Effect of $CuFe_2O_4$ Nanoparticles on Fronth Stability in Wastewater Treatment by Flotation

CRISTINA ILEANA COVALIU[1]*, IOANA CORINA MOGA[2], EUGENIU VASILE[3], MIHAI GABRIEL MATACHE[4], GABRIEL PETRESCU[2]

[1] University Politehnica of Bucharest, Faculty of Biotehnichal Systems Engineering, 313 Splaiul Independentei, 060042, Bucharest, Romania

[2] SC DFR Systems SRL, 46 Drumul Taberei Str., ap. 23, Bucharest, Romania

[3] University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Polizu Str., 011061, Bucharest, Romania

[4] National Institute of Research-Development for Machines and Installations Designed to Agriculture and Food Industry, 6 Ion Ionescu de la Brad, 013811, Bucharest, Romania

Flotation is a method applied very often in wastewater treatment. One way of improving the efficiency of wastewater treatment by flotation is increasing the quantity and stability of foam. For this purpose, in this paper was studied $CuFe_2O_4$ oxide nanomaterial for treatment of wastewater containig oil as pollutant. $CuFe_2O_4$ was prepared by coprecipitation method and their structural and morphological characterisation was done by XRD and TEM analyses. In order to evaluate their potential of application in wastewater treatment by flotation were invesigated the separation efficiency of oil from wastewater and the quantity and foam stability.

Keywords: wastewater treatment, oxide nanomaterials, copper ferrite, flotation

The amounts of oil in municipal and industrial wastewater effluents are carefully 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 daily maximum of 42 mg L^{-1} and monthly average of 29 mg· L^{-1} [7]. To comply with these stringent discharge limits, oily substances can be separated from wastewater using following technologies:

1. Gravity settling [8];
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 bioreactor [27-32] and activated sludge);
7. Media Filtration (resin, polymer, sand, clay, garnet, silica, walnut shell [33, 34]).

Nanotechnologies are considered at the moment *emerging technologies* which can revolutionize a large number of application areas. In the field of wastewater treatment, as regarding the flotation, nanoparticles may act as surfactant molecules during wastewater treatment by flotation, being incorporated into surfactant-stabililised foams for some years [35-37]. Some studies found in the scientific literature presented the ability of nanoparticles to act as foams/emulsion stabilisers [36,38]. The formation and the stability of foams are dependent of the particles size, surfactant type and concentration [39-47].

Wastewater resulting from the food industry is represented by washing water of raw material, technological waters, condensation or cooling water, water from washing and disinfection of processing facilities, machinery and packaging, water from sanitary facilities.

Oily wastewater is wastewater with oils or fats resulted from various industries. Oily wastewater has an increased potential to degrade the environment especially soil and water. Because of this reason oily wastewater is considered an environmental problem and for preventing this type of pollution, oily wastewater treatment is unavoidable.

The efficiency of treating wastewater using flotation systems is mainly given by the structure and stability of a froth phase. Therefore, the separation efficiency and selectivity of the flotation process relates directly to froth stability, bubble coalescence and bubble size distribution [48, 49].

One way to ensure the existence of a stable froth is to use frothers (foam stabilizers), which have a positive effect on froth stability, bubble coalescence, mobility and also on the adhesion, entrainment and drainage of suspended matter.

In order to investigate the application of nanomaterials as froth stabiliser in flotation, our experimental study was based on testing the copper ferrite ($CuFe_2O_4$) nanomaterial for the removal of oil from wastewater.

$CuFe_2O_4$ nanomaterial was prepared by coprecipitation method. Copper ferrite structural and morphological characterisation was done by XRD and TEM analyses. In order to evaluate their potential of application in oil removal from wastewater by flotation were evaluated various parameters such as: the separation efficiency of oil from wastewater and the quantity and foam stability.

Experimental part

Material and methods

Ferric chloride ($FeCl_3 \cdot 6H_2O$), copper chloride ($CuCl_2 \cdot 6H_2O$), polyethylene glycol 200 (PEG200) and polyvinylpyrrolidone (PVP), sodium hydroxide (NaOH) pellets were supplied from Sigma Aldrich and were used as received.

The preparation of copper ferrite nanomaterial tested in the flotation process was done by precipitation method.

The precipitation was accomplished using 0.7 mol L^{-1} aqueous solution of sodium hydroxide and the reaction pH was 12. The molar ratio Cu^{2+}: Fe^{3+}: PEG: PVP unit was 1:2:7:7. The precipitate was separated by centrifugation and washed several times with water. Finally, $CuFe_2O_4$ powder was obtained by precursor calcination at 550^0C for 3 h.

* email: cristina_covaliu@yahoo.com

The X-ray diffraction (XRD) analysis was obtained using a X'PERT PRO MPD with Cu-Kαradiation (λ = 0.15418 nm) and transmission electron microscopy (TEM) investigation was done on FEI Tecnai ™G²F30 S-TWIN with EDAX energy dispersive X-ray spectrometer.

The experiments were done on a synthetic wastewater containing a concentration of oil of 10% in the presence and in the absence of $CuFe_2O_4$ nanomaterial. Dissolved air flotation system contained also 0.1% of anionic surfactant and 0.1 % of amphoteric surfactant.

Results and discussions

X-ray diffraction

The nano-powder obtained from synthesis was analyzed by XRD. The XRD pattern has proved the formation of single phase compound with inverse spinel structure and tetragonal symmetry for $CuFe_2O_4$ (fig. 1). The average crystallite size was 14 nm.

TEM investigation

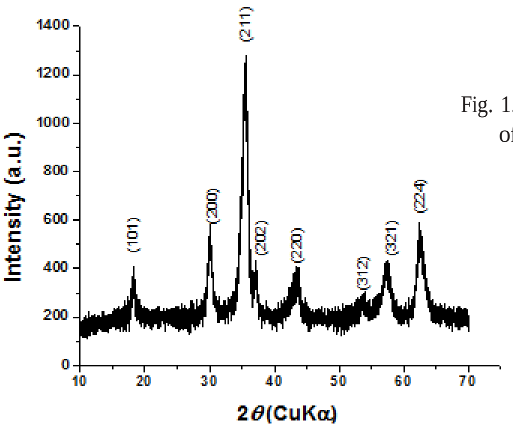

Fig. 1. XRD pattern of $CuFe_2O_4$

The morphology of the obtained ferrite nanoparticle was investigated by TEM. Copper ferrite powder presents a uniform size distribution and a mean particles size of 18 nm (fig.2). The synthesized magnetic nanoparticles show both spherical and polyhedral shape.

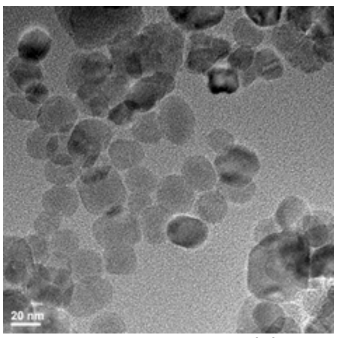

Fig. 2. TEM image of $CuFe_2O_4$

The investigation of flotation process for treatment of oily wastewater with and without copper ferrite has led to the following conclusions:

a) the decreasing of time for wastewater treatment when the copper ferrite particles were used in the flotation process, 2,5 min in comparison with 10 min;

b) the increasing of stability of the formed foam when were used copper ferrite nanoparticle in the flotation process (5 h in comparison with 40 min). This aspect is important for the large-scale wastewater treatment processes when is needed sufficient time to remove the foam having the pollutant on the surface of wastewater;

c) the obtaining of a wastewater efficiency treatment of 100 % only in the testes in which was used copper ferrite nanomaterial. The investigation of flotation applied to oily wastewater without using copper ferrite conducted to 90 % treatment efficiency.

d) the obtaining of an identical value of the amount of foam formed in the flotation process in both situations.

Conclusions

The preliminary study of the influence of using $CuFe_2O_4$ nanomaterial in the wastewater treatment by flotation revealed that the main advantages were observed in the increasing the stability of the foam containing the oil pollutant, the decreasing of the time needed for wastewater treatment and the increasing of wastewater treatment efficiency. The results sustain further research on this subject of interest by investigating other several types of nanoparticles having different morphologies for wastewater treatment by flotation.

Acknowledgement: We hereby acknowledge the found project of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-PTE-2016-0183, No. 25 PTE/2016, Improved technology for treatment by flotation of highly loaded wastewater.

References

1.DIYA'UDDEEN, B.H., DAUD, W.M.A.W, ABDUL AZIZ, A.R., Process Safety and Environmental Protection, **89**, 2011, p. 95.

2.FARMAKI, E., KALOUDIS, T., DIMITROU, K., THANASOULIAS, N., KOUSOURIS, L., TZOUMERKAS, F., Desalination, **210**, 2007, p. 52.

3.BINKS, B.P., Current Opinion in Colloid & Interface Science, **7**, 2002, p. 21.

4.MUELLER, S.A., KIM, B.R., ANDERSON, J.E., GASLIGHTWALA, A., SZAFRANSKI, M.J., GAINES, W.A., Practice Periodical Hazardous Toxic and Radioactive. Waste Management, **7**, 2003, p. 156.

5.RAHA, D., Environmental Forensics, **8**, 2007, p. 371.

6.RINCON, G.J., La MOTTA, E.J., Journal of Environmental Management, **144**, p. 50.

7.HANK, C.R., Mechanisms for flotation of fine oil droplets. SME Annual Meeting & Exhibit, Denver, 2011, p. 1.

8.STEWAR, T.M., ARNOLD, K., Elsevier, 2009, p. 107.

9.BAI, Z., WANG, H., TU, S.T., Chemical Engineering Research and Design, **89**, 2011, p. 55.

10.BELAIDI, A., THEW, M.T., MUNAWEERA, S.J., The Canadian Journal of Chemical Engineering, **81**, 2003, p. 1159.

11.HUSVEG, T., RAMBEAU, O., DRENGSTIG, T., BILSTAD, T., Mining Engineering, **20**, 2007, p. 368.

12.MOSTEFA, N.M., TIR, M., Desalination, **161**, 2004, p. 115.

13.SANTO, C.E., VILAR, V.J.P., BOTELHO, C.M.S., BHATNAGAR, A., KUMAR, E., BOAVENTURA, R.A.R., Chemical Engineering Journal, **183**, 2012, p. 117.

14.ZOUBOULIS, A., AVRANAS, A., Colloids and Surfaces A: Physicochemical and Engineering Aspects, **172**, 2000, p. 153.

15.MA, S., KANG, Y., CUI, S., Journal of Dispersion Science and Technology, 2013.

16.OWENS, N., LEE, D.W., Produced Water Workshop, 1–19 Aberdeen, 2007, Scotland.

17.ZHANG, L., ZHU, T., SUN, Y., JIANG, B., Journal of Dispersion Science and Technology, **36**, 2014, p. 182.

18.CASTILLO, A., NIEVA, A.D., CAPARANGA, A.R., AIChE 2012-2012 AIChE Annual, Meeting Conference Proceedings, 2012.

19.El-KAYAR, A., HUSSEIN, M., ZATOUT, A.A., HOSNY, A.Y., AMER, A.A, Separation Science and Technology, 1993, 3, p. 25.

20.HOSEINI, S.M., SALARIRAD, M.M., ALAVI, MOGHADDAM, M.R., Desalination Water Treatment, **53**, 2013, p. 300.

21.MEYSSAMI, B., KASAEIAN, A.B., Bioresource Technology, **96**, 2005, p. 303.

22.PAINMANAKUL, P., SASTARAVET, P., LERSJINTANAKARN, S. KHAODHIAR, Chemical Engineering Research and Design, **88**, 2010, p. 693.

23.ABO-EL ELA, S.I., NAWAR, S.S, Environment International, **4**, 1980, p. 47.
24.BEHIN, J., BAHRAMI, S., Chemical Engineering and Processing: Process Intensification, **59**, 2012, p. 1.
25.MULTON, L.M., VIRARAGHAVAN, T., Waste Management, **12**, 2008, p. 25.
26.YOUNKER, J.M., WALSH, M.E., Journal of Environmental Chemical Engineering, **2**, 2014, p. 692.
27.KOSE, B., OZGUN, H., ERSAHIN, M.E., DIZGE, N., KOSEOGLU-IMER, D.Y., ATAY, B., KAYA, R., ALTINBAS, M., SAYILI, S., HOSHAN, P., ATAY, D., EREN, E., KINACI, C., KOYUNCU, I., Desalination **285**, 2012, p. 295.
28.PENDASHTEH, A.R., ABDULLAH, L.C., FAKHRU'L-RAZI, A., MADAENI, S.S., ZAINAL ABIDIN, Z., AWANG BIAK, D.R., Process Safety and Environmental Protection, **90**, 2012, p. 45.
29.SOLTANI, S., MOWLA, D., VOSSOUGHI, M., HESAMPOUR, M., Desalination, **250**, 2010, p. 598.
30.ZHIDONG, L., NA, L., HONGLIN, Z., DAN, L., Petroleum Science and Technology, **27**, 2009, p. 1274.
31.TELLEZ, G.T., NIRMALAKHANDAN, N., GARDEA-TORRESDEY, J.L., Advanced in Environmental Research, **6**, 2002, p. 455.
32.ZHANG, H., XIANG, H., ZHANG, G., CAO, X., MENG, Q., Journal of Hazardous Materials, **167**, 2009, p.217.
33.ANGELOVA, D., UZUNOV, I., UZUNOVA, S., GIGOVA, A., MINCHEV, L., Chemical Engineering Journal, **172**, 2011, p. 306.
34.BLUMENSCHEIN, C.D., SEVERING, K.W., BOYLE, E., AISE Steel Technolology, **78**, 2001, p. 33.
35.BINKS, B. P., Current Opinion in Colloid & Interface Science, **7**, 2002, p. 21.
36.DICKINSON, E., ETTELAIE, R., KOSTAKIS, T., MURRAY, B.S., Langmuir, **20**, 2004, p. 8517.
37.HOROZOV, T.S., Current Opinion in Colloid & Interface Science, **13**, 2008, p. 134.
38.LIU, Q., ZHANG, S., SUN, D., XU, J., Colloids and Surfaces A: Physicochemical and Engineering Aspects, **355**, 2010, p. 151.
39.PAUNOV, V.N., BINKS, B.P., ASHBY, N.P., 2002, Langmuir **18**, p. 6946.
40.SATHTHASIVAM, J., LOGANATHAN, K., SARP, S., Chemosphere, **144,** 2016, p. 671.
41.WANG, L.K., SHAMMAS, N.K., SELKE, W.A., AULENBACH, D.B., 2010., http://dx.doi.org/10.1007/978-1-60327-133-2.
42.ZECH, O., HAASE, M.F., SHCHUKIN, D.G., ZEMB, T., MOEHWALD, H, Colloids and Surfaces A: Physicochemical and Engineering Aspects, **413**, 2012, p. 2.
43.BEJINARIU, C., SANDU, A.V., BACIU, C., SANDU, I., TOMA, S.L., SANDU, I.G., Rev. Chim (Bucharest), **61**, no. 10, 2010, p. 961.
44.ABDULLAH, M.M.A., NORDIN, N., TAHIR, M.F.M., KADIR, A.A., SANDU, A.V., International Journal of Conservation Science, **7**, no. 3, 2016, p. 753.
45.SAGEATA, R., DAMIAN, N., MITRICA, B., Urbanism Architecture Constructions, **7**, no. 3, 2016, p. 199.
46.SAHU, P.C., International Journal of Conservation Science, **8**, no. 1, 2017, p. 145.
47.PETRISOR, A.I., International Journal of Conservation Science, **7**, no. 3, 2016, p. 759.
48.CILEK, E.C., KARACA S., International Journal of Mineral Processing, **138**, 2015, p. 6.
49.FARROKHPAY, S., Advances in Colloid and Interface Science, **166**, 2011, p. 1.

Manuscript received: 10.04.2017