

# Magnetically Separable Nanoparticles for Wastewater Treatment

Marco Barozzi<sup>a</sup>, Martina S. Scotton<sup>a</sup>, Elisabetta Sieni<sup>b</sup>, Paolo Sgarbossa<sup>c</sup>, Annalisa Sandon<sup>c</sup>, Sabrina Copelli<sup>a,\*</sup>

<sup>a</sup>Department of Science and High Technology, Università degli Studi dell'Insubria, Como, Italy

<sup>b</sup>Department of Theoretical and Applied Sciences, Università degli Studi dell'Insubria, Varese, Italy

<sup>c</sup>Department of Industrial Engineering, Università degli Studi di Padova, Padova, Italy

sabrina.copelli@uninsubria.it

Water is a vital source for both human life and environment, with 10% of the water globally available for domestic use. World Health Organization and UNICEF mention, in a report on Progress on Sanitation and Drinking Water, that approximately 768 million people do not have access to clean water, and companies are working for finding and implementing circular economies in order to save water for a sustainable production. In this context, the optimization of wastewaters recovery and their recycling are among the most crucial aspects to improve. Industrial wastewater can be also a resource for recovering valuable materials and components and, when properly purified, can be almost entirely recycled, setting the basis for a circular economy from the water re-use point of view. In recent years, environmental remediation research studies have been focused on the design and development of nanosized materials for adsorption of both organic and heavy metal pollutants. Their small dimension on one side allows for a low resistance to mixing but it also represents a limit for their final separation from the aqueous mixture, potentially becoming additional pollutants. In this study, a new set of selective magnetized nanoadsorbents/nanoparticles (MNPs), potentially capable of removing a wide series of pollutants (both organic and inorganic) from wastewaters, have been developed and tested at lab scale.

## 1. Introduction

Over the years, the focus on the environment has increased and, thanks to the progress of scientific knowledge, humankind is now able to remove different types of pollutants adopting increasingly complex and sophisticated technologies. Among the various environmental matrices, water, because of its limited availability, covers a particular importance and, therefore, needs interventions aimed at preserving its usability, often compromised by contamination of both natural and anthropogenic origin. For this reason, the treatment of civil and industrial wastewater is essential to reuse this resource and ensure the safety of both humankind and environment.

According to a report (Climate Change: Impacts, Adaptation and Vulnerability (2014) by the Intergovernmental Panel on Climate Change (IPCC), a warning which states that 80% of the world suffers of water scarcity (Jaspal and Malviya, 2020) has been issued. The European Environmental Agency (EEA) constantly promotes the development and the application of sustainable technologies, through the State of Environment reporting (SOER): a yearly report which describes, for each Eionet country (26 in total), topics inquiring environmental issues and solutions. In particular, the SOER for Italy emphasizes the importance of the topic related to waste and industrial pollution. In this framework, wastewater takes a huge part in water wastes, being involved in almost all food, agriculture (Wang and Serventi, 2019), fine chemicals, oil, textile (Chandanshive et al., 2020) and pharmaceutical industries. At the current state, wastewater management in Europe is performed through the definition of thresholds limit values of pollutant concentration in water for human use, defined within dedicated standards (European Council Directives 91/271/EEC and 98/15/EC). In Italy, acceptable pollutant concentrations in wastewater are defined in both D. Lgs. 152 – 2006 and G.U. 88 (2006). These limits account for concentrations of both organic toxic substances (such as PAHs, Polycyclic

Aromatic Hydrocarbon), and heavy metals. The presence of certain substances highly depends upon the territory, and it is due to specific local anthropogenic activities. As an example, textile industries, with the widespread use of dyes, will determine the presence in wastewater of both organic substances and nickel, copper and chromium ions (Ali et al., 2019). The most used methods for wastewater treatment include ultrafiltration, flocculation, coagulation (Lee et al., 2012), adsorption methods and biological processes (Copelli et al., 2015; Rada et al., 2014). Currently, chemical and biological methods are expensive and exhibit a poor removal efficiency at full plant scale (Mohammadi et al., 2020). But, among them, adsorption is considered an optimal method, as it is easy to operate, cost-effective and efficient for the removal of both organic and inorganic substances in aqueous media (Mohammadi et al., 2020). In recent years, environmental remediation research studies have been focused on the design and development of nanosized materials for adsorption of both organic and heavy metal pollutants (Ali et al., 2019). Nanomaterials are characterized by at least one dimension smaller than 100 nm and exhibit peculiar properties produced by the high surface area/volume ratio. In fact, if compared to massive material, the amount of surface atoms and their properties make them the best candidates as adsorption systems. Their small dimension on one side allows a low resistance to mixing but also represents a limit for their final separation from the aqueous mixture, potentially becoming additional pollutants. For these reasons, additional properties such as a magnetic behavior are desirable, in order to permit a different and effective separation method that avoids the use of filters or membranes and, therefore, the related fouling problems (Torretta et al., 2013). Magnetic separation is already largely used in mineral industry and foundries to separate magnetic ores from non-magnetic materials (Svoboda and Fujita, 2003) and it has been proposed to extract pollutants from liquids using magnetic nanoparticles to collect the substance; a static magnetic field is used to separate and extract the magnetic part from the fluid (Wang et al., 2012) and send it to a suitable regeneration treatment and/or disposal. As a consequence, it is important to think about the subsequent removal and reuse of nanoparticles, which are relevant aspects when facing a real industrial separation.

Among the pollutants involved, it is possible to include both organic compounds and heavy metals which are widely spread and difficult to remove. In industrialized areas, heavy metals are a major source of water pollution, because of their toxicity even at low concentrations. Among them, chromium, contained in many types of industrial effluents, is of particular concern as its use in various sectors (galvanic, tanning, etc.) contributed to the pollution of both water bodies and soil. This heavy metal may exhibit different oxidation states; however, the prevailing forms in the natural environment appears to be trivalent (Cr(III)) and hexavalent (Cr(VI)), different in terms of toxicity and mobility. Trivalent chromium is relatively less soluble and less toxic in water systems other than hexavalent chromium, characterized by high solubility and a high toxicity, which may induce carcinogenicity and mutagenesis (Chen et al., 2017).

In this work, MNPs were tested to assess their removal efficiency with respect to chromium III ions. Both artificially made samples of chromium trichloride and real industrial wastewaters have been tested, performing experiments with different amounts of nanoparticles, contact time and pollutant concentrations, in order to establish the best set for a future real plant design.

## 2. Methods and Materials

The nanoadsorbent used within this work is based on Graphene Oxide decorated with magnetite nanoparticles (MNPs, for short), resulting in a material with high surface area and a very cost-effective one-step co-precipitation method.

The method makes use of cheap iron (II/III) salts (chlorides) and a base (sodium or ammonium hydroxide solutions) to decorate a dispersion of graphene oxide in water (GO is obtained from graphite by a modified Hummer's method) at room temperature (Spizzo et al., 2017). Figure 1 shows a TEM micrograph, acquired using a Transmission electron microscopy (TEM, TECNAI FEI G2 microscope, Hillsboro, Oregon, USA), of the obtained composite.

The preliminary testing was conducted with the main aim of addressing the water purification extent on synthetic water and on wastewater samples from an industrial sewage treatment plant.

Firstly, it was hypothesized to perform experiments at different concentrations of the pollutant and nanoadsorbents. Tests were also performed at different contact times among contaminated water and nanoparticles, in order to study the adsorption phenomenon over time. Polluted water was artificially reconstructed by preparing mixtures of water and chromium (III) chloride ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ). Tests were performed in an EasyMax™ workstation (Mettler Toledo), and measurements were carried out with an ICP-MS. In order to perform a limited number of tests but with a significant result, the Design of Experiment (DoE) (Plackett and Burman, 1946; Montgomery, 2013) approach was applied, thus obtaining three representative combinations: initial concentration of chromium, amount of MNPs per total liquid mixture and stirring time.

During this preliminary phase, it was also decided to maintain a constant stirring velocity equal to 100 RPM to avoid structural brakes of the nanoadsorbents and maintain a uniform distribution of the particles in the suspension.

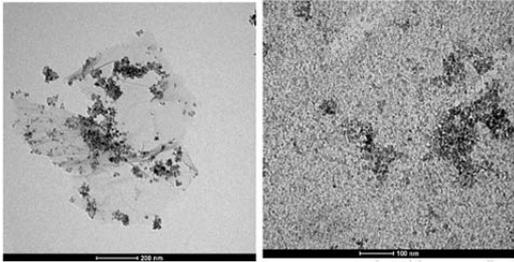


Figure 1- Picture of the nanoadsorbent used for the test

In the following, a brief overview of the preliminary experimental protocol is presented:

- preparation of the solution, chromium chloride and water at the target concentration;
- separation of a blank sample;
- loading of 50 mL of solution into an EasyMax™ reactor (a glass, blade-shaped stirrer was used);
- loading of nanosized adsorbent;
- stirring activation for the required time;
- separation of MNPs through a magnet (a classic Neodymium magnet was used);
- preparation of both blank sample and purified water sample for ICP-MS analyses.

## 2.1 Synthetic water experimental conditions

Four tests with synthetic water were carried out taking into account data reported in Table 1, while Table 2 shows the matrix used to determine the tests to be carried out based on DoE. DoE analysis is carried out in order to reduce the number of experiments to investigate the influence of the different experimental parameters and set the suitable values of these parameters. The first analysis investigates the influence of parameters that will be exploited in more accurate future experiments.

Given the range of each experimental parameter in Table 2, “+” means the “upper level of the parameter range” and “-” the “lower level of the range”. For example, in test #1.1, stirring time of 30 minutes, Cr(III) concentration of 18.40 mg/L and MNPs amount of 10 mg per 50 mL of solution were adopted.

Table 1: Data used in the DoE methodology

Variable	Value (-)	Value (+)
Time	5 min	30 min
Cr (CrCl <sub>3</sub> • 6H <sub>2</sub> O)	9.00 mg/L	18.40 mg/L
MNPs (magnetite/GO)	5 mg / 50 mL	10 mg / 50 mL

The chromium concentrations in Table 1 were arbitrarily decided as starting concentrations; anyway, 10 mg/L and 20 mg/L are considered typical values encountered in real wastewaters coming from textile industry.

The removal efficiency,  $\eta$ , was evaluated as:

$$\eta = 100 \left| \frac{C_{bk} - C_{NP}}{C_{bk}} \right| \quad (1)$$

Where  $C_{bk}$  is the Cr(III) concentration of the blank sample (non-treated) and  $C_{NP}$  is the Cr(III) concentration after the treatment with MNPs.

In DoE evaluation it is important to establish the relative sensitivity of the system in terms of separation efficiency with respect to its main operative parameters. Such a sensitivity can be calculated using the following formula:

$$S = \sqrt{\sum_{j=1}^N \left| \frac{\sum_{k=1}^{M+} \eta_{+,j,k}}{M+} - \frac{\sum_{k=1}^{M-} \eta_{-,j,k}}{M-} \right|^2} = \sqrt{\sum_{j=1}^N \left| \frac{s\eta_+}{M+} - \frac{s\eta_-}{M-} \right|^2} \quad (2)$$

Where N is the number of the parameters (stirring time, Cr concentration, MNPs amount) moved in the tests, i.e N=3 in this case,  $\eta_-$  corresponds to the removal efficiency evaluated using (1) considering the test for

which the  $j$ -th parameter was considered with its ‘-’ value (inferior extreme of the variation range) in Table 2, the same is for  $\eta_+$  but with a “+” in the test (superior extreme of the variation range));  $M+$  and  $M-$  are the numbers of efficiency values that have a ‘+’ for the considered parameter in the corresponding column in Table 2. In practice, for each parameter in Table 2 the following quantities are computed:

1. Considering a column in Table 2, the sum of the efficiency for which the parameter  $j$ -th appears with ‘+’,  $s_{\eta_+,j}$ , and the sum of the efficiency for which the parameter appears with ‘-’,  $s_{\eta_-,j}$ ;
2. Difference between the ratio  $s_{\eta_+,j}/M+$  e ratio  $s_{\eta_-,j}/M-$ .
3. The points 1-2 are repeated for each of the  $j$ -th columns in Table 2.

Table 2: Matrix used for the selection of experiments to be carried out with synthetic water

Test	Time	Cr	MNPs
#1.1	+	+	+
#1.2	-	+	-
#1.3	-	-	+
#1.4	+	-	-

### 3. Experiments and results

#### 3.1 Synthetic water

During each trial, it was possible to observe how the nanoadsorbents were not well distributed inside the liquid to be treated. This can be due to the low stirring speed, which was selected conservatively to not compromise the nanoadsorbent structure, which is quite delicate. As the adsorbent separation was carried out manually, it has been tried to scrupulously remove all the nanoadsorbents present into the liquid solution.

At the end of the trials, treated and untreated waters were sent to an IPC-MS analysis, showing the removal efficiencies reported in Table 3. Blank is the sample before the treatment with MNPs, whereas ‘treated sample’ identifies the sample after the treatment with MNPs.

Table 3: Test results based on DoE

Test	Cr concentration in the blank sample [mg/L]	Cr concentration in the treated sample [mg/L]	Removal efficiency ( $\eta$ )
#1.1	18.40	11.70	37%
#1.2	18.40	13.20	29%
#1.3	9.00	1.85	79%
#1.4	9.00	4.05	55%

It is important to state that, within this first set of tests, the main aim is not to obtain high removal efficiencies for all combinations: the goal is to establish the relative sensitivity of the system in terms of separation efficiency with respect to its main operative parameters. According to Eq. (2), the sensitivity with respect to the stirring time was about 0.08, that one with respect to initial Cr concentration was 0.35 and, finally, that one with respect to the amount of MNPs per 50 mL of solution is 0.16. This demonstrates how the most influencing operating parameters is the initial Cr concentration, followed by the amount of MNPs and the stirring speed. From a practical point of view, the ratio between initial Cr concentration and the amount of MNPs should be taken into account for a real process optimization; therefore the following experimental tests were carried out using 5 min of stirring and MNPs amount of 10 mg / 50 mL solution: A) Cr(III) 6.3 mg/L.; B) Cr(III) 0.598 mg/L. Results showed an overall removal efficiency of 74.7% and 96.7%, respectively. This proves the effectiveness of the proposed MNPs for the removal of Cr(III) from wastewaters, highlighting an optimal Cr(III) concentration / MNPs amount ratio of 0.05.

#### 3.2 Wastewater sample

The previous trials provide useful information on both the most influencing operating parameters and the effectiveness of MNPs in the chromium (III) removal; however, it should be noted that the conditions analyzed are excessively ideal (synthetic water). In real cases, the presence into the contaminated water of pollutants of different types (both organic and inorganic) could cause huge drops in the removal efficiencies with respect to the metal of interest (in this case Cr(III)). For this reason, MNPs were also tested on a sample of water from a

plant that receives wastes from textile and tanning industries, as well as liquid waste of different types, thus deviating considerably from the ideal situation studied in the laboratory.

In the sample taken in account both suspended and dissolved chromium were present, so it was decided to focus on the last one, that is the total chromium after membrane filtration, which was 0.52 mg/L.

Two tests, called #A and #B, were conducted, as shown in Table 4.

*Table 4: Industrial wastewater tests*

Test	Time [min]	Cr concentration after membrane filtration [mg/L]	MNPs [mg/50 mL]
#A	5	0.52	20
#B	30	0.52	10

From the results, reported in Table 5, it possible to notice that there is an important reduction in the removal efficiency compared to the experiments with synthetic water; this could be due to numerous factors, such as the presence of organic material, solids, Ni, Cu, chlorides, fluorides, sulphates, etc.. which can adsorb onto the MNPs surface affecting their ability to selectively bind Cr (III).

*Table 5: Test results of the industrial wastewater samples*

Test	Cr concentration on "white" sample after membrane filtration [mg/L]	Cr concentration after membrane filtration [mg/L]	Removal efficiency ( $\eta$ )
#A	0.52	0.45	12%
#B	0.52	0.43	16%

As GO/magnetite MNPs are at an early stage of study, their removal efficiency with respect to either other metals or organic substances is unknown; maybe such pollutants could have been removed faster with respect to Cr (III) leading to the saturation of the MNPs, therefore no longer available to remove chromium.

In addition, it should be remembered that, in the actual wastewater, there are both dissolved chromium and suspended. Analyses, carried out only after membrane filtration, did not allow to understand the overall effect of the MNPs on the abatement of metal, but only on its dissolved form (the magnetic nanoadsorbent may have acted effectively on chromium suspended but not on the dissolved one). The results reported in Table 5 would seem to lead to opposite considerations if compared to those inferred from the tests with synthetic water as the latter indicate a better removal efficiencies at lower amounts of MNPs. In addition to the reasons just described, it is necessary to underline that, compared with synthetic water trials, in the same volume, 50 mL, was more difficult to ensure chromium-MNPs contact as the dissolved chromium concentrations are significantly low. Agitation time seems to play a more important role: its increase corresponded to a greater possibility of obtaining chromium- MNPs contact; in fact, the results show a better removal efficiency of the metal for longer stirring time (30 min).

#### 4. Conclusions

Preliminary results from the use of graphene magnetite/oxide nanocomposites were presented in this work. Since this material is still in the early experimental phase, firstly, it was decided to test it on synthetic water, obtained from the addition of chromium trichloride hexahydrate ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ), very water soluble, to deionized water. In addition to these guidance tests, the use of this magnetic nanoadsorbents on the effluent from an industrial wastewater treatment plant was also tested in order to assess its efficiency for a possible chemical-physical treatment refinement downstream of biological treatment.

From the tests with chromium chloride samples (synthetic water), it has been highlighted that removal efficiencies above 96% can be reached with only 5 minutes of contact time and, it was also evidenced, through DOE methodology, a great influence of the Cr(III) concentration / MNPs amount ratio on the Cr (III) removal efficiencies. This is confirmed by the trend reported in Table 3 which shows an increase in the removal efficiency, increasing MNPs amounts per unit volume of solution; in particular, amounts of nanoadsorbent equal to 5 mg/50 mL and 10 mg/50 mL were more suitable for an initial chromium concentration of 9.00 mg/L, and, unsuitable at 18.40 mg/L, due to saturation of the material. For what concerns the tests made with industrial wastewaters, the original mixture contained chromium, nickel, copper and iron ions. The nanoadsorbent was found very selective with respect to  $\text{Cr}^{+3}$  ions, even if the removal efficiencies were tested for the dissolved chromium only. Comparing the use of chemicals, normally employed in industrial plants, with that of magnetic nanoadsorbent in a possible chemical-physical refining treatment, it appears that, while the adoption of chemicals, studied with the Jar Test, led to a removal efficiency of

dissolved chromium between 16-20% approximately, the use of magnetite/GO MNPs resulted in an abatement of 12-16%. It is important to point out that, in a refinement, while the use of chemicals unlikely lead to a good margin of improvement, as consisting only in the dosing of coagulants and flocculants, the action of the magnetic nanoadsorbent could be improved by performing other tests to understand the optimal dosage, as well as any interference.

The results of the tests carried out on this innovative material are very encouraging. Obviously, as these are preliminary studies, it is necessary to investigate variables such as treatable pollutants, interferences, conditions (pH, Temperature, pollutant concentration, etc.), optimal dosages as well as the engineering solutions to be adopted in order to ensure its safe use in real-scale plants.

## References

- Ali, I., Basheer, A.A., Mbianda, X.Y., Burakov, A., Galunin, E., Burakova, I., Mkrtchyan, E., Tkachev, A., Grachev, V., 2019. Graphene based adsorbents for remediation of noxious pollutants from wastewater. *Environment International* 127, 160–180.
- Chandanshive, V., Kadam, S., Rane, N., Jeon, B.-H., Jadhav, J., Govindwar, S., 2020. In situ textile wastewater treatment in high rate transpiration system furrows planted with aquatic macrophytes and floating phytobeds. *Chemosphere* 252, 126513.
- Chen, H., Dou, J., Xu, H., 2017. Removal of Cr(VI) ions by sewage sludge compost biomass from aqueous solutions: Reduction to Cr(III) and biosorption. *Applied Surface Science* 425, 728–735.
- Copelli, S., Raboni, M., Urbini, G., 2015. Water Pollution: Biological Oxidation and Natural Control Techniques, in: Reference Module in Chemistry, Molecular Sciences and Chemical Engineering. Elsevier.
- IPCC, n.d. AR5 Climate Change 2014: Impacts, Adaptation, and Vulnerability. URL <https://www.ipcc.ch/report/ar5/wg2/> (accessed 1.22.21).
- Jaspal, D., Malviya, A., 2020. Composites for wastewater purification: A review. *Chemosphere* 246, 125788.
- Lee, K.E., Morad, N., Teng, T.T., Poh, B.T., 2012. Development, characterization and the application of hybrid materials in coagulation/flocculation of wastewater: A review. *Chemical Engineering Journal* 203, 370–386.
- Mohammadi, S.Z., Safari, Z., Madady, N., 2020. A novel Co<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> magnetic nanoparticle-nylon 6 for high efficient elimination of Pb(II) ions from wastewater. *Applied Surface Science* 514, 145873.
- Montgomery, D.C., 2013. Design and analysis of experiments. Eighth edition. Hoboken, NJ: John Wiley & Sons Inc.
- Plackett, R.L., Burman, J. P., 1946. The Design of Optimum Multifactorial Experiments. *Biometrika* 33(4), 305–325.
- Rada, E., Raboni, M., Torretta, V., Copelli, S., Ragazzi, M., Caruson, P., Istrate, I., 2014. Removal of Benzene from Oil Refinery Wastewater Treatment Plant Exhausted Gases with a Multi-stage Biofiltration Pilot Plant. *Revista de Chimie -Bucharest- Original Edition-* 65, 68–70.
- Spizzo, F., Sgarbossa, P., Sieni, E., Semenzato, A., Dughiero, F., Forzan, M., Bertani, R., Del Bianco, L., 2017. Synthesis of Ferrofluids Made of Iron Oxide Nanoflowers: Interplay between Carrier Fluid and Magnetic Properties. *Nanomaterials (Basel)* 7.
- Svoboda, J., Fujita, T., 2003. Recent developments in magnetic methods of material separation. *Minerals Engineering* 16, 785–792.
- Torretta, V., Urbini, G., Raboni, M., Copelli, S., Viotti, P., Luciano, A., Mancini, G., 2013. Effect of Powdered Activated Carbon to Reduce Fouling in Membrane Bioreactors: A Sustainable Solution. *Case Study. Sustainability* 5, 1501–1509.
- Wang, Q., Guan, Y., Ren, X., Yang, M., Liu, X., 2012. Application of magnetic extractant for the removal of hexavalent chromium from aqueous solution in high gradient magnetic separator. *Chemical Engineering Journal* 183, 339–348.
- Wang, Y., Serventi, L., 2019. Sustainability of dairy and soy processing: A review on wastewater recycling. *Journal of cleaner production*.
- World Health Organization, UNICEF, 2013. Progress on sanitation and drinking-water: 2013.
- European Council Directives 91/271/EEC 'concerning urban waste water treatment', (on line) <https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:01991L0271-20140101&from=EN>
- Commission Directive 98/15/EC of 27 February 1998 amending Council Directive 91/271/EEC with respect to certain requirements established in Annex I thereof (Text with EEA relevance) (on line) <https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:31998L0015&from=EN>
- DECRETO LEGISLATIVO 3 aprile 2006, n. 152, Norme in materia ambientale., GU Serie Generale n.88 del 14-04-2006 - Suppl. Ordinario n. 96, 2006