



The application of hematite ($\alpha\text{-Fe}_2\text{O}_3$) nanoparticles in coagulation and flocculation processes of River Nile Rosetta branch surface water

Ahmed A. Almarasy¹ · Saleh A. Azim¹ · El-Zeiny M. Ebeid^{1,2}

© Springer Nature Switzerland AG 2018

Abstract

The aim of this paper is to investigate the performance of hematite nanoparticles in coagulation process in turbidity removal from naturally and artificially turbid raw surface water. Alum is widely used as coagulant in drinking water treatment processes in Egypt. To avoid residual aluminum problems, hematite nanoparticles have been used as coagulant. In this study, the prepared hematite nanoparticles before and after agglutination are characterized by using electron microscope (TEM, SEM). In addition to quality tests of treated water by hematite nanoparticle after coagulation process, tests were also conducted in comparison to alum. Effect of hematite nanoparticles dosage on the coagulation ability was studied to determine the highest turbidity removal. The results show the highest turbidity removal by hematite nanoparticles of values up to 93.8%.

Keywords Coagulant · Flocculation · Hematite · Nanoparticles · Raw surface water · Turbidity removal

1 Introduction

Coagulation and flocculation are predominant methods used for removing colloidal material during drinking water treatment. Particles removal depends on particles surface, stability and the coagulant type [1]. Flocculation is the process of destabilizing suspended particle systems and bridging the aggregated flocs to form larger agglomerates that settle down under gravity [2]. The coagulation process creates agglomerates or flocs, which can be bridged or linked together by flocculants to form bigger agglomerates that precipitate faster under gravity [3].

Many parameters affect the quality of drinking water. Turbidity is considered the most important parameter for measuring the quality of water. Turbidity is caused by suspended particles, inorganic matter and microscopic organisms. Coagulation/flocculation process is considered the primary process in drinking water treatment steps. Settling and filtration are steps that come after coagulation process [4, 5].

There are many coagulants that are widely used in the coagulation process such as aluminum and iron salts [6]. Mixing speed and water pH, the efficiency of the coagulation process depends on the nature and the dosage of coagulants. Hybrid flocculants are considered another type of flocculant that depends on inorganic salts and organic flocculant as combination [7, 8]. There are many environmental consequences that result from using of these chemicals particularly aluminum such as Alzheimer disease and carcinogenic properties [9].

Nanoremediation has been very important in recent years due to their high adsorption capacity and their large surface area [10]. The unique properties of nanomaterials in water decontamination enable nanomaterials not just to play an important role in water treatment but also allow for a more cost-effective clean-up process [11–14].

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) colloids have the tendency to form complexes with natural organic matter (NOM) which are precursor compounds that form by-products like hazardous trihalomethanes (THMs) [15]. Thiruvengkatchari et al.

✉ Ahmed A. Almarasy, proahmed1989@yahoo.com | ¹Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt. ²Misr University for Science and Technology (MUST), 6th of October City, Egypt.

reported the application of hematite ($\alpha\text{-Fe}_2\text{O}_3$) colloids as a flocculent in cross-flow microfiltration (CFMF) which is a very useful process for removing colloids and suspended solids in water [15, 16]. Application of iron oxide nanoparticles-based nanomaterials for removal of heavy metals is well-known adsorbents for remediation of water [17]. Free chlorine can react with numerous organic materials such as amino acids, humus, environmental pollutants in raw surface water to yield halogenated organics [18].

In the present study, we report the application of hematite nanoparticles on their own as efficient coagulant in surface water treatment showing the highest turbidity removal as high as 93.8%.

2 Materials and methods

2.1 Description of drinking water treatment plant

Drinking water in Egypt is overwhelmingly provided by the River Nile. In the present study, water samples were collected from River Nile Rosetta Branch at Basyoun City at the uptake site of Basyoun's Drinking Water Company. The uptake site is located 5 m from canal bank, and samples were collected in the period 3–15 of August.

Sample	Values Prior to treatment
Temperature ($^{\circ}\text{C}$)	24.1 ± 0.05
Initial turbidity (NTU)	12.19 ± 0.095
Final turbidity (NTU)	9 ± 0.005
Total dissolved solids (mg L^{-1})	208 ± 0.5
Conduct. ($\mu\text{S cm}^{-1}$)	354 ± 1
$(\text{PO}_4)^{-3}$ (mg L^{-1})	0.10 ± 0.005
Alkalinity (mg L^{-1})	134 ± 1
Ammonia (mg L^{-1})	0.27 ± 0.005
Nitrate (mg L^{-1})	0.27 ± 0.005
Nitrite (mg L^{-1})	0.23 ± 0.01
pH	7.55 ± 0.005
Fe^{2+} (mg L^{-1})	0.54 ± 0.005
Ca^{2+} hardness (mg L^{-1})	81 ± 0.5
Mg^{2+} hardness (mg L^{-1})	44 ± 0.5
Total hardness	125 ± 0.5

2.2 Preparation of hematite nanoparticles

Hematite nanoparticles were prepared by using a solution FeCl_3 as described before [19]. Briefly, 15 mL from (0.1 M) FeCl_3 was added to 100 mL stirred boiling distilled water drop by drop. The solution colour was yellow and then turned to red, and upon excess addition of FeCl_3 , the final colour of solution changed to dark red. Then

this solution was heated to reflux for 30 min. The resulting solution was kept at room temperature to cool [19, 20]. The solution can exist in colloidal state without any of precipitation. Given hematite having trigonal hexagonal crystal structure with cell parameters $a = 5.038 \text{ \AA}$, $c = 13.772 \text{ \AA}$; $Z = 6$ [21], the concentration of as-prepared hematite nanoparticles under the present experimental conditions was $2.98 \times 10^{-6} \text{ M}$.

2.3 Characterization of prepared hematite nanoparticles

The structure of hematite nanoparticles was confirmed by several techniques such as UV–Vis spectra, which was recorded using a CARY Bio 100 spectrophotometer. X-ray diffraction was recorded using a Philips PW 1390 X-ray diffractometer using copper target with nickel filter. FTIR spectra were carried out using FTIR spectrophotometer model 670 (NEXUS) Nicolet in transmittance mode with a resolution of 4 cm^{-1} and 34 scans min^{-1} in the $4000\text{--}400 \text{ cm}^{-1}$. Transmission electron microscopy (TEM) was applied on transparent samples prepared as suspended solution in distilled water. TEM micrographs were taken with high-resolution transmission electron microscope (JEOL JEM-2100) at an accelerating voltage of 80 kV (Tanta university, Egypt).

2.4 Coagulation flocculation experiments (jar tests)

Fill the beakers with test water. After placing beakers on their position, the paddles should be in their position identically. As soon as the different dosages flocculent was added to beakers as shown in Table 1, mix the solution at 150 rpm for 2 min and then mix slowly the solution at 45 rpm for 30 min. Allow settling to occur for 30 min and then remove the supernatant of the solution from the top by siphoning. Turbidity was analyzed by using turbidity meter (Nephelometers NTU).

Originally, five concentrations of flocculants were tested to locate the optimum flocculent dosage. Measurements were then taken in duplicate in two authorized water analysis laboratories; one is Basyoun's Drinking Water Company Laboratory, and the other is Gharbia Drinking and Waste Water Central Laboratory. The methods used to evaluate TDS, conductivity, $(\text{PO}_4)^{-3}$, alkalinity, total hardness, ammonia, nitrate, nitrite and Fe^{2+} are those adopted by these two professional laboratories according to standard methods. Routine assessment of these contaminants is also carried out on weekly basis.

Table 1 Effect of hematite nanoparticles dosage on water sample turbidity, alkalinity, pH and total dissolved solids (TDS) according to jar test and settling time of 30 min

Volume of hematite nanoparticles solution (mL) added to 1 L water sample	Concentration of hematite nanoparticles (M)	Turbidity (NTU)	Percentage turbidity removal (%)
20	5.85×10^{-8}	1.29 ± 0.01	89.4 ± 0.01
25	7.25×10^{-8}	1.22 ± 0.01	89.9 ± 0.01
30	8.7×10^{-8}	0.75 ± 0.005	93.8 ± 0.005
35	1.01×10^{-7}	0.80 ± 0.02	93.4 ± 0.02
40	1.15×10^{-7}	0.86 ± 0.01	92.9 ± 0.01

2.5 Characterization of prepared hematite nanoparticles after agglutination

Scanning electron microscopy (SEM) was applied on samples that prepared as suspended solution in distilled water. It was investigated using JEOL scanning electron microscope, of the model JSM 6510 LV.

3 Results and discussion

3.1 Characterization of iron oxide nanoparticles

UV–Vis spectrum of 9-nm-diameter iron oxide nanoparticles aqueous solutions a characteristic absorption

band centered at $\lambda_{\max} = 405$ nm. The XRD pattern of iron oxide nanoparticles is shown in Fig. 1a. Hematite nanoparticles ($\alpha\text{-Fe}_2\text{O}_3$) showed the hexagonal phase (Fig. 1b) with the peaks around $2\theta = 32^\circ, 35^\circ, 40^\circ$ and 50° [22, 23]. No other phase was detected for prepared hematite nanoparticles, indicating the sample high purity. The FTIR spectrum of as-prepared hematite nanoparticles (Fig. 1c) shows bands at 570 cm^{-1} and 630 cm^{-1} due to Fe–O stretching mode of hematite. The band at 468 cm^{-1} results from lattice mode of FeO_6 . The band at 3420 cm^{-1} is due to adsorbed water that also gives rise at 3217 cm^{-1} and 1640 cm^{-1} which indicates the hydroxyl stretching mode and the hydroxyl bending mode, respectively [24, 25]. The transmission electron microscopy (TEM) images (Fig. 1d) show a 9-nm-diameter iron oxide nanoparticles.

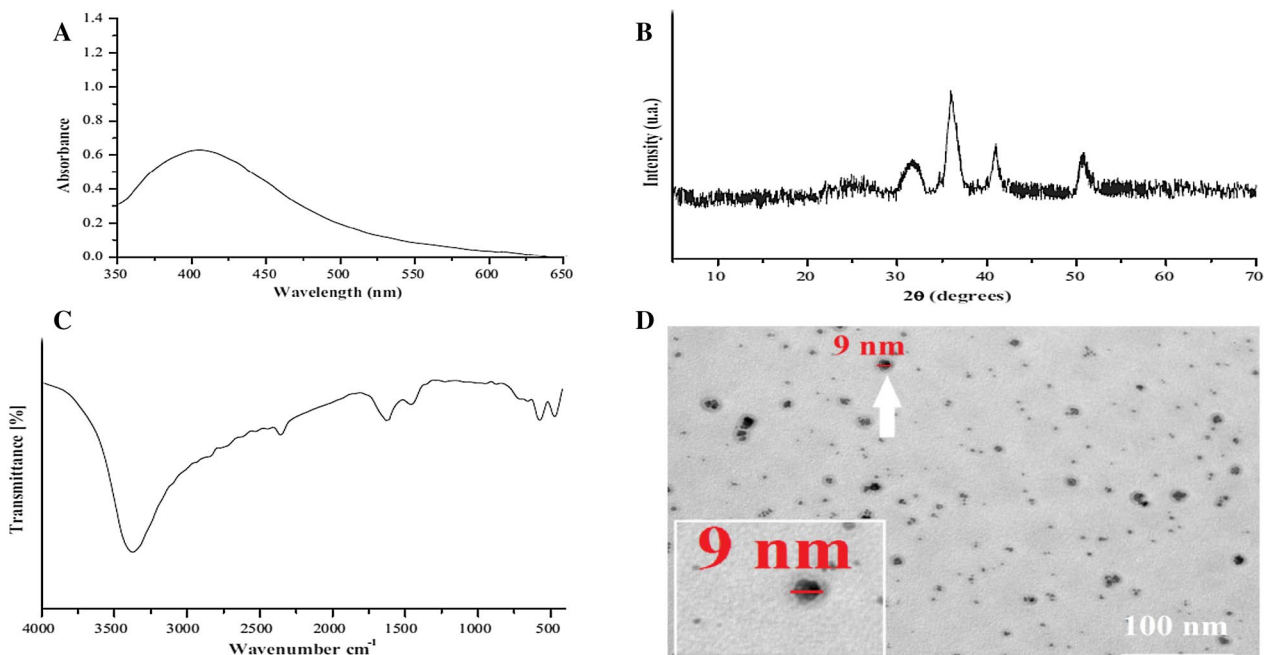


Fig. 1 Structural and spectroscopic data of the as-prepared hematite nanoparticles **a** UV–Vis spectrum, **b** XRD patterns, **c** FTIR spectrum and **d** transmission electron microscopy (TEM) images for as-prepared hematite nanoparticles

3.2 Investigation of the optimum coagulant conditions

3.2.1 Effect of hematite nanoparticles dosage

The coagulant dosage is considered the most critical parameters in the coagulation and flocculation processes. Variety of concentration of 0–40 mL of hematite nanoparticles (2.98×10^{-6} M) was examined using jar test at pH=7.55. According to WHO (World Health Organization) recommendations, turbidity should be less than 5 NTU before water can be adequately cleared. After using different volumes of hematite nanoparticles as coagulant added to 1L water samples, the percentage of turbidity removal ranges from 89.4 ± 0.01 to $93.8 \pm 0.005\%$ [26].

The highest turbidity removal of $93.8 \pm 0.005\%$ was achieved upon using 30 mL of hematite nanoparticles concentration of 2.98×10^{-6} M per liter of water sample. This is compared to a highest turbidity removal of

95.4% that occurs upon using 2.0×10^{-4} M alum solution as shown in Table 1 and Fig. 2.

3.2.2 Discussions of values of quality tests

The extent of agglutination and subsequent turbidity removal is affected by the volume of coagulants whether hematite nanoparticles or alum. Table 2 shows the turbidity changes as a function of hematite nanoparticle dosages according to jar test following 30-min settling time. The data together with some other parameters such as total dissolved solids (TDS), conductivity, $(\text{PO}_4)^{3-}$ concentration, alkalinity, ammonia concentration, nitrate concentration, nitrite concentration, pH and Fe^{2+} concentration are summarized in Tables 2.

Very slight rise in total dissolved solids concentration, conductivity and alkalinity occurs after using alum and hematite nanoparticles as shown in Fig. 3 and Table 2.

Ammonia concentration was measured prior and after addition of 30-mL hematite nanoparticles (2.98×10^{-6} M).

Fig. 2 **a** Comparison between turbidity of blank water sample and water samples after coagulation process using alum and hematite coagulants. **b** Turbidity changes as a function of hematite nanoparticle (2.98×10^{-6} M) dosages according to jar test and 30-min settling time

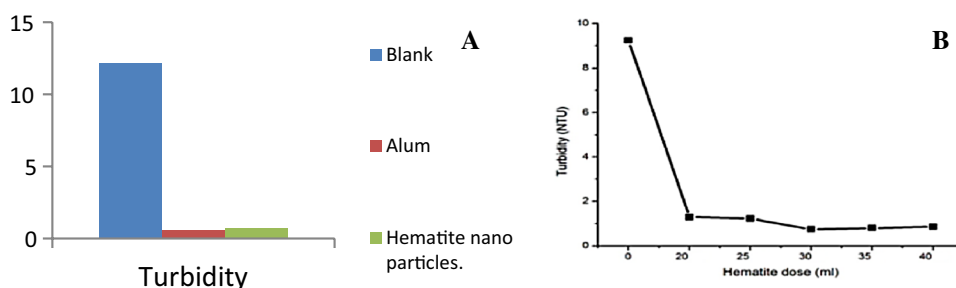


Table 2 shows some quality criteria of as-collected and water sample treated by addition of 10 mL of alum solution (0.02 M) to 1 L water sample from Rosetta branch of River Nile in comparison with addition of 30 mL of hematite nanoparticles solution (2.98×10^{-6} M) to 1 L water sample

Sample	Values prior to treatment	Values after treatment by alum	Values after treatment by hematite
Temperature (°C)	24.1 ± 0.05	24.2 ± 0.05	24.3 ± 0.05
Initial turbidity (NTU)	12.19 ± 0.095	12.19 ± 0.095	12.19 ± 0.095
Final turbidity (NTU)	9 ± 0.005	0.56 ± 0.005	0.75 ± 0.005
Total dissolved solids (mg L ⁻¹)	208 ± 0.5	180 ± 0.5	217 ± 0.5
Conduct. (µS cm ⁻¹)	354 ± 1	340 ± 3.5	410 ± 2.5
(PO ₄) ⁻³ (mg L ⁻¹)	0.10 ± 0.005	0.02 ± 0.0005	0.005 ± 0.0003
Alkalinity (mg L ⁻¹)	134 ± 1	120 ± 0.5	112 ± 2.5
Ammonia (mg L ⁻¹)	0.27 ± 0.005	0.16 ± 0.005	0.65 ± 0.005
Nitrate (mg L ⁻¹)	0.27 ± 0.005	0.29 ± 0.005	7.45 ± 0.01
Nitrite (mg L ⁻¹)	0.23 ± 0.01	0.21 ± 0.005	0.20 ± 0.005
pH	7.55 ± 0.005	7.42 ± 0.01	6.88 ± 0.01
Fe ²⁺ (mg L ⁻¹)	0.54 ± 0.005	0.02 ± 0.0005	0.05 ± 0.0005
Ca ²⁺ hardness (mg L ⁻¹)	81 ± 0.5	86 ± 0.5	80 ± 0.5
Mg ²⁺ hardness (mg L ⁻¹)	44 ± 0.5	38 ± 0.5	42 ± 0.5
Total hardness	125 ± 0.5	124 ± 0.5	122 ± 0.5

The end concentration of hematite nanoparticles is (8.7×10^{-8} M). The samples under study were collected and analyzed in the same time and just after collection giving criteria

The value of ammonia concentration prior to nanoparticle addition was measured as 0.27 mg L^{-1} . The value of ammonia concentration after nanoparticle addition was measured as 0.65 mg L^{-1} . The increased ammonia concentration upon using hematite nanoparticle as coagulant may result from the catalytic action of hematite nanoparticles on nitrite and/or the action of ammonium-oxidizing bacteria resulting in ammonium ion generation [27, 28].

Nitrate concentration was measured prior and after addition of 30-mL hematite nanoparticles ($2.98 \times 10^{-6} \text{ M}$). The value of nitrate concentration prior to nanoparticle addition was measured as 0.29 mg L^{-1} . The value of nitrate concentration after nanoparticle addition was measured as 7.45 mg L^{-1} . So, there is an increase in nitrate concentration upon using hematite nanoparticle as coagulant and this may be due to the oxidation of nitrite to nitrate in nanoparticle media.

Phosphate (PO_4^{3-}) ion concentration decreases after treatment either by hematite nanoparticles or by alum as shown in Table 2 and Fig. 3. In case of hematite nanoparticles, the capping Fe^{3+} ions interact with phosphate ion forming insoluble iron(III) phosphate. This process is of dual purpose; it helps in flocculation by destabilizing the colloidal iron oxide nanoparticles and also reduces the phosphate content in water samples under treatment. Once hematite is released into solution, it rapidly hydrolyzes and precipitates as an oxide. The iron cycle is closely tied to oxygen, carbon, phosphorus, sulfur and heavy metals, as well as biological organisms [29].

3.3 Coagulation mechanism of hematite nanoparticles

A red colloidal system is formed if FeCl_3 solution is added slowly to boiling water. This occurs because of a chemical reaction in which the hydrated iron(III) ions lose water and hydrogen ions to form a hydrated oxide: $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. As

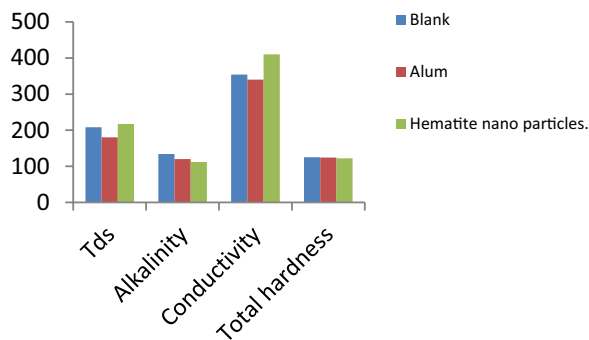


Fig. 3 Left: comparison between total dissolved solids, alkalinity, conductivity and total hardness of blank water sample and water samples after coagulation process using alum and hematite coag-

the particles of Fe_2O_3 begin to grow, they adsorb Fe^{3+} ions on their surfaces, which makes them positively charged. Because each of the oxide particles acquires the same electrical charge, they repel each other and the nanoparticle system shows indefinite stability. Hydrated iron(III) oxide particles can be coagulated by electrolytes that are capable of neutralizing the charges on the surfaces of their particles such as phosphate ions [30]. The scanning electron microscopy (SEM) after agglutination is shown in Fig. 4. The agglutination process is associated with the reduction in turbidity.

4 Conclusion

In this study, experiments were conducted on nanoparticle of hematite ability as flocculant for drinking water treatment of raw water. Hematite nanoparticles showed high efficiency in turbidity removal giving percentage turbidity removal as high as 93.8% when used as a coagulant. The efficiency of turbidity removal is highly dependent on hematite nanoparticle dosage. This is compared to a highest turbidity removal by using $2.0 \times 10^{-4} \text{ M}$ alum solution. The application of hematite nanoparticles as

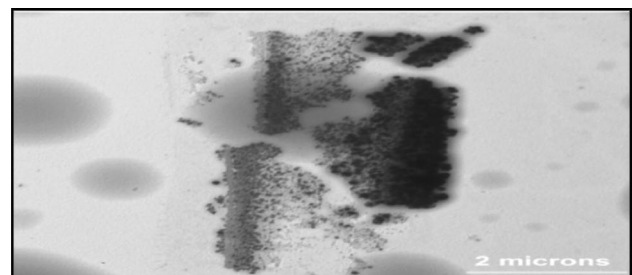
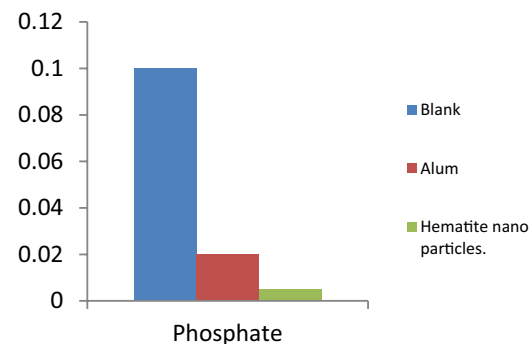


Fig. 4 Scanning electron microscopic (SEM) images for hematite nanoparticles after agglutination



ulants; right: comparison between phosphate concentrations of blank water sample and water samples after coagulation process using alum and hematite coagulants

flocculent/coagulant in surface water treatment avoids the risks of using aluminum or organic derivatives. Aside from turbidity removal upon using hematite nanoparticles in flocculation, other sharp reductions in concentrations of phosphate ion contaminant occur due to reaction with Fe^{3+} ions capping hematite nanoparticles. Hematite nanoparticles satisfy many crucial requirements including non-toxicity, indefinite stability, low cost and ease of production.

Acknowledgements The authors would like to express their gratitude to the Basyoun's drinking water company, Basyoun, Gharbiya, Egypt, for helpful evaluation standard methods.

Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest regarding the publication of this paper.

References

- Ariel RD, Craig DA, Yinfa M, Chady S, Todd E, Honglan S (2018) Fate of nanoparticles during alum and ferric coagulation monitored using single particle ICP-MS. *Chemosphere* 195:531–541
- Liang CZ, Sun SP, Li FY, Ong YK, Chung TS (2014) Treatment of highly concentrated waste water containing multiple synthetic dyes by a combined process of coagulation/flocculation and nano filtration. *J Mem Sci* 469:306–315
- Liang CZ, Sun SP, Zhao BW, Chung TS (2015) Integration of nanofiltration hollow fiber membranes with coagulation–flocculation to treat colored wastewater from a dyestuff manufacturer: a pilot-scale study. *Ind Eng Chem Res* 54:11159–11166
- Wang JP, Chen YZ, Ge XW, Yu HQ (2007) Optimization of coagulation–flocculation process for a paper-recycling wastewater treatment using response surface methodology. *Colloids Surf A* 302:204–210
- Zheng H, Zhu G, Jiang S, Tshukudu T, Xiang X, Xiang P (2011) Surfactant templating effects on the encapsulation of iron oxide nanoparticles within silica microspheres. *Desalination* 269:148–156
- Duan J, Gregory J (2003) Coagulation by hydrolysing metal salts. *Adv Colloid Interface Sci* 100:475–502
- Kasiri M, Khataee A (2011) Photo oxidative decolorization of two organic dyes with different chemical structures by UV/ H_2O_2 process: experimental design. *Desalination* 270:151–159
- Lee KE, Teng TT, Morad N, Poh BT, Mahalingam M (2011) Flocculation activity of novel ferric chloride polyacrylamide (FeCl_3 -PAM) hybrid polymer. *Desalination* 266:108–113
- Renault F, Sancey B, Badot P-M, Crin G (2009) Chitosan for coagulation/flocculation processes—an eco-friendly approach. *Eur Polym J* 45:1332–1348
- Kumar R, Shampa S (2018) Adsorptive removal of carbamazepine using biosynthesized hematite nanoparticles. *Environ Nanotechnol Monit Manag* 9:122–127
- Savage N, Diallo MS (2005) Nanomaterials and water purification: opportunities and challenges. *J Nanopart Res* 7:331–342
- Zhang W (2003) Nanoscale iron particles for environmental remediation: an overview. *J Nanopart Res* 5:323–332
- Zheng T, Pang J, Tan G, He J, McPherson GL, Lu Y, John VT (2007) Surfactant templating effects on the encapsulation of iron oxide nanoparticles within silica microspheres. *Langmuir* 23:5143–5147
- Mayo JT, Yavuz CT, Yean S, Cong L, Shipley H, Yu W, Falkner A, Kanb A, Tomson M, Colvina VL (2007) The effect of nanocrystalline magnetite size on arsenic removal. *Sci Technol Adv Mater* 8:71–75
- Thiruvengkatachari R, Ngo HH, Hagare P, Vigneswaran S, Benaim R (2002) Flocculation cross-flow microfiltration hybrid system for natural organic matter (NOM) removal using hematite as a flocculent. *Desalination* 147:83–88
- Hagare P, Thiruvengkatachari R, Ngo HH (2001) A feasibility study of using hematite to remove dissolved organic carbon in water treatment". *J Sep Sci Technol* 36:2547–2559
- Valerie AG, Jinxuan H, Karen EE, Heather JS (2012) Adsorption and desorption of bivalent metals to hematite nanoparticles. *Environ Toxicol Chem* 31:86–92
- Hua GH, Reckhow DA (2007) Comparison of disinfection byproduct formation from chlorine and alternative disinfectants. *Water Res* 41:1667–1678
- Al-Kady AS, Gaber M, Hussein MM, Ebeid EM (2011) Structural and fluorescence quenching characterization of hematite nanoparticles. *Spectrochim Acta A Mol Biomol Spectrosc* 83:398–405
- Oshtrakh MI, Alenkina IV, Kuzmann E, Klencsar Z, Semionkin VA (2014) Anomalous Mössbauer line broadening for nanosized hydrous ferric oxide cores in ferritin and its pharmaceutical analogue Ferrum Lek in the temperature range 295–90 K. *J Nanopart Res* (16) 2363:1–8
- Anthony WJ, Bideaux AR, Bladh WK, Nichols CM (2011) "Hematite". *Handbook of mineralogy* (PDF). III (halides, hydroxides, oxides). Mineralogical Society of America, Chantilly, VA. ISBN 0962209724
- Wolska E (1988) Relations between the existence of hydroxyl ions in the anionic sublattice of hematite and its infrared and X-ray characteristics. *Solid State Ionics* 28:1349–1351
- Gualtieri AF, Venturelli P (1999) In situ study of the goethite-hematite phase transformation by real time synchrotron powder diffraction. *Am. Mineral.* 84:895–904
- Kustova GN, Sadykov VA, Poryvaev SG (1992) Vibrational spectroscopic investigation of the goethite thermal decomposition products. *Phys Chem Miner* 18:379–382
- Ruan HD, Forst RL, Kloprogge JT, Duong L (2002) Infrared spectroscopy of goethite dehydroxylation: III. FT-IR microscopy of in situ study of the thermal transformation of goethite to hematite. *Spectrochim Acta A* 58:967–981
- Aboubaraka AE, Aboelfetoh EF, Ebeid EM (2017) Coagulation effectiveness of graphene oxide for the removal of turbidity from raw surface water. *Chemosphere* 181:738–746
- Speijers GJA (2002) Guidelines for drinking-water quality, 2nd edn, vol 2. Health criteria and other supporting information. World Health Organization, Geneva
- Reichert J, Lochtmann S (1984) Auftreten von Nitrit in Wasserversorgungssystemen. 'Occurrence of nitrite in water distribution systems'. Gas- und Wasserfach, Wasser- Abwasser 125:442–446
- Stumm W, Sulzberger B (1992) The cycling of iron in natural environments: considerations based on laboratory studies of heterogeneous redox processes. *Geochim Cosmochim Acta* 56:3233–3257
- Liang L, Morgan JJ (1990) Chemical aspects of iron oxide coagulation in water: laboratory studies and implications for natural systems. *Aquat Sci* 55:32–55