Magnetic recoverable $Ag_3PO_4/Fe_3O_4/\gamma\text{-}Fe_2O_3$ nanocomposite

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Abstract:

The use of nanomaterials in water treatment is an alternative for the development of new materials that optimize the purification process. Heterogeneous photocatalysis is used for the treatment of wastewaters contaminated with recalcitrant pollutants that cannot be removed in conventionally. Ag_3PO_4 has been reported to use visible light. Another important challenge of heterogeneous photocatalysis is to find a proper support for the photocatalysts to reduce the expense associated with the separation and reuse of these materials. However, the immobilization of the catalyst leads to lower reaction rates because the surface area exposed decreases and the material used as support can also interfere. In the last years, the use of magnetic materials to support photocatalysts has attracted special attention because it allows high surface areas to be exposed. Only few authors have reported the use of Ag_3PO_4/magnetic nanocomposites for photocatalysis and these need to be continued to improve their efficiency. In this work we synthesized Ag_3PO_4 and supported it on Fe_3O_4.

Fe_3O_4 was synthesis at pH 12 by the addition of $FeCl_3$ and $FeCl_2$. The magnetic material was washed with water and dried at 80ºC. Ag_3PO_4 was synthesised over Fe_3O_4 from the reaction between $AgNO_3$ and Na_2HPO_4. The final material was washed, recovered magnetically and dried at 80ºC. For characterization, a SEM and XRD studies were carried out.

Ag_3PO_4 was synthesised and satisfactorily supported over $Fe_3O_4/\gamma\text{-}Fe_2O_3$. The photodegradation of 10 mg·L-1 of methylene blue was achieved, although the apparent reaction rate constant was slightly lower for the magnetic composite than for the Ag_3PO_4 alone. This is explained because the composite contained 48% of the active Ag_3PO_4 material, as depicted form DRX studies.

Keywords:

Photocataysis, wastewater treatment, magnetic nanomaterials,

1. Introduction

Water is a scarce resource and for many countries supply is not enough to satisfy demand. Water resources location and their quality are factors that limit their availability. This problem is further complicated by climate

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change, rapid industrialization, population growth and pollution of existing water resources [1]. To solve this question different solutions are proposed which include repairing water distribution infrastructures and conservation of existing water sources. However, these options can not increase resources. Supply water can only be increased beyond hydrological cycle by desalination and water reuse. For this, a series of conventional water treatment technologies are used which include among others: ultraviolet radiation, chemical treatments, distillation and membrane processes (reverse osmosis, ultrafiltration, microfiltration, electrodialysis...), but all of them show specific disadvantages [2].

The continuous deterioration of the environment is a problem with greater relevance every day, and that requires short-term solutions. Most of the harmful contaminants found are anthropogenic compounds that have low biodegradability and therefore cannot be eliminated by conventional treatments. This is the case of the so-called emerging pollutants, which are found in low concentrations in the environment; these have the potential to carry an ecological impact, as well as adverse effects on health [3]. These contaminants include: drugs, additives, pesticides and a wide variety of compounds that, even at low concentrations, can alter endocrine functions [4] and increase the presence of resistant bacteria [5].

Elimination and control of these substances in aqueous media is complex due to their presence in large bodies of water. In recent years, emerging contaminants have been found in practically all the bodies of water studied. In Spain, among others, more than 30 emerging contaminants have been found in groundwater [6], 100 in wastewater treatment plants [7], more than 100 in wastewater already treated in conventional treatment plants [8], several in aquaculture areas [9] and 144 in river water fish [10].

Due to the nature of these contaminants, most have proven to be poorly biodegradable, and cannot be eliminated by conventional purification systems and therefore require advanced oxidation processes for their treatment [11]. Advanced oxidation processes are part of the tertiary treatment of purified water and seek to eliminate compounds that are difficult to biodegrade and reduce microbiological contamination, often with the aim of reusing the water. Among the most common tertiary processes we find ozonation, photocatalysis or membrane filtration, among others.

Based on this situation and nanotechnology development, nanomaterials use for water treatment is an alternative that allows solving drawbacks of methods traditionally used. Due to their new properties nanomaterials can contribute in obtaining stronger, lighter, cleaner and smarter surfaces and systems [12]. They have many applications ranging from automotive and aircraft (for example, reinforced and lighter materials, antifouling paints or more durable pneumatic) to biomedicine (drug released as specific organs, biosensors or prosthesis).

In water treatment, nanotechnology is finding applications through different routes [13] such as the use of large surface area of nanoparticles to adsorb contaminants (they allow retaining a higher rate of contaminants than conventional adsorbent), the use of membranes with nanomaterials (several studies have fixed nanomaterials to different polymer membranes and have obtained a greater water flow than conventional membranes) and the use of catalytic nanoparticles to decompose contaminants (nanomaterials have a higher photoactivity than conventional catalysts). Nanomaterials such as silver nanoparticles [14], TiO_2 nanoparticles and carbon nanotubes [15] have bactericidal effects that make it possible to eliminate microorganisms present in water. They also have better adsorption capacities than conventional adsorbents for low concentrations of heavy metals: porous carbon nanomaterials have been used efficiently for lead, cadmium, nickel and zinc elimination [16]. Another application is oils and organic solvents treatment: SiO_2 nanoparticles fixed to a polysulfone membrane improve antifouling properties and increase permeability from 1.08 to 17.32 $l/m^2 \cdot h$ [17]. On the other hand, boron nitride nano-slides have been shown to adsorb up to 33 times their own weight in oils and organic solvents while repelling water [18]. The use of nanomaterials has also been evaluated for emerging contaminants in water treatment: a combination of titanium dioxide nanotubes on a graphene base eliminates, with the help of the sun, traces of drugs and pesticides that escape from the current purification systems.

Of all the mentioned water treatment processes, we will focus on the use of nanomaterials in heterogeneous photocatalysis.Heterogeneous photocatalysis is used for the treatment of wastewaters contaminated with recalcitrant pollutants that cannot be removed in conventionally. One of the main drawbacks is that most photocatalysts need to be illuminated with wavelengths shorter than 388 nm [19]. Ag_3PO_4 has been reported to use visible light [20]. Another important challenge of heterogeneous photocatalysis is to find a proper support for the photocatalysts to reduce the expense associated with the separation and reuse of these materials. However, the immobilization of the catalyst leads to lower reaction rates because the surface area exposed decreases and the material used as support can also interfere [21]. In the last years, the use of magnetic materials to support photocatalysts has attracted special attention because it allows high surface areas to be

exposed. Only few authors have reported the use of $AgPO_4$/magnetic nanocomposites for photocatalysis [20], [22], [23] and these need to be continued to improve their efficiency.

In this work we synthesized Ag_3PO_4 and supported it on Fe_3O_4, performing the characterization of the synthesized material

2. Bibliometric Analysis

Bibliometric analysis is defined as a statistical evaluation of published scientific documents that enables the measure of the influence of publication in the scientific community.
The data obtained from the bibliometric analysis of the terms "silver nanoparticles" and water treatment are presented below. The scientific database used to search for the terms was Scopus (search conducted on May 23, 2021), and the software used to analyze the results was VOS Viewer®.

A growing trend is observed in the number of documents published as of 2008, with the number of documents published up to that date being less than 200. Regarding the countries with the most publications on this subject, Spain is in position number 10 , with 265 publications. Regarding the research groups or institutions with the greatest scientific production in the field, the first Spanish institution is found in position 23, this being the Higher Council for Scientific Research (CSIC).

However, if we add the term “emerging pollutants” to the previous search, the number of documents is reduced to 454 (from the year 2000 to the present). Thus, up to the year 2010, only 6 references were found in Scopus related to the study of silver nanoparticles for the treatment of emerging contaminants in water. As of that year, the number of documents begins to increase, finding in 2020, 90 documents published on this subject. In this regard, Spain is the fourth country with the most documents (27 documents in total).

Figure 1 shows the bibliometric network obtained from the keywords found in the documents resulting from the search. It is observed that the most commonly used materials for the application of silver nanoparticles are membranes (95 occurrences), graphene oxide (192 occurrences), titanium dioxide (327 occurrences) or magnetite (122 occurrences). Regarding the final application of these materials, we mainly found keywords related to disinfection processes (E. coli, antibacterial activity, etc.), although words related to emerging contaminants (antibiotics, tetracycline) and dyes (blue of methylene, dyes).

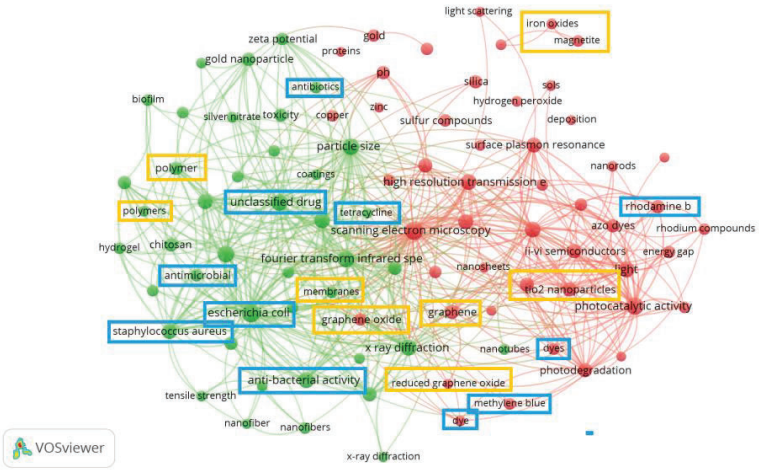

Figure 1. Bibliometric analysis of the terms “silver nanoparticles” and “water treatment”.

3. Experimental

3.1. Sample preparation

Fe_3O_4 nanoparticles were synthesized using a solvothermal method [24], Fe_3O_4 was synthesis at pH 12 by the addition of $FeCl_3$ and $FeCl_2$. The magnetic material was washed with water and dried at 80ºC.

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The synthesized Fe_3O4 nanoparticles were then dispersed in distilled water, and added to the NaH_2PO_4 solution (0,15M, pH = 4.12). And then, $AgNO_3$ aqueous solution (0.15 M) was added with drop by drop to the above solution under continuous mechanical vibration, and then the solution was maintained at room temperature and under continuous mechanical vibration for 4 h. The magnetic material was dried at 200ºC.
The as-prepared Fe_3O_4@ Ag_3PO_4 nanoparticles were separated by an external magnetic field, The final material was washed with water to remove excess phosphate ions. The obtained Fe_3O_4@Ag_3PO_4 was separated by an external magnetic field, then dried for 6 h at 80 °C.

3.2. Analysis

Powder X-ray diffraction (XRD) measurements were obtained on an X-ray diffractometer PANalytical Empyrean diffractometer (Cu Kα1, λ = 1.5406 Å). Crystallite sizes were estimated using the Scherrer equationand the fractions of the different phases were obtained from analysis with Match! 3® software.
UV-vis diffuse reflectance spectra (DRS) was measured using a Varian Cary E5 spectrophotometer in the range 200 – 2000 nm.
SEM microscopic observation allowed the visualization of the ground material surface morphology. For scanning electron microscopy (SEM) measurements a Sigma 300 VP FESEM Zeiss instrument was used. It was equipped with energy dispersive X-ray spectroscopy (EDX).

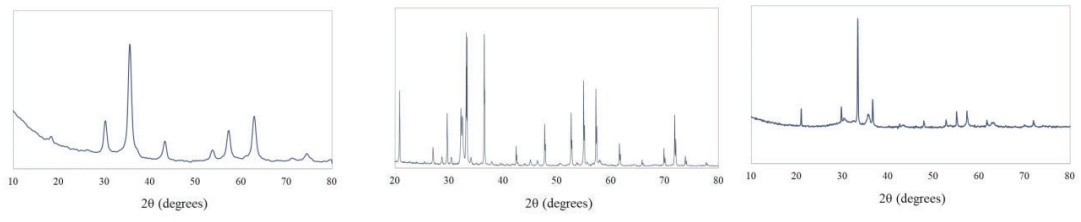
3.3. Degradation experiment

The photocatalytic activities of the samples were evaluated by degradation of MB under a simulated solar lam. A 60 W Hapro Solarium HB175 equipped with four 15 W Philips CLEO fluorescent tubes with emission spectrum from 300 to 400 nm (maximum around 365 nm) and with an average irradiation of about 90 $W \cdot m^{-2}$ was used.. A photocatalyst (0.1 g) was added to an aqueous solution of MB (100 mL, 10mgL−1) at room temperature in air. The suspension was magnetically stirred for 30 min in the dark to establish an adsorption desorption equilibrium to eliminate the influence of adsorption. A lamp was switched on to initiate the reaction. During irradiation, samples were taken at different time intervals for 180 min or until complete degradation was observed. Samples were centrifuged and then the decolorization of MB was measured with a UV–vis spectrophotometer (Cary 60, Varian, USA). To investigate the stability and recyclability of the as-prepared composite magnetic photocatalysts (Fe_3O_4@Ag_3PO_4), recycling experiments were also performed. In the recycling experiments, after the photocatalysts were separated from the solution by an external magnetic field, the remaining solution was removed. Separated photocatalysts were washed five times with distilled water, and then used in the next degradation experiment

4. RESULTS AND DISCUSSION

4.1 Characterization

XRD was used to investigate the phase structures of the samples. Fig. 2. shows typical XRD patterns of the samples at various stages. Fig. 2 shows the XRD pattern of Fe_3O_4 nanoparticles, Fig. 2B shows the XRD pattern of Ag_3PO_4. The successful coating and subsequent crystallization of Ag_3PO_4 and Fe_3O_4 were also confirmed (Fig. 2C).



(a) *(b)* *(c)*

Figure 2. XRD patterns of the samples: (a) Fe_3O_4 spheres, (b) Ag_3PO_4, (c) Ag_3PO_4/Fe_3O_4/γ-Fe_2O_3

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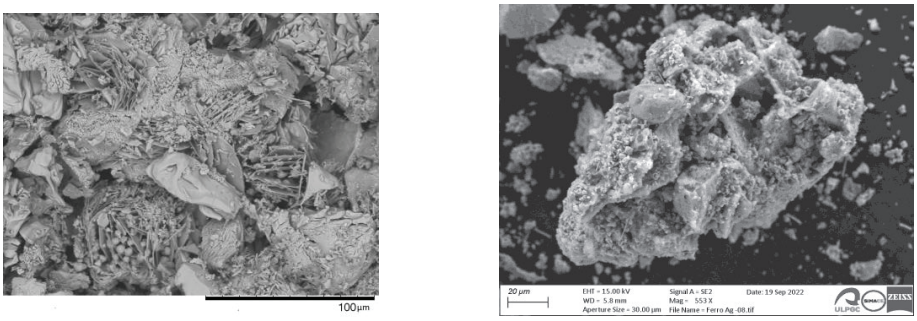
For the Ag_3PO_4 material alone, DRX studies revealed that 100% Ag_3PO_4 was present. For the magnetic composite, the phases found in DRX studies were Ag_3PO_4 (47,8%), magnetite, Fe_3O_4 (42,6%) and maghemite, γ-Fe_2O3 (9,5%). Although we initially synthesized Fe_3O_4, it is known that this structure can oxidize to γ-Fe_2O_3, also magnetic, even at ambient temperature. The size of the crystals obtained from Ag_3PO_4 is 54 nm and in the case of Fe_3O_4 and γ-Fe_2O_3 crystals it is 18 nm.

Thus, the maghemite crystalline phase (γ-Fe_2O_3) can be intuited in the diffractograms of the catalysts synthesized by calcination in a nitrogen atmosphere. The formation of maghemite can occur as a consequence of the oxidation of magnetite particles, according to equation 1 [25]. This process can occur at room temperature [26], although it usually occurs more favorably in an oxidizing environment above 200 ºC, with the optimum temperature for maghemite formation being between 375-400 ºC [27].

$$2\ Fe_3O_4 + ½\ O_2 \rightarrow 3\ \gamma\text{-}Fe_2O_3 \qquad (1)$$

The SEM image of the $Ag_3PO_4/Fe_3O_4/\gamma\text{-}Fe_2O_3$ composite is shown in Fig. 3.



(a) *(b)*

Figure 3. SEM Images of: (a) Ag_3PO_4 (b) $Ag_3PO_4/Fe_3O_4/\gamma\text{-}Fe_2O_3$

It is observed that there is a coating of silver phosphate on the ferromagnetite. Table 1 shows the elemental composition of Fe_3O_4@Ag_3PO_4 synthesized material.

Table 1. Composition of Fe_3O_4@Ag_3PO_4

Element	Weight %	Atomic %	Error %
O K	38.97	71.81	11.71
P K	9.23	8.78	7.67
Fe K	20.63	10.89	7.56
Ag L	31.17	8.52	6.87

UV–vis absorption spectra of the studied catalysts are depicted in Fig. 4. Pure Ag_3PO_4 absorbs solar energy with a wavelength shorter than approximately 500 nm. In contrast to pure Ag_3PO_4, the absorption edge of Fe_3O_4@Ag_3PO_4 and Fe_3O_4 generates red shift, Fe_3O_4@Ag_3PO_4 and Fe_3O_4 also exhibit higher absorption in the visible region than the pure Ag_3PO_4.

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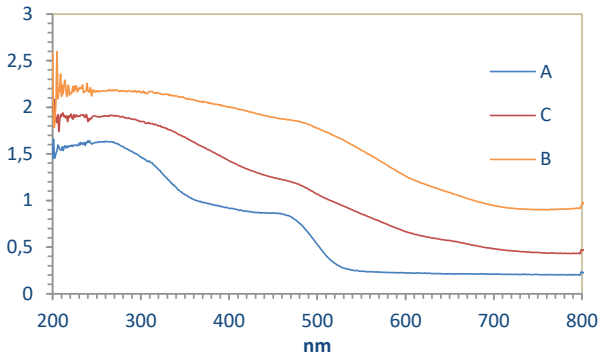

Figure 4. UV–Vis absorption spectra of: (A) pure Ag_3PO_4, (B) pure Fe_3O_4 and (C) $Ag_3PO_4/Fe_3O_4/\gamma\text{-}Fe_2O_3$

The hysteresis curves of the magnetic materials are shown in Fig. 5. We observe that the magnetization saturation is 43 emu·g^{-1} for Fe_3O_4 and 15 emu·g^{-1} for $Ag_3PO_4/Fe_3O_4/\gamma\text{-}Fe_2O_3$.

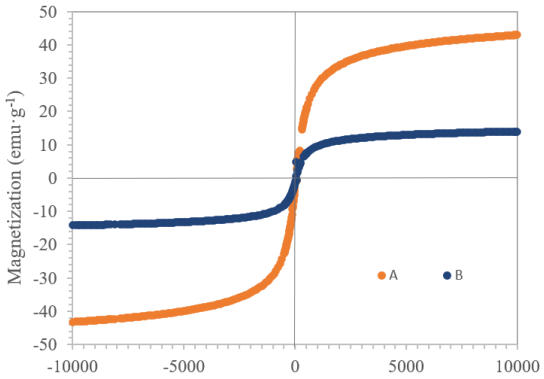

Figure 5. Hysteresis curves of: (A) Fe_3O_4 and (B) $Ag_3PO_4/Fe_3O_4/\gamma\text{-}Fe_2O_3$

4.2 Degradation Experiment

The photocatalytic degradation of MB by $Fe_3O_4@Ag_3PO_4$ under simulated solar irradiation at room temperature was investigated (Fig. 5). For comparison, the Fe_3O_4 and Ag_3PO_4 photocatalyst was also investigated. About 48% of MB was removed by $Fe_3O_4@Ag_3PO_4$ after 180 min irradiation. In contrast, pure Ag_3PO_4 exhibited the highest photocatalytic activity of the catalysts, about 96% of MB within 180 min under simulated solar irradiation.

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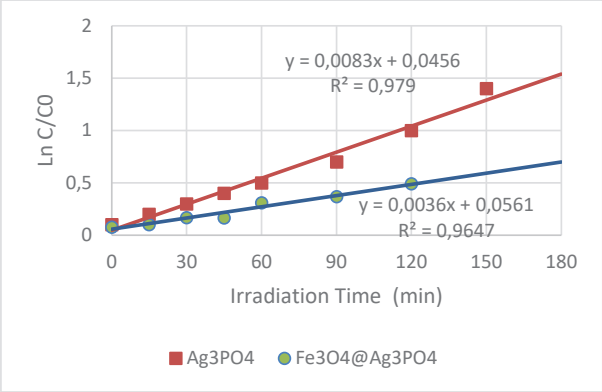

Figure 5. Photocatalytic degradation of MB over Fe_3O_4 spheres, pure Ag_3PO_4 and Fe_3O_4@Ag_3PO_4

The apparent fist-order reaction rate constant for the degradation of methylene blue was 0.0077 min^{-1} for Ag_3PO_4 and 0.0034 min^{-1} for Ag_3PO_4/Fe_3O_4/γ-Fe_2O_3. No photolysis was observed under the studied conditions.

4.3 Separation and reuse

The recyclability of the magnetic photocatalysts was investigated. The Fe_3O_4@Ag_3PO_4 photocatalysts can be rapidly separated under an applied magnetic field in 20 s.

Fig. 6 shows the recyclability of the Fe_3O_4@Ag_3PO_4 for photocatalytic degradation of MB. The degradation activity of Fe_3O_4@Ag_3PO_4 decreased sharply only after 1 cycle.The decoloration efficiency decreased to about 32%, 25%, 19% and 14% for the 2nd, 3rd,4th and 5th degradation cycles, respectively.

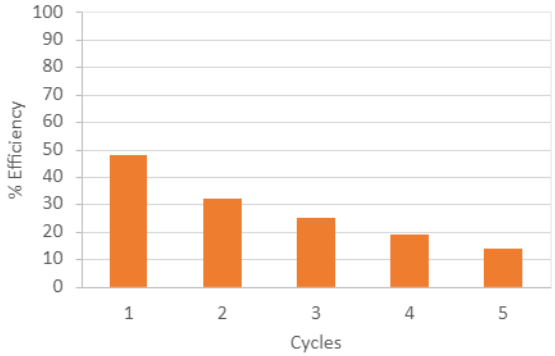

Figure 6. Recyclability of the Fe_3O_4@Ag_3PO_4

Efficiency decreases with reuse, it can be observed that the catalyst darkens due to the photocorrosion of silver by irradiation. This occurs because silver phosphate is slightly soluble in water, and silver ions can react with the generated photoelectrons reducing to elemental silver [28].

5. Conclusions

Ag_3PO_4 was synthesised and satisfactorily supported over Fe_3O_4/γ-Fe_2O_3. The photodegradation of 10 $mg \cdot L^{-1}$ of methylene blue was achieved, although the apparent reaction rate constant was slightly lower for the magnetic composite than for the Ag_3PO_4 alone. This is explained because the composite contained 47.8% of the active Ag_3PO_4 material, as depicted form DRX studies.

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References

[1] Q. Zaib and H. Fath, "Application of carbon nano-materials in desalination processes," *Desalin. Water Treat.*, vol. 51, pp. 627–636, Jan. 2012, doi: 10.1080/19443994.2012.722772.

[2] R. Das, M. E. Ali, S. B. A. Hamid, S. Ramakrishna, and Z. Z. Chowdhury, "Carbon nanotube membranes for water purification: A bright future in water desalination." 2014.

[3] D. Birkholz, S. M. Stilson, and H. S. Elliott, "Analysis of Emerging Contaminants in Drinking Water - A Review," in *Comprehensive Water Quality and Purification*, vol. 2, 2010, pp. 212–229.

[4] C. García-Gómez, P. Gortáres-Moroyoqui, and P. Drogui, "Contaminantes emergentes: efectos y tratamientos de remoción," *Química Viva*, vol. 10, no. 2, pp. 96–105, Mar. 2011, [Online]. Available: https://www.redalyc.org/articulo.oa?id=86319141004.

[5] M. Taheran, M. Naghdi, S. K. Brar, M. Verma, and R. Y. Surampalli, "Emerging contaminants: Here today, there tomorrow!," *Environmental nanotechnology, monitoring & management*, vol. v. 10. Elsevier B.V.

[6] A. Jurado, E. Vàzquez-Suñé, J. Carrera, M. López de Alda, E. Pujades, and D. Barceló, "Emerging organic contaminants in groundwater in Spain: a review of sources, recent occurrence and fate in a European context.," *Sci. Total Environ.*, vol. 440, pp. 82–94, Dec. 2012, doi: 10.1016/j.scitotenv.2012.08.029.

[7] M. J. M. Bueno, M. J. Gomez, S. Herrera, M. D. Hernando, A. Agüera, and A. R. Fernández-Alba, "Occurrence and persistence of organic emerging contaminants and priority pollutants in five sewage treatment plants of Spain: two years pilot survey monitoring.," *Environ. Pollut.*, vol. 164, pp. 267–273, May 2012, doi: 10.1016/j.envpol.2012.01.038.

[8] Y. Cabeza, L. Candela, D. Ronen, and G. Teijon, "Monitoring the occurrence of emerging contaminants in treated wastewater and groundwater between 2008 and 2010. The Baix Llobregat (Barcelona, Spain).," *J. Hazard. Mater.*, vol. 239–240, pp. 32–39, Nov. 2012, doi: 10.1016/j.jhazmat.2012.07.032.

[9] Y. Aminot *et al.*, "Environmental risks associated with contaminants of legacy and emerging concern at European aquaculture areas." 2019, doi: 10.1016/j.envpol.2019.05.133.

[10] Y. Pico *et al.*, "Contaminants of emerging concern in freshwater fish from four Spanish Rivers," *Sci. Total Environ.*, vol. 659, pp. 1186–1198, 2019, doi: https://doi.org/10.1016/j.scitotenv.2018.12.366.

[11] A. Gogoi, P. Mazumder, V. K. Tyagi, G. G. Tushara Chaminda, A. K. An, and M. Kumar, "Occurrence and fate of emerging contaminants in water environment," *A Rev.*, vol. 6, pp. 169–180, Mar. 2018, doi: 10.1016/j.gsd.2017.12.009.

[12] E. Roduner, "Size matters: why nanomaterials are different.," *Chem. Soc. Rev.*, vol. 35 7, pp. 583–592, 2006.

[13] A. Smith, "Opinion: Nanotech – the way forward for clean water?," *Filtr. Sep.*, vol. 43, no. 8, pp. 32–33, 2006, doi: https://doi.org/10.1016/S0015-1882(06)70976-4.

[14] T. Ahmed, S. Imdad, K. Yaldram, N. M. Butt, and A. Pervez, "Emerging nanotechnology-based methods for water purification: a review," *Desalin. Water Treat.*, vol. 52, no. 22–24, pp. 4089–4101, Jul. 2014, doi: 10.1080/19443994.2013.801789.

[15] Q. Li *et al.*, "Antimicrobial nanomaterials for water disinfection and microbial control: potential applications and implications.," *Water Res.*, vol. 42, no. 18, pp. 4591–4602, Nov. 2008, doi: 10.1016/j.watres.2008.08.015.

[16] J. P. Ruparelia, S. P. Duttagupta, A. K. Chatterjee, and S. Mukherji, "Potential of carbon nanomaterials for removal of heavy metals from water," *Desalination*, vol. 232, no. 1, pp. 145–156, 2008, doi: https://doi.org/10.1016/j.desal.2007.08.023.

[17] A. L. Ahmad, M. A. Majid, and B. S. Ooi, "Functionalized PSf/SiO2 nanocomposite membrane for oil-in-water emulsion separation," *Desalination*, vol. 268, no. 1, pp. 266–269, 2011, doi:

https://doi.org/10.1016/j.desal.2010.10.017.

[18] W. Lei, D. Portehault, D. Liu, S. Qin, and Y. Chen, “Porous boron nitride nanosheets for effective water cleaning,” *Nat. Commun.*, vol. 4, no. 1, p. 1777, 2013, doi: 10.1038/ncomms2818.

[19] C. B. Anucha, I. Altin, E. Bacaksiz, and V. N. Stathopoulos, “Titanium dioxide (TiO_2)-based photocatalyst materials activity enhancement for contaminants of emerging concern (CECs) degradation: In the light of modification strategies,” *Chem. Eng. J. Adv.*, vol. 10, p. 100262, 2022, doi: https://doi.org/10.1016/j.ceja.2022.100262.

[20] X. Guo *et al.*, “Performance of magnetically recoverable core–shell Fe3O4@Ag3PO4/AgCl for photocatalytic removal of methylene blue under simulated solar light,” *Catal. Commun.*, vol. 38, pp. 26–30, 2013, doi: https://doi.org/10.1016/j.catcom.2013.04.010.

[21] D. E. Santiago, M. R. Espino-Estévez, G. V González, J. Araña, O. González-Díaz, and J. M. Doña-Rodríguez, “Photocatalytic treatment of water containing imazalil using an immobilized TiO2 photoreactor,” *Appl. Catal. A Gen.*, vol. 498, pp. 1–9, 2015, doi: https://doi.org/10.1016/j.apcata.2015.03.021.

[22] E. Abroshan, S. Farhadi, and A. Zabardasti, “Novel magnetically separable Ag3PO4/MnFe2O4 nanocomposite and its high photocatalytic degradation performance for organic dyes under solar-light irradiation,” *Sol. Energy Mater. Sol. Cells*, vol. 178, pp. 154–163, 2018, doi: https://doi.org/10.1016/j.solmat.2018.01.026.

[23] Z. Liu *et al.*, “The triple-component Ag3PO4-CoFe2O4-GO synthesis and visible light photocatalytic performance,” *Appl. Surf. Sci.*, vol. 458, pp. 880–892, 2018, doi: https://doi.org/10.1016/j.apsusc.2018.07.166.

[24] B. Lv, Y. Xu, H. Tian, D. Wu, and Y. Sun, “Synthesis of Fe3O4\SiO2\Ag nanoparticles and its application in surface-enhanced Raman scattering,” *J. Solid State Chem.*, vol. 183, no. 12, pp. 2968–2973, 2010, doi: https://doi.org/10.1016/j.jssc.2010.10.001.

[25] S. Laurent *et al.*, “Magnetic Iron Oxide Nanoparticles: Synthesis, Stabilization, Vectorization, Physicochemical Characterizations, and Biological Applications,” *Chem. Rev.*, vol. 108, no. 6, pp. 2064–2110, Jun. 2008, doi: 10.1021/cr068445e.

[26] A. Haneda, K. & Morrish, “Magnetite to maghemite transformation in utrafine particles.,” *J. Phys. Colloq.*, vol. 38, pp. 321–323, 1977, doi: https://doi.org/10.1051/jphyscol:1977166.

[27] H. Lepp, “Stages in the oxidation of magnetite,” *Am. Mineral.*, vol. 42, pp. 679–681, 1957.

[28] X. Chen, Y. Dai, and X. Wang, “Methods and mechanism for improvement of photocatalytic activity and stability of Ag3PO4: A review,” *J. Alloys Compd.*, vol. 649, no. C, pp. 910–932, 2015, doi: 10.1016/j.jallcom.2015.07.174.

 https://doi.org/10.52202/069564-0279