Comparative performance and eco-toxicity assessment of $Y_2(CO_3)_3$, ZnO/TiO$_2$, and Fe$_3$O$_4$ nanoparticles for arsenic removal from water

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Abstract

The application of nanomaterials to remove arsenic (As) from the water represents one of the most promising remediation methods nowadays. In this study, three active materials, including $Y_2(CO_3)_3$, ZnO/TiO$_2$, and Fe$_3$O$_4$, with different structural and morphological properties, were evaluated for their As(V) adsorption capacity in contaminated water. Thus, the adsorption behaviour was evaluated, including the influence of pH, absorption kinetics, and isotherms. This work demonstrates that the active materials show a high adsorption performance, with adsorption efficiencies always close to 100%, leading to maximum adsorption capacities of 32.8, 37.3, and 35.8 mg/g for $Y_2(CO_3)_3$, ZnO/TiO$_2$, and Fe$_3$O$_4$, respectively. The effects of these suspended sorbent nanomaterials on $Daphnia magna$ allowed us to estimate the lethal concentration that kills 50% of the test specimens ($LC_{50}$) of 6.57$x10^3$ mg/L, 28.7 mg/L, and...
1.91x10^6 mg/L, for Fe_3O_4, ZnO/TiO_2 and Y_2(CO_3)_3, respectively. Overall, it is confirmed the suitability of the investigated materials for arsenic water remediation applications.

**Keywords:** adsorption, arsenic, ecotoxicity, heavy-metals, nanomaterials, water remediation

1. Introduction

Water quality is a growing concern throughout the world, and the problems caused by the scarcity of potable water imply that 1.2 billion people do not have access to drinkable water. Additionally, 2.6 billion people have little or no sanitation, and approximately 4000 children die every day due to diseases caused by bacteria and viruses transmitted through contaminated water [1].

Arsenic (As) is a ubiquitous element naturally found in the lithosphere (soil, rocks and water) and is one of the twenty most abundant elements in the environment [2]. It is present in the atmosphere, hydrosphere and biosphere in different concentrations and as compound or elemental [3]. It is unusual to find arsenic in elemental form; it is typically conjugated with oxygen, sulphur, and iron. The arsenic compounds most commonly present in nature are arsenite (+3) and arsenate (+5) [4]. The predominance of each form depends on the environment to which they are exposed. Arsenate is generally the most stable state in oxidative environments, while in reductive environments, it is reduced to its most toxic form: As (III). These ionised forms are the reference for the technologies for removing arsenic from water [5].

Arsenic is present in water due to both natural and anthropogenic causes [3]. Naturally arsenic occurrence is due to the weathering and dissociation of rocks or minerals that contain arsenic. Anthropogenically, arsenic occurs mainly due to mining activity and industry. The natural concentration of As in the soils is typically between 5 and 10 mg/kg, while in groundwater ranges from 0.5 to 5000 μg/L [6]. Arsenic is one of the most potential carcinogens, and it presents a complicated metabolism when compared with the “big four” toxic non-essential elements (As, cadmium (Cd), mercury (Hg) and lead (Pb)), being classified as Group
I human carcinogen by the World Health Organization (WHO) [7]. Long term arsenic exposure, which can occur through water, air, and soil, causes skin lesions, cancer, cardiovascular diseases, pulmonary problems, neurological deficiencies, and developmental and reproductive toxicity [8-10]. As a result, the WHO has set its maximum concentration level (MCL) in drinking water to 10 µg/L [6]. Water exposure is the most critical way arsenic gets into the human body since most of the compounds are easily dissolved in water. In this context, the United Nations International Children Emergency Fund (UNICEF) has been developing efforts with governments in countries where this chemical is a severe problem, such as Bangladesh, India, China and Vietnam, promoting the adoption of filtration technologies to treat contaminated water [10].

Different techniques for As removal from groundwater have been proposed, including oxidation [11], coagulation-flocculation [12], ion-exchange [13], membrane [10] and adsorption [14]. Among these, adsorption is one of the most promising techniques for removing inorganic pollutants, such as arsenic, due to its consistent efficiency, cost-effectiveness and simple operation [15]. Adsorption is a physicochemical process where solid or liquids surfaces retain dissolved substances. It can be classified into physical adsorption or van der Waal’s adsorption and chemical adsorption or chemisorption [16]. Usually, gases and dissolved substances are adsorbed on a surface by weak van der Waal’s adsorption, essentially depending on the surface area of the adsorbent at a given temperature and pressure. In the case of arsenic adsorption, the primary mechanism is the bound of the arsenic species to the surface of the adsorbent with the help of van der Waal’s forces, which is separated from the solution by filtration or another separation process. This process depends on different factors, such as arsenic concentration, pH of the solution, temperature, and presence of other ionic species in the solution. The size of the adsorbents is usually in the nanometre range and with large porosity, providing a large surface area. There are a large variety of adsorbents with potential
efficiency in arsenic removal from water. These include activated carbon [17], activated alumina [18], fly ash [19], red mud [20], rice husk [21], kaolinite [22], goethite [23], chitosan [24] and cation-exchange resins [25]. Micro/nanomaterials as iron and aluminium oxides [26, 27], zinc oxide [28], yttrium [29], zeolites [30], clinoptilolite [31] and titanium dioxide-based materials [32] are being investigated for arsenic removal from water due to their high affinity towards inorganic species of arsenic and their high specific surface area.

In this work, the As(V) adsorption efficiency of nano/microparticles of yttrium carbonate \((Y_2(CO_3)_3)\), zinc oxide/titanium dioxide \((ZnO/TiO_2)\), and magnetite \((Fe_3O_4)\), with different structural and morphological properties, was evaluated. The selection of the adsorbent materials has been carried out considering that yttrium-based adsorbents have been reported as materials with As adsorption capacity in all ranges of pH [33]. In addition, TiO_2-based materials also have been reported for As remediation due to their stability, high affinity for arsenic, and ability to oxidise As(III) and organic arsenic to As(V) [34], and that iron oxides are a well-known adsorbent for arsenic due to their high affinity for arsenic oxyanions and low cost [35]. The characterisation of the materials was performed and related to the As(V) adsorption efficiency under different experimental conditions such as pH, time of contact and arsenic concentrations. In addition, the potential toxicity of materials was examined using the model organism *Daphnia magna* and standard toxicity tests.

2. Materials and methods

2.1. Materials and reagents

Yttrium (III) carbonate, \((Y_2(CO_3)_3)\), 99.9%, 100–120 nm, 35–65 m²/g) was purchased from Sigma-Aldrich. 10 wt. % ZnO/TiO_2 nanoparticles were synthesised following the procedure reported in [36]. Magnetite nanoparticles \((Fe_3O_4)\), 97.0%, 50–100 nm, 6–8 m²/g) were obtained from Nanostructured & Amorphous Materials, Inc. Arsenic standard solution \((H_3AsO_4)\), 1000
mg/L) was supplied by Merck. Sodium hydroxide (NaOH, ≥ 95%) and hydrochloric acid (HCl 37%) were acquired from Panreac and Sigma-Aldrich.

2.2. Materials characterisation

The crystalline structure of the micro/nanomaterials was characterised by X-ray diffraction (XRD), using a Philips Analytical X-Ray PW1710 BASED diffractometer with Cu Kα radiation, λ = 1.5406 Å (40 kV, 30 mA), over the scanning range 2θ = 10-80° with a step width of 2°/min.

Transmission Electron Microscopy (TEM) was performed with a TECNAI G2 20 TWIN apparatus operated at 200 kV and equipped with LaB₆ filament, EDAX EDS microanalysis system and high angle annular dark-field-scanning transmission electron microscopy (HAADF-STEM). The samples for the TEM experiments were prepared by dispersion into ethanol and keeping the suspension in an ultrasonic bath for 15 min. Then, a drop of the suspension was poured onto a TEM copper grid (300 mesh) covered by a pure carbon film and dried under vacuum.

The zeta (ζ) potential was measured using a Zetasizer NANO ZS-ZEN3600, Malvern (Malvern Instruments Limited, UK), equipped with a He–Ne laser (wavelength 633 nm) and backscatter detection (173°). Nanoparticles were dispersed in ultra-pure water, and the solutions were prepared at different pH values (3, 5, 7, 9 and 11) using HCl (1M) and NaOH (1M) solutions. The results were obtained using the Smoluchowski theory approximation, and each sample was measured ten times at 22 °C. The manufacturer software (Zetasizer 7.12) was used to assess zeta potential values.

The specific surface area of the micro/nanomaterials was determined by the Brunauer-Emmett-Teller (BET) method. The samples were analysed at -176 °C by nitrogen adsorption-
desorption in a Micromeritics TriStar analyser (Micromeritics). Before adsorption experiments, 0.5 g of each sample was outgassed at 26.7 Pa and 350 °C for six hours.

2.3. Arsenic removal efficiency evaluation

To evaluate the arsenic (As) removal efficiency of the materials, As(V) solutions were prepared by diluting a commercial standard solution of 1000 mg/L in ultrapure water.

Then, 50 mg of each adsorbent material was added to 50 mL of an As(V) standard solution. The solution was placed under magnetic stirring for 30 minutes and filtered to remove the materials from the solution. Three micro/nanomaterials were tested to evaluate their arsenic adsorption efficiency: Y$_2$(CO$_3$)$_3$, ZnO/TiO$_2$, and Fe$_3$O$_4$. Atomic absorption spectroscopy (AAS) was used to quantify the final As concentration in solutions and, therefore, to determine the adsorption capacity of the materials. The measurements were performed in a Thermo M Series AA Spectrometer coupled to a graphite furnace Thermo GF95Z Zeeman Furnace in a coated cuvette with defined conditions: $\lambda = 193.7$ nm; drying temperature = 100 °C; pyrolysis temperature = 1200 °C; atomising temperature = 2600 °C; cleaning temperature = 2800 °C.

Arsenic adsorption efficiency (E) and arsenic adsorption capacity ($Q_e$) were evaluated according to equations 1 and 2:

$$E (\%) = \frac{(C_i-C_f)}{C_i} \times 100 \quad (1)$$

$$Q_e = \frac{(C_i-C_f)V}{m} \quad (2)$$

where $C_i$ and $C_f$ are the final and initial arsenic concentration (mg/L), respectively, m is the mass (g) of adsorbent, and V is the volume (L) of the solution.

Experiments were performed under varying conditions, including different pH (2, 4, 7, and 10), contact times (2, 4, 6, 8, 10, 15, 20, 25, and 30 minutes), and As(V) initial concentrations (0.1, 0.25, 0.5, 0.75, 1, 2, 5, and 10 mg/L).
The kinetic behaviour was fitted according to non-linear forms of pseudo-first-order [37], pseudo-second-order [38], Elovich [39], and Bangham models [40] described in Supplementary Information. The isotherm curves were fitted according to non-linear forms of Langmuir [41], Freundlich [42], Temkin [43], and Dubinin-Radushkevich [44] models, described in Supplementary Information.

2.4. Acute lethality tests

Acute lethality tests were performed to evaluate the sensitivity of the *Daphnia magna* to the different nanoparticles (Fe$_3$O$_4$, ZnO/TiO$_2$ and Y$_2$(CO$_3$)$_3$). Individuals of *D. magna* were placed in containers with 10 mL of nanosuspensions (n=5). For each concentration, four replicates were used. Subsequently, they were exposed to the nanoparticle’s suspensions prepared in autoclaved mineral water (6 concentrations ranging from 0 to 2000 mg/L of Fe$_3$O$_4$; 0.1 to 50 mg/L of ZnO/TiO$_2$; and 0.005 to 1.5 mg/L of Y$_2$(CO$_3$)$_3$). The tests ran for 48 h at 21 ºC under a 12 h:12 h photoperiod. The animals were not fed during exposure. Individuals that did not show any movement when mechanically stimulated at 24 h intervals were considered dead. At the beginning and after 48 h, the pH of the nanosuspensions was measured (Table S1). *Daphnia magna* mortality recorded in the acute toxicity tests was used to calculate the mean concentration and 95% of confidence interval (C.I.), inducing the death of 50% of the test specimens (LC$_{50}$) within 48 h of exposure. PriProbit 1.63 [45] was used to estimate toxicity parameters. Repeated measurements analysis of variance (ANOVA) was used to test for effects of nanoparticles concentrations on the percentage of animal survival in the acute lethality test [46].

3. Results and discussion

3.1. Nanomaterial’s characterisation
Materials characterisation was carried out through TEM, XRD, BET surface area and zeta potential measurements. Figure 1 (a, b, c) shows representative TEM images of Fe$_3$O$_4$, ZnO/TiO$_2$ and Y$_2$(CO$_3$)$_3$. TEM images of Fe$_3$O$_4$ show spherical and hexagonal particles, with diameters ranging from 80 to 150 nm. For ZnO/TiO$_2$ nanoparticles, round-shaped particles are observed, presenting widths from 100 to 350 nm. Y$_2$(CO$_3$)$_3$ nanoparticles exhibit a shape like nanorods with varying sizes and lengths ranging from 50 to 200 nm.

Figure 1. TEM images of (a) Fe$_3$O$_4$, (b) ZnO/TiO$_2$ and (c) Y$_2$(CO$_3$)$_3$; (d) XRD patterns and (e) zeta potential measurements of magnetite, 10% ZnO/TiO$_2$ and Y$_2$(CO$_3$)$_3$.

The characterisation of the different nano/micro materials performed by XRD is shown in Figure 1 (d). Y$_2$(CO$_3$)$_3$ diffractogram presents peaks at 11.6º, 15.7º, 19.4º, 22.8º, 25.0º, 30.1º and 35.5º, which are characteristic of its crystalline form and agree with Y-Tengerite (Y$_2$(CO$_3$)$_3$·2·3H$_2$O) [47-49]. Magnetite shows peaks at $2\theta = 33.0^\circ$, 35.6º, 40.7, 49.3 53.9º, 62.4º and 63.9º, characteristic of a rhombohedral crystalline structure [50, 51]. The ZnO/TiO$_2$ diffractogram
shows the characteristic peaks of TiO$_2$ at $\theta = 25.3^\circ$, 37.8$^\circ$, 54.1$^\circ$, 55.0$^\circ$ and 62.8$^\circ$ [52, 53] and one characteristic peak of ZnO at $\theta = 48.1^\circ$ [53, 54]. Just one peak of ZnO is present in the ZnO/TiO$_2$ nanocomposite diffractogram, related to the low amount of ZnO.

The zeta potential measurements are paramount to estimate the surface charge of the particles. Figure 1 (e) shows a similar surface charge dependency on the pH for $Y_2$(CO$_3$)$_3$, ZnO/TiO$_2$, and Fe$_3$O$_4$. All the nanomaterials present positive zeta potential values at acidic pH values. The point of zero charges (PZC) of ZnO/TiO$_2$ is approximately at pH 6 and, consequently, at pH values higher than PZC this nanomaterial is negatively charged. $Y_2$(CO$_3$)$_3$ and Fe$_3$O$_4$ show the PZC at pH 10, and just in highly alkaline conditions, these materials are negatively charged. The surface area of these three materials was determined using the BET method. The surface area of ZnO/TiO$_2$ is 88.28 m$^2$/g, showing a very low microporosity (the micropore area is 9.911 m$^2$/g). The total pore volume is 0.144 cm$^3$/g, and pore distribution of 2 to 6 nm is observed, which is related to the nanoparticle size distribution. Both Fe$_3$O$_4$ and $Y_2$(CO$_3$)$_3$ show no microporosity and a surface area of 1 m$^2$/g. In related studies, surface area values of 31 m$^2$/g have been obtained using iron oxide for water treatment [55]. Previous works with similar crystalline structures of $Y_2$(CO$_3$)$_3$ have reported surface area values ranging from 0.1 to 10 m$^2$/g [56, 57]. The synthesis process and the crystalline arrangement leads to different morphologies and surface areas. A higher surface area promotes more interaction between the adsorbent and the arsenic species, and better efficiency is expected. To overcome the smaller surface area, the affinity of functional groups of $Y_2$(CO$_3$)$_3$ and Fe$_3$O$_4$ must also play a relevant role to achieve effective arsenic adsorption.

3.2. Arsenic removal efficiency evaluation
An initial evaluation of the active materials was performed to identify the best pH of the media that leads to better arsenic removal efficiencies. After that, the adsorption kinetics and isotherms were evaluated under the optimised conditions.

3.2.1. Effect of pH

Arsenic species exist as neutral and anionic forms in the pH range of 2-10 [58]. Also, pH is an essential parameter because the functional groups and surface charge of active materials are affected by the pH of the solution, as previously mentioned in section 3.1. [59]. It is thus necessary to understand the influence of initial pH values on adsorption efficiency. Therefore, the three active materials were subjected to different pH values: 2, 4, 7 and 10 (Figure 2).

Since the pH values affect the surface charges of the adsorbents and arsenic species, pH will directly affect the adsorption of As(V). As shown in Figure 2, for almost all materials, the As (V) adsorption capacity depends on pH, and the adsorption is significantly better under acidic and neutral environments. For pH 2, pH 4, and pH 7, all materials present adsorption efficiencies higher than 97%. Under alkaline conditions, at pH 10, the adsorption efficiency
decreases for almost all materials, except for ZnO/TiO$_2$. Thus, the performance of ZnO/TiO$_2$ is independent of the pH; contrarily, the adsorption efficiency of Y$_2$(CO$_3$)$_3$ and Fe$_3$O$_4$ depends on pH. The electrostatic repulsions between materials and As(V) species with increased pH explain this dependence. When pH < 7, the primary forms of As(V) in water are anions (AsO$_4^{3-}$, HAsO$_4^{2-}$ and H$_2$AsO$_4^-$), favouring the protonation of the adsorbent surface. The protons increase results in multiplying positively charged sites, leading to the enhanced attractive force between adsorbents and arsenic species [60]. Hence, at acidic pH values, there are many positive charges on the surface of the materials, promoting a strong attraction to the arsenic anions in the solution. However, the amount of OH$^-$ increases with increasing pH, resulting in a competition for the As(V) adsorption on materials surface. When pH $\geq$ 10, positive charges appear on the surface of Y$_2$(CO$_3$)$_3$ and Fe$_3$O$_4$, and the adsorption capacity decreases. The independence of ZnO/TiO$_2$ from pH could be due to the larger surface area of this material, which allows better contact between arsenic species and the surface of the active material. These results evidence the role of electrostatic interaction, surface charge and surface area of the materials in the adsorption process.

3.2.2. Adsorption kinetics

The contact time is an essential parameter defining the adsorption efficiency. The effect of contact time between arsenic and the active materials was evaluated at contact times of 2, 4, 6, 8, 10, 15, 20, 25, and 30 minutes, as represented in Figure 3 (a).
Figure 3. (a) Effect of contact time on arsenic adsorption by the active materials; (b) Pseudo-second order adsorption kinetics of Y\(_3\)(CO\(_3\))\(_3\), ZnO/TiO\(_2\) and Fe\(_3\)O\(_4\) (pH = 7; [As] = 100 µg/L; adsorbent dosage; 1 g/L).

Figure 3 (a) shows an initial high adsorption rate for all materials, as shown by the high adsorption efficiencies in the first 10 minutes of contact. For all materials, 100% of arsenic removal was achieved after the first 15 min. This faster adsorption occurs because, at the beginning of the process, a high number of active binding sites are available for adsorption and more As species are adsorbed. As the adsorption process continues, the active sites of the adsorbents begin to be unavailable. As a result, the adsorption rate slows down until it reaches equilibrium. This two-stage adsorption process has been described for arsenic adsorption [61, 62].

Adsorption kinetics is an important parameter to understand the behaviour of adsorption over time. Based on Figure 3 (a), most As(V) adsorption occurs in the first 10 minutes of contact with the active materials. With this data, As(V) adsorption kinetics was analysed using pseudo-first, pseudo-second-order, Elovich, and Bangham kinetic models. Figure 3 (b) presents the kinetics fitting using a pseudo-second-order model, whilst Figure S1 and Table S2 provide the adsorption kinetics fitting for all the simulated models. Table S1 also summarises the adsorption rate constants (k, α), the correlation coefficient (R\(^2\)), and the root-mean-square errors (RMSE) for each model.
Based on $R^2$ and RMSE values, the adsorption kinetics fits well with all the models. Among all, the pseudo-second-order model presents better $R^2$ and RMSE values for all active materials. As this model defines adsorption as a chemical process, it is reasonable to consider chemisorption as the main driving force for As(V) adsorption on active materials surfaces [63]. However, as $R^2$ and RMSE values of pseudo-second and pseudo-first-order models are similar, arsenic adsorption can be explained as a combination of electrostatic interactions (physical adsorption) and chemisorption [64, 65].

3.2.3. Adsorption isotherms

The adsorption capacity of the three active materials was evaluated through adsorption experiments using different As(V) concentrations, and the results are presented in Table S3. It was found that all active materials can remove As(V) completely, regardless of the initial concentration, as efficiencies higher than 97% are always obtained. The results show that all active materials remove As(V) to values below the MCL when the initial concentration is lower than 1 mg/L, which means that all materials are efficient to remove As in under concentrations that are typically found in arsenic polluted water sources around the world [66]. The fitting of As(V) adsorption isotherms using different models was performed with the obtained data. The fitting of Langmuir isotherm model to the experimental results is presented in Figure 4, whilst Figure S2 and Table S4 provide the adsorption isotherm fitting for all the simulated models.
Figure 4. As(V) adsorption Langmuir isotherm of \( Y_2(\text{CO}_3)_3 \), ZnO/TiO\(_2\) and Fe\(_3\)O\(_4\) (pH = 7; contact time: 30 min; adsorbent dosage: 1 g/L).

R\(^2\) and RMSE parameters were used to determine the fit quality of isotherm models. Langmuir and Freundlich present R\(^2\) close to 1 and smaller RMSE values, suggesting the suitability of both methods. As Langmuir model present the smallest RMSE values, it is considered the most suitable model to describe As(V) adsorption. However, as R\(^2\) and RMSE values of Langmuir and Freundlich models are similar, arsenic adsorption can be described as a combination of electrostatic interactions and chemisorption – as demonstrated by the results of adsorption kinetics. Based on Langmuir results, the maximum adsorption capacities (\( Q_{\text{max}} \)) achieved were 32.8, 37.3, and 35.8 mg/g for \( Y_2(\text{CO}_3)_3 \), ZnO/TiO\(_2\), and Fe\(_3\)O\(_4\), respectively.

Langmuir isotherm assumes that adsorption occurs on a homogeneous surface and that all binding sites have an equal affinity for adsorbate, leading to the formation of an arsenic monolayer on the surface of the active material. Thus, this model considers adsorption as a chemisorption process [58]. On the other hand, Freundlich isotherm assumes that adsorption occurs on a heterogeneous surface and that the adsorption process is multilayer.

Many efforts have been devoted to the development of different adsorbents for arsenic removal from water. Previous works using similar adsorbents to those used in this work are presented in Table 1.
### Table 1. Comparison of maximum adsorption capacities of different adsorbents for As removal from water.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity (mg/g)</th>
<th>Adsorbent dosage (g/L)</th>
<th>Initial concentration of As (mg/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄ magnetite</td>
<td>0.147</td>
<td>10</td>
<td>1</td>
<td>[67]</td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>2.7</td>
<td>0.5</td>
<td>0.1 – 20</td>
<td>[65]</td>
</tr>
<tr>
<td>Hematite</td>
<td>14.46</td>
<td>1</td>
<td>1.5 – 12</td>
<td>[68]</td>
</tr>
<tr>
<td>Magnetite</td>
<td>35.76</td>
<td>1</td>
<td>0.1 – 10</td>
<td>This study</td>
</tr>
<tr>
<td>Fe₂O₃ – TiO₂</td>
<td>15.73</td>
<td>2</td>
<td>10 – 50</td>
<td>[69]</td>
</tr>
<tr>
<td>TiO₂ – ZrO₂</td>
<td>21.6</td>
<td>0.5</td>
<td>1</td>
<td>[70]</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.85</td>
<td>2</td>
<td>0.2 – 2</td>
<td>[71]</td>
</tr>
<tr>
<td>ZnO/TiO₂</td>
<td><strong>37.30</strong></td>
<td>1</td>
<td><strong>0.1 – 10</strong></td>
<td>This study</td>
</tr>
<tr>
<td>Yttrium</td>
<td>35.56</td>
<td>4</td>
<td>1 – 60</td>
<td>[72]</td>
</tr>
<tr>
<td>Y₂(CO₃)₃</td>
<td><strong>32.83</strong></td>
<td>1</td>
<td><strong>0.1 – 10</strong></td>
<td>This study</td>
</tr>
</tbody>
</table>

Previous works using iron oxides for As adsorption present lower Qₘₐₓ values when compared with the Fe₃O₄ used in this work, using similar conditions [65, 67, 68]. The different shapes of the magnetite used in this work and the higher PZC explain the highest Qₘₐₓ values. There is no previous report of the use of the ZnO/TiO₂ nanocomposite for As removal. However, previous works using TiO₂ [69, 70] and ZnO [71] based nanocomposites for As(V) removal present lower Qₘₐₓ values. The superior surface area explains the higher Qₘₐₓ values achieved with this material compared with previous works. A previous work using yttrium-based adsorbents presents a higher Qₘₐₓ value than yttrium carbonate used in this work. However, the experimental conditions used a higher adsorbent dosage (4 g/L) and contact time (2 hours) when compared to this work (1 g/L and 30 minutes, respectively) [72]. Thus, the sorbents used in this work achieved better or similar adsorption capacities when compared to previous works using similar materials and experimental conditions, proving their affinity for As(V) species adsorption. It is essential to notice that the adsorption capacity of the materials used in this work was evaluated under arsenic concentrations and pH conditions similar to As-contaminated water sources found worldwide, particularly in America [73], Europe [74], and Asia [75].

### 3.3. Adsorption mechanism
FTIR spectroscopy was accessed to elucidate the adsorption mechanism of As(V) by the active materials. Figure 5 presents the FTIR spectra of all active materials before and after the As(V) adsorption experiments.

**Figure 5.** FTIR spectra of (a) $\text{Y}_2(\text{CO}_3)_3$, (b) ZnO/TiO$_2$, and (c) Fe$_3$O$_4$ before and after As(V) adsorption experiments.

FTIR spectra of $\text{Y}_2(\text{CO}_3)_3$ (Figure 5 a) shows a slight difference before and after adsorption of arsenic, decreasing peaks intensity at ≈ 1500 cm$^{-1}$. This group of peaks is associated with the carbonate groups of $\text{Y}_2(\text{CO}_3)_3$, which suggest the adsorption of As(V) on active material via ligand/anion exchange between CO$_3^-$ groups and As(V) oxyanions [76]. In addition, an increase of peaks intensity was observed between ≈ 700 and 850 cm$^{-1}$, related to monodentate inner-sphere complex Y–O–As bonding [77]. These changes indicated that CO$_3^-$ groups of Y-based active material are involved on As(V) adsorption via H-bonds interaction, by a chemisorption process, as described in equation 3 [29]:

$$
\equiv Y - \text{CO}_3^2- + \text{As} \left(\text{V}\right) \rightarrow Y - \text{As} \left(\text{V}\right) + \text{CO}_3^2- \quad (3)
$$

$$
\equiv Ti - \text{OH} + \text{As} \left(\text{V}\right) + H^+ \rightarrow Ti - \text{As} \left(\text{V}\right) + H_2O \quad (4)
$$

$$
\equiv Fe - \text{OH} + \text{As} \left(\text{V}\right) + H^+ \rightarrow Fe - \text{As} \left(\text{V}\right) + H_2O \quad (5)
$$

Comparing the FTIR spectra of ZnO/TiO$_2$, two significant differences are observed before and after As(V) adsorption (Figure 5 b). A significant peak intensity decreases at ≈ 1600 and
3400 cm$^{-1}$ is associated with H–O–H bonds and O–H stretching vibration of TiO$_2$. This indicates that the hydroxyl groups of the active material and the As(V) oxyanions are linked by a monodentate and bidentate complex on the adsorbent surface (equation 4) [78, 79].

FTIR spectra of Fe$_3$O$_4$ (Figure 5 c) present a substantial increase of intensity at peaks below $\approx 850$ cm$^{-1}$, related to the coordination of Fe–O–As stretching vibration (equation 5) [80]. Further, two minor variations were observed, a decrease of peak intensity was found at $\approx 1500$ cm$^{-1}$, associated with the complexation of Fe–OH groups with As(V) species [81]. The intensity increase of two peaks at $\approx 2950$ cm$^{-1}$ was related to As–O bonds between OH$^-$ groups of Fe-based active material and arsenic oxyanions [82]. With this information, a complete understanding of the adsorption mechanism for all the active materials was established.

3.4. Acute lethality tests

To evaluate the putative toxic effects of Fe$_3$O$_4$, ZnO/TiO$_2$ and Y$_2$(CO$_3$)$_3$ nanoparticles, D. magna was exposed to water suspensions of these nanomaterials for 48 h. The pictures obtained after this exposure period are shown in Figure 6.
Figure 6. *Daphnia magna* exposed to (a) medium without nanoparticles and exposed to medium with nanoparticles: (b) Fe₃O₄, (c) ZnO/TiO₂, and (d) Y₂(CO₃)₃ after 48h.

Comparing Figure 6 (a) with Figure 6 (b – c), it is possible to realise that Fe₃O₄ and ZnO/TiO₂ nanoparticles uptake by *D. magna* occurred all over its body for both materials. Figure 6 (c) indicates that Y₂(CO₃)₃ nanoparticles accumulate mainly on the *D. magna* gut, which agrees with previous studies employing nanomaterials [76, 83].

Figure 7. Acute lethal effects of (a) Fe₃O₄, (b) ZnO/TiO₂, and (c) Y₂(CO₃)₃ nanoparticles on *Daphnia magna* exposed to contaminated water for up to 48 hours (concentrations on mg/L).

*Daphnia magna* has been used as a model organism in ecotoxicity studies [84]. The present study shows that exposure to nanoparticles strongly affects *D. magna* survival, especially at the
highest tested concentrations of Fe$_3$O$_4$ (< 250 mg/L), ZnO/TiO$_2$ (< 25 mg/L) and Y$_2$(CO$_3$)$_3$ (1.5 mg/L) (Figure 7) (repeated-measurements ANOVA, p < 0.05). Mortality was higher for ZnO/TiO$_2$ (Figure 7 b) than for the remaining tested materials (Figure 7 a, c). However, mortality was low or absent at lower, environmentally relevant concentrations. The LC$_{50}$ (95% C.I.) for Fe$_3$O$_4$, ZnO/TiO$_2$ and Y$_2$(CO$_3$)$_3$ was: 6.57 x 10$^3$ mg/L (2.73 – 20.31 x 10$^3$ mg/L), 28.66 mg/L (21.12 – 32.66 mg/L), and 1.91 x 10$^6$ mg/L (1.63 – 3.09 x 10$^6$ mg/L), respectively. Therefore, the toxicity tests show that the used micro/nanoparticles, besides their efficiency on As removal, do not threaten aquatic organisms, reinforcing their use for water treatments.

4. Conclusions

Three different active materials have been prepared and characterised, and their arsenic adsorption capacity evaluated. Magnetite nanoparticles show spherical and hexagonal shapes, with sizes ranging from 80 to 150 nm and a point of zero charges of ≈ 10. The prepared ZnO/TiO$_2$ nanoparticles are round-shaped with widths from 100 to 350 nm. A surface area of 88.28 m$^2$/g and a PZC of 6 characterises the nanocomposite. Yttrium carbonate exhibits shapes like nanorods with lengths ranging from 50 to 200 nm, and a PZC of 10. The pH proved to be an important parameter determining the adsorption capacity, and just the ZnO/TiO$_2$ nanocomposite presents high adsorption capacity for all the pH ranges. Contact time tests allow concluding that both yttrium and ZnO/TiO$_2$ present higher adsorption rates, achieving efficiencies close to 100% after 10 minutes of contact. Changing the initial concentration of As solution, ZnO/TiO$_2$ shows high performance on adsorption, with adsorption efficiencies always close to 100% in all ranges of concentrations (0.1 – 10 mg/L) and leading to maximum adsorption capacities of 32.83, 37.30, and 35.76 mg/g for Y$_2$(CO$_3$)$_3$, ZnO/TiO$_2$, and Fe$_3$O$_4$, respectively. In addition, toxicity tests using the model species *D. magna* showed that the micro/nanoparticles do not constitute a threat to aquatic organisms, reinforcing their use for
water remediation applications. The remarkable adsorption results indicate the suitability of all
active materials for arsenic removal from contaminated water.

Credit author statement
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Mendez; Funding acquisition: S. Lanceros-Mendez and Fernanda Cássio; Investigation: H.
Salazar, Daniela Batista, A. Fidalgo-Marijuan, Krishnapriya R., K. P. Shejale; Methodology:
P. M. Martins, H. Salazar, K. P. Shejale, A. Fidalgo-Marijuan; Project administration: S.
Lanceros-Mendez; Resources: S. Lanceros-Mendez, Fernanda Cássio, R. K. Sharma and G.
Botelho; Software: H. Salazar, A. Fidalgo-Marijuan; Supervision: S. Lanceros-Mendez,
Fernanda Cássio, R. K. Sharma, S. Ferdov and G. Botelho; Validation: S. Lanceros-Mendez,
Fernanda Cássio and G. Botelho; Visualization: P. M. Martins; H. Salazar; Roles/Writing: H.
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References


Supplementary Information

1. Supplementary information for sub-chapter 2.3.

The kinetic curves were fitted according to nonlinear forms of pseudo-first, pseudo-second-order, Elovich, and Bangham models described in equations 1, 2, 3, and 4, respectively:

\[ Q_t = Q_e \left(1 - \exp\left(-k_1 t\right)\right) \quad (1) \]

\[ Q_t = \frac{Q_e^2 k_2 t}{1 + Q_e K_2 t} \quad (2) \]
\[ Q_t = \frac{\ln \alpha \beta}{\beta} + \frac{1}{\beta} \ln t \]  

(3)

\[ Q_t = k t^\nu \]  

(4)

where \( Q_e \) and \( Q_t \) (mg/g) are the capacities for arsenic adsorption at equilibrium and at a correspondent time, respectively. \( K_1 \) (min\(^{-1}\)) is the pseudo-first-order adsorption rate constant, \( K_2 \) (g/mg min) is the pseudo-second-order adsorption rate constant, \( \alpha \) is the initial adsorption rate (mg/g min), and \( \beta \) is the desorption constant (g/mg), \( k \) (mg/g) and \( \nu \) (min\(^{-1}\)) are constants.

The isotherm curves were fitted to the following models: Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich, which are defined by the equations 5 to 9, respectively:

\[ q_e = \frac{q_{\text{max}} b C_e}{1 + b C_e} \]  

(5)

\[ q_e = K_F C_e^{1/n} \]  

(6)

\[ q_e = \frac{R T}{b_T} \ln(K_T C_e) \]  

(7)

\[ q_e = Q_S \exp\left(-B_D \varepsilon^2\right) \]  

(8)

\[ \varepsilon = R T \ln \left(1 + \frac{1}{C_e}\right) \]  

(9)

where \( q_e \) (mg/g) is the As adsorption capacity at a given equilibrium concentration, \( C_e \) (mg/L) is the arsenic equilibrium concentration, \( q_{\text{max}} \) (mg/g) is the maximum adsorption capacity, \( K_L \) (L/mg) is the adsorption rate for Langmuir isotherm model, \( K_F \) (L\(^{1/n}\) mg\(^{(1-1/n)}\) g\(^{-1}\)) is the adsorption capacity of the adsorbent for Freundlich isotherm model, and \( I/n \) is a measure of the adsorption intensity, \( b \) (J/mol) is Temkin constant, \( K_T \) (L/g) Temkin isotherm constant, \( Q_S \) (mg/g) is the maximum adsorption capacity, \( B_D \) (mol\(^2\)/kJ\(^2\)) is Dubinin-Radushkevich constant, \( \varepsilon \) (kJ/mol) is the adsorption potential, \( R \) (8.314 J/mol K) is the universal gas constant, \( T \) (K) is the temperature, \( k \) and \( \nu \) are constants. Regarding \( I/n \) value, the closer its value to 0, the more heterogeneous is the surface of the nanocomposite membrane.
2. Supplementary information for sub-chapter 2.4.

Table S2. pH of the nanosuspensions measured at the beginning and after 48h of exposure.

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Concentrations (mg/L)</th>
<th>Initial</th>
<th>48 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>8.29</td>
<td>8.07</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8.20</td>
<td>7.81</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>8.11</td>
<td>7.80</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>7.77</td>
<td>7.84</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>7.45</td>
<td>7.99</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>7.18</td>
<td>7.64</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>6.78</td>
<td>7.49</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>0.1</td>
<td>8.09</td>
<td>7.63</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>8.12</td>
<td>7.71</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>8.12</td>
<td>7.69</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>8.09</td>
<td>7.74</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>8.03</td>
<td>7.84</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>7.93</td>
<td>7.96</td>
</tr>
<tr>
<td>ZnO/TiO$_2$</td>
<td>0.005</td>
<td>8.02</td>
<td>7.74</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>8.10</td>
<td>7.79</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>8.11</td>
<td>7.77</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>8.12</td>
<td>7.83</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>8.11</td>
<td>7.86</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>8.10</td>
<td>7.88</td>
</tr>
<tr>
<td>Y$_2$(CO$_3$)$_3$</td>
<td>0.005</td>
<td>8.02</td>
<td>7.74</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>8.10</td>
<td>7.79</td>
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<tr>
<td></td>
<td>0.1</td>
<td>8.11</td>
<td>7.77</td>
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<tr>
<td></td>
<td>0.5</td>
<td>8.12</td>
<td>7.83</td>
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<tr>
<td></td>
<td>1</td>
<td>8.11</td>
<td>7.86</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>8.10</td>
<td>7.88</td>
</tr>
</tbody>
</table>

3. Supplementary information for sub-chapter 3.2.2.

Figure S8. Adsorption kinetics of (a) Y$_2$(CO$_3$)$_3$, (b) ZnO/TiO$_2$, and (c) Fe$_3$O$_4$, for As (V) removal ([As] = 100 µg/L; contact time: 30 min; pH = 7).
Table S3. Pseudo-first-order, pseudo-second-order, Elovich, and Bangham kinetics models for As(V) adsorption by $Y_2$($CO_3$)$_3$, ZnO/TiO$_2$, and Fe$_3$O$_4$ active materials.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$Y_2$($CO_3$)$_3$</th>
<th>ZnO/TiO$_2$</th>
<th>Fe$_3$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pseudo First Order</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$k_1$ (min$^{-1}$)</td>
<td>0.269</td>
<td>0.361</td>
<td>0.407</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.95</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.459</td>
<td>0.307</td>
<td>0.257</td>
</tr>
<tr>
<td><strong>Pseudo Second Order</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_2$ (g/mg min)</td>
<td>0.054</td>
<td>0.085</td>
<td>0.104</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.97</td>
<td>0.994</td>
<td>0.991</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.292</td>
<td>0.123</td>
<td>0.158</td>
</tr>
<tr>
<td><strong>Elovich</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$ (mg/g min)</td>
<td>8.831</td>
<td>23.908</td>
<td>42.488</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.97</td>
<td>0.98</td>
<td>0.97</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.301</td>
<td>0.222</td>
<td>0.276</td>
</tr>
<tr>
<td><strong>Bangham</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k$ (mg/g)</td>
<td>0.240</td>
<td>3.457</td>
<td>3.632</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.97</td>
<td>0.98</td>
<td>0.97</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.312</td>
<td>0.271</td>
<td>0.317</td>
</tr>
</tbody>
</table>

4. Supplementary information for sub-chapter 3.2.3.

Table S4. Effect of As (V) concentration on efficiency (E) and adsorption capacity ($Q_e$) of active materials.

<table>
<thead>
<tr>
<th>[As] (mg/L)</th>
<th>$Y_2$($CO_3$)$_3$</th>
<th>ZnO/TiO$_2$</th>
<th>Fe$_3$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E (%)</td>
<td>$Q_e$ (mg/g)</td>
<td>E (%)</td>
</tr>
<tr>
<td>0.1</td>
<td>99.6</td>
<td>0.10</td>
<td>99.9</td>
</tr>
<tr>
<td>0.25</td>
<td>98.9</td>
<td>0.25</td>
<td>98.7</td>
</tr>
<tr>
<td>0.5</td>
<td>98.7</td>
<td>0.49</td>
<td>99.4</td>
</tr>
<tr>
<td>0.75</td>
<td>98.9</td>
<td>0.74</td>
<td>99.3</td>
</tr>
<tr>
<td>1</td>
<td>98.9</td>
<td>0.99</td>
<td>99.4</td>
</tr>
</tbody>
</table>
Table S5. Isotherm models parameters for As (V) removal by Y$_2$(CO$_3$)$_3$, ZnO/TiO$_2$, and Fe$_3$O$_4$.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Y$_2$(CO$_3$)$_3$</th>
<th>ZnO/TiO$_2$</th>
<th>Fe$_3$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$Q_{\text{max}}$ (mg/g)</td>
<td>32.83</td>
<td>37.30</td>
<td>35.76</td>
</tr>
<tr>
<td></td>
<td>$K_L$ (L/mg)</td>
<td>1.49</td>
<td>1.67</td>
<td>1.54</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.994</td>
<td>0.99</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>0.149</td>
<td>0.328</td>
<td>0.133</td>
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<tr>
<td>Freundlich</td>
<td>$K_F$ (mg$^{n-1}$L$^n$/g)</td>
<td>26.83</td>
<td>33.25</td>
<td>31.93</td>
</tr>
<tr>
<td></td>
<td>$1/n$</td>
<td>0.80</td>
<td>0.79</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.998</td>
<td>0.994</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>0.169</td>
<td>0.286</td>
<td>0.160</td>
</tr>
<tr>
<td>Temkin</td>
<td>$b_T$ (J/mol)</td>
<td>1.35</td>
<td>1.16</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>$K_T$ (L/g)</td>
<td>436.49</td>
<td>943.92</td>
<td>539.42</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.7</td>
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<td>0.6</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>1.720</td>
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<td>1.938</td>
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<tr>
<td>Dubinin –</td>
<td>$Q_S$ (mg/g)</td>
<td>15.38</td>
<td>16.52</td>
<td>16.14</td>
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<tr>
<td>Radushkevich</td>
<td>$B_0$ (mol$^2$/kJ$^2$)</td>
<td>0.21</td>
<td>0.18</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.97</td>
<td>0.97</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>0.528</td>
<td>0.616</td>
<td>0.440</td>
</tr>
</tbody>
</table>

Figure S9. Adsorption isotherm models simulation for (a) Y$_2$(CO$_3$)$_3$, (b) ZnO/TiO$_2$, and (c) Fe$_3$O$_4$, for As (V) removal (contact time: 30 min; pH = 7).