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Synthesis and Technological Innovation of Applying Oxide Nanomaterials in Wastewater Treatment by Flotation

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Abstract. The appearance and development of nanotechnology gave new and efficient modalities for pollutants removal from wastewaters by using new compounds called nanomaterials which possess unique structural and morphological properties. In this paper we investigated the application of $CoFe_2O_4$ nanomaterial for increasing the efficiency of oily wastewater treatment by flotation. $CoFe_2O_4$ nanomaterial was prepared by precipitation method. Prior testing their application in wastewater treatment by flotation, the oxide nanomaterial was structural and morphological characterized by XRD and TEM analyses. The influence of $CoFe_2O_4$ nanomaterial on oily wastewater depollution by flotation process was investigated by measuring the following parameters: treatment efficiency [%] and the stability of froth.

1. Introduction

Society today faces the extensive growth of wastewater generated from various industries and from household use. This has become a very important issue from the environmental point of view and has led to the enforcement of new and stricter rules and standards limiting the pollution caused by these wastewaters. Oily wastewater results from various industries and has a high potential to degrade the environment especially soil and water. As such, they represent a major environmental problem. To protect the environment, oily wastewater treatment is unavoidable.

The concentrations of oil in municipal and industrial wastewater effluents are strictly monitored [1-6] as they could cause serious health and environmental problems. For example, in the water resulting from petroleum plants the discharge limits of these substances are regulated at a monthly average of 29 mg/l with a daily maximum of 42 mg/l [7]. To meet these stringent discharge limits, oil substances can be effectively separated from wastewater using following practical technologies:

1. Gravity settling [8] and corrugated plate interceptors;
2. Centrifugal separation using hydrocyclone [9-11];
3. Chemical pre-treatment (coagulation-flocculation) [12-14];
4. Coalescing media [15-17];
5. Gas flotation (induced gas flotation [18-22] and dissolved gas flotation [23-26];

6. Biological processes (membrane bio-reactor [27-32] and activated sludge;
7. Media Filtration (resin, polymer, sand, clay, garnet, silica, walnut shell) [33, 34].

The conventional process of wastewater treatment consists in a series of combined physical, chemical and biological steps. The existence of suspended solids and stable fats emulsion in wastewaters makes their treatment to be extremely difficult in term of technical concerns [35].

Nowadays, the challenge is to find new, low cost and more efficient technologies for the treatment of wastewaters to decrease pollution and comply with the existing regulations. Dissolved air flotation system can be used as process for removing finest suspended particles and fats from water. When air is introduced in water forms small bubbles that contact suspended particles in water so by decreasing their density these particles gain enough energy to be floated. Flotation extraction represents a highly efficient method for the treatment of dilute aqueous solutions with the help of flotation devices [36]. By passing air through the solution (wastewater), a high interface is created between the solution and the surfactants that are intended to collect the unwanted components.

Low molar mass surfactants and surface-active polymers are used to facilitate the dispersion of powdered materials in a liquid solution and are very often used as emulsifiers for preparing emulsions and as stabilizers in the production of foams [3]. The use of solid (nano- or micro-) particles in the production and stabilization of foams is not exploited as much as the use of low molar mass surfactants or surface-active polymers and represents a new and promising perspective. The incorporation of solid particles into surfactant-stabilized aqueous foams has been used for a long time, and their influence on the formation and stability of the foam depends on the type of surfactant, on the size of the particles and on the concentration [37]. Concerning spherical particles that adsorb to water-air or water-oil interfaces, the most relevant parameter is considered to be the contact angle θ, which is formed at the contact between the particle and the interface. For hydrophilic particles, θ angle measured into the aqueous phase is normally $<90^o$ and a larger fraction of the particle surface resides in water than in the nonpolar phase. For hydrophobic particles, θ is generally greater than 90^o and the particle resides more in air or oil than in water [3]. By analogy with surfactant molecules, the monolayers will curve such that the larger area of the particle surface remains on the external side, giving rise to air or oil-in-water when $\theta<90^o$ and water-in-air or oil when $\theta<90^o$ (Figure 1). The first include aqueous foams and o/w emulsions, respectively, whilst the latter include aerosols and w/o emulsions (Figure 2) [1].

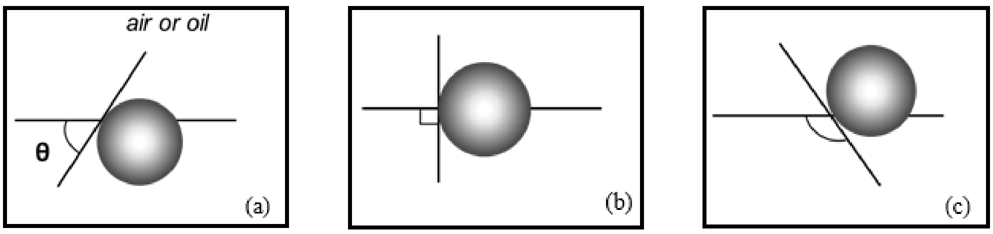

Figure 1. Position of a small spherical particles at a planar fluid-water interface for a contact angle measured through the aqueous phase: less than 90^o – (a), equal to 90^o – (b), and greater than 90^o – (c) [1].

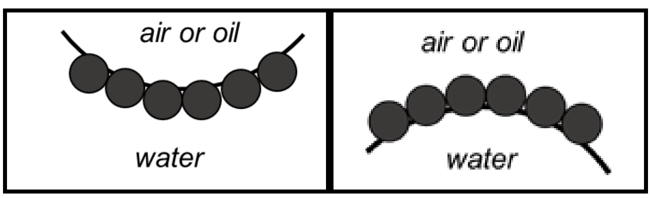

Figure 2. Corresponding probable positioning of particles at a curved fluid-water interface.

For θ <90°, solid-stabilized aqueous foams or o/w emulsions may form (Figure 1, a). For θ>90°, solid-stabilized aerosols or w/o emulsions may form (Figure 1, c) [1].

For testing the influence of nanomaterials in the wastewater treatment by flotation, we chose cobalt ferrite, having the formula $CoFe_2O_4$ obtain by precipitation method.

2. Materials and methods

The preparation of cobalt ferrite nanomaterial tested was already published in another article [38]. The chemical reagents used in this study are ferric nitrate ($Fe(NO_3)_3$. $9H_2O$), cobalt nitrate ($Co(NO_3)_2$. $6H_2O$), ammonia solution 28%, polyvinylpyrrolidone (PVP), polyethylene glycol (PEG). The average crystallite size of $CoFe_2O_4$ obtained by calcination at 400^0C calculated by Scherrer formula was 18 nm. By TEM investigation was revealed that cobalt ferrite particles are nearly monodisperse and the mean particle size is 21 nm. Also, was observed that the cobalt ferrite nanoparticles tend to agglomerate due to their magnetic properties forming honeycomb structure [38].

The experiments were done on a synthetic wastewater containing a concentration of oil of 25% in the presence and in the absence of CoFe2O4 nanomaterial. Dissolved air flotation system contained also 5% of anionic surfactant and 5 % of amphoteric surfactant.

3. Results and discussion

During the experiments we observed the following: the decreasing of time needed for treatment of wastewater when the cobalt ferrite nanoparticles were used in the flotation process, from 10 min to 2 min; the increasing of stability of the formed foam when were used cobalt ferrite nanoparticles in the flotation process (7 h in comparison with 40 min). In the large-scale wastewater treatment technologies is needed sufficient time to remove the foam having the pollutant on the surface of wastewater; the the yield of wastewater treatment when was used cobalt ferrite nanomaterial was 100%.

The tested nanomaterials will be further tested by the authors in situ conditions. An experimental installation was designed, and the simplified process diagram is presented in Figure 3. The main components of the dissolved air flotation (DAF) unit are: the pressured capsule (in which air and water are introduced under pressure), the nanoparticle dosing system and the lamellar settler (Figure 4).

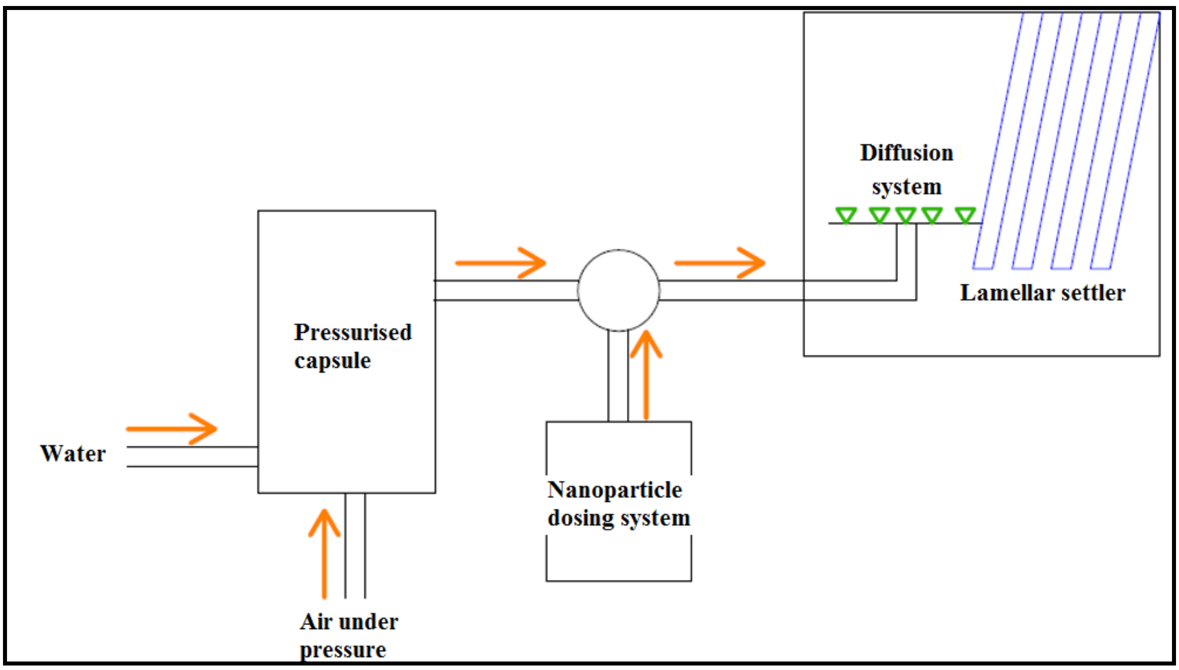

Figure 3. The process diagram for an improved DAF.

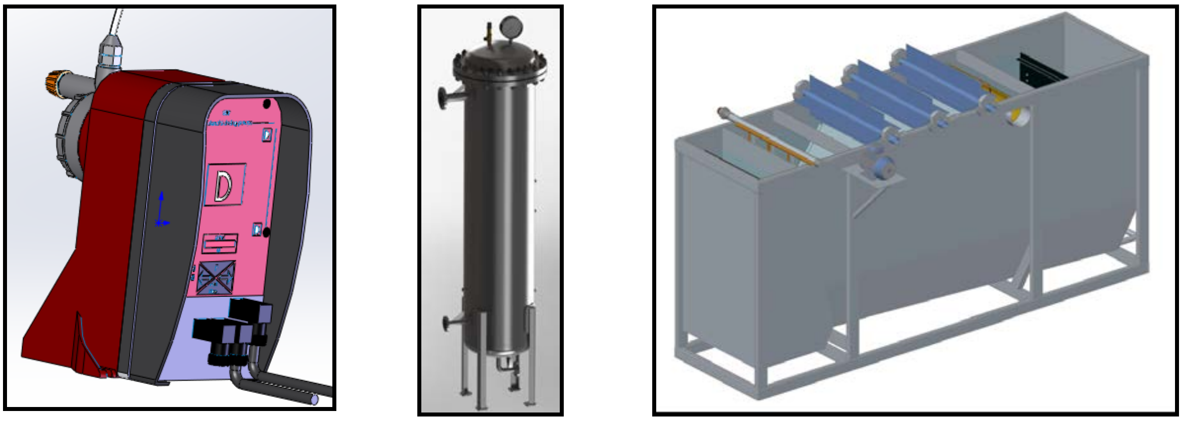

Figure 4. The main components of an improved dissolved air flotation unit (from left to right: nanomaterial solution dosing pump, pressured capsule, lamellar settler).

4. Conclusions

The investigation of applying $CoFe_2O_4$ nanomaterial in the wastewater treatment by flotation showed two important advantages: in the increasing the stability of the foam containing the oil pollutant and the decreasing of the time needed for wastewater treatment.

5. References

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