvement depends on different factors like PH, temperature, coagulant efficiency, but high-energy and rapid-mix to properly disperse coagulant and promote particle collisions is needed to achieve good coagulation what is followed by flocculation process but with different mixing velocity and energy to prevent floc from tearing apart.

Anyway, flash and effective dispersion of coagulant improve collision of particles and then micoflocs formation that will improve flocculation what finally will improve sedimentation as more efficient water treatment [21].

Refer to coagulation efficiency as an important factor for flocculation then sedimentation, nowadays though different nanoparticles usage make all these processes more efficient, but method of ultrasonic treatment gives the possibilities to increase the size of nanoparticles moving in the water [22]. That means better mixing and 20% lower scattering intensity (Fig 4) then more homogenous solution.

On the other hand, flocs growing during flocculation as a significant process needs precise control that could be achieved via accurate mechanism like ultra-sonication.

Therefore, all of them conduct coagulation improvement, more efficient flocculation and sedimentation then less plant construction that means plant that is more feasible.

4. Conclusions

Ultra-sonication is an effective method of water treatment from different nanoparticles used for cleaning the water from different toxic and pathogenic substances. Along with sound waves parameters (frequency, harmonic modes etc.) the effectiveness of ultrasonic treatment is very depend of general power and density of ultrasound flow.

Development of construction of transducing systems with flexible electromagnetic and mechanical properties will give the possibilities to build new precise instruments and ultrasonic sources allow purification of water from Nano sized particles of different origin as well as from their clusters and conglomerates.

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