Iron oxides are a group of minerals composed of Fe together with O and/or OH. They have high points of zero charge, making them positively charged over most soil pH ranges. Iron oxides also have relatively high surface areas and a high density of surface functional groups for ligand exchange reactions. In recent time, many studies have been undertaken on the use of iron oxides to remove harmful oxyanions such as chromate, arsenate, phosphate, and vanadate, etc., from aqueous solutions and contaminated waters via surface adsorption on the iron oxide surface structure. This review article provides an overview of synthesis methods, characterization, and sorption behaviours of different iron oxides with various oxyanions. The influence of thermodynamic and kinetic parameters on the adsorption process is appraised.

Keywords: oxyanions, iron oxides, adsorption, isotherm, points of zero charge

Introduction

Iron oxides are a group of minerals composed of iron and oxygen and/or hydroxide. They are widespread in nature and are found in soils and rocks, lakes and rivers, on the seafloor, in air, and in organisms. Iron oxides are of great significance for many of the processes taking place in the ecosystem. They are ubiquitous in soils and sediments, where they are important regulators of the concentration and distribution of plant nutrients and pollutants such as heavy metals [1]. Iron oxides can be both beneficial and undesirable. There are 17 known iron oxides differing in composition, valence of Fe, and – most importantly – in crystal structure [2]. Iron oxides have been studied for their potential use in a wide range of important uses such as pigments in ceramic glaze, catalysis, electrochemistry, magnetization, biomedical science, and environmental applications [3-8].

Iron oxides have been used as catalysts in the chemical industry [9, 10], and a potential photoanode for possible electrochemical cells [11, 12]. In medical applications, nanoparticle magnetic and superparamagnetic iron oxides have been used for drug delivery in the treatment of cancer [13, 14]. There also has been considerable interest in using iron oxides to remove environmental contaminants since environmental pollution has emerged as an important issue in recent decades. Increasing interest has recently been diverted to evaluating the ability of iron oxides to remove contaminants such as arsenite, arsenate, chromate, vanadate, and phosphate etc., from aqueous solution by the process of adsorption. This is because iron oxides have exhibited a great potential to efficiently remove harmful oxyanions due to the earlier-mentioned characteristic of high surface area.

The aim of this review is therefore to discuss iron oxide composition and structure, synthesis and characterization with specific emphasis on their ability to adsorb oxyanions.
from aqueous solution. Several factors that play important roles in the adsorption process, such as pH, competitive anions, temperature, and particle size, will also be discussed in light of literature results.

**Composition and Structure of Iron Oxides**

Most of the iron oxides contain Fe (III); only in FeO and Fe(OH)₂ is iron exclusively present in the divalent state, whole green rusts and magnetite are mixed Fe (II) – Fe (III) minerals. There are five polymorphs of FeOOH and four of Fe₂O₃. Nearly all iron oxides are crystalline (with the exception of ferrihydrite and schwertmannite, which are poorly crystalline). The degree of crystal order is, however, variable and depends on the conditions under which the iron oxides are formed [2]. Table 1 shows an overview of different iron oxides, hydroxides, and oxy-hydroxides.

Iron oxides consist of arrays of iron and oxygen or hydroxides. Since oxygen and hydroxides are much larger than the iron atoms, the crystal structure of the oxides is controlled by the arrangement of the oxygens and hydroxides. The sheets of oxygen and hydroxide are mostly stacked ABCABC. (hexagonal close packing, or hcp) or ABAB. (cubic close packing, or ccp), while Fe is placed in the interstices between the oxygen and hydroxide sheets. To fulfill the charge balance requirement, only part of the interstices is filled with Fe. The various iron oxides differ in the arrangement of Fe in the interstices, and to a lesser extent differences in the stacking of oxygen and hydroxide sheets [2].

Fe is predominantly octahedrally (FeO₆ or FeO₃(OH)₃), and in some cases tetrahedrally (FeO₄) coordinated in the iron oxides, and the resultant octahedral and tetrahedral constitute the basic structural unit of iron oxides. An alternative way of considering the iron oxide crystal structure is the linkage of these basic structural units, since the linkage by sharing either corners, edges, or faces results in different iron oxides. Figs. 1 a-c show the structure of goethite, hematite, and magnetite according to Ghose et al. [15].

**Properties and Uses of Iron Oxides**

Iron (II) oxide (FeO) or ferrous oxide is also known as wustite in its mineral form. As a powder, this black oxide can cause an explosion as it readily ignites. Iron (III) oxide (Fe₂O₃) or ferric oxide is also known as hematite (alpha form) or maghemite (gamma form) in its mineral form. As an industrial chemical it is commonly called ‘rouge’ or red. Iron (II,III) oxide (Fe₃O₄) or ferrous ferric oxide is also known as magnetite or lodestone in its mineral form. Magnetite forms readily when iron oxidizes under water, and so it is often found inside tanks or below the waterline of ships. Color is one of the most striking features of the iron oxides. Iron oxides are responsible for the vivid colors of rocks and soils. The most common shades are red, brown, and yellow, but purple, black (magnetite) and even greenish blue (green rust) also occur. Due to their color (and also their opacity and light fastness), natural iron oxides have been used for decoration since prehistoric times [1]. The most industrially important iron ores are chemically iron oxides. Some iron oxides are widely used in ceramic applications, particularly in glazing. Many metal oxides provide the colors in glazes after being fired at high temperatures. Iron (II) oxide is black, while iron (III) oxide is red or rust colored. Iron compounds other than oxides can have other colors. Iron oxides yield pigments, and natural iron oxide pigments are called ‘ochre.’ Many classic paint colors, such as raw and burnt siennas and umbers, are iron oxide pigments. These pigments have been used in art since prehistoric times. Iron pigments are also widely used in the cosmetic field. They are considered to be non-toxic, moisture-resistant, and non-bleeding. Iron oxides graded safe for cosmetic use are produced synthetically in order to avoid the inclusion of ferrous or ferric oxides and impurities normally found in naturally occurring iron oxides. The iron oxide cycle (FeO₂/O₂/FeO) is a two-step thermo-chemical process used for hydrogen production [2].

**Synthesis of Iron Oxides**

Iron oxides can be regarded as a class of minerals that are simple to synthesize in the laboratory, although not always as pure phases. In general, there are several approaches to preparing iron oxides. Recently, a thorough review has been prepared by Cornell and Schwertmann [1] on the preparation of iron oxides. The preparation and properties of iron oxides continue to attract considerable interest and attention because of their importance in magnetic mate-

---

Table 1. Overview of iron oxides.

<table>
<thead>
<tr>
<th>Oxides-hydroxides and hydroxides</th>
<th>Oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite (α-FeOOH)</td>
<td>Wüstite (FeO)</td>
</tr>
<tr>
<td>Akaganéite (β-FeOOH)</td>
<td>Magnetite (Fe₃O₄)</td>
</tr>
<tr>
<td>Lepidocrocite (γ-FeOOH)</td>
<td>Hematite (α-Fe₂O₃)</td>
</tr>
<tr>
<td>Feroxyhydrate (δ'-FeOOH)</td>
<td>Maghemite (γ-Fe₂O₃)</td>
</tr>
<tr>
<td>- (δ-FeOOH)</td>
<td>(- β-Fe₂O₃)</td>
</tr>
<tr>
<td>Ferrihydrite (Fe₇OH₈·4H₂O)</td>
<td>(- θ-Fe₂O₃)</td>
</tr>
<tr>
<td>High-pressure FeOOH</td>
<td></td>
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<tr>
<td>Benalite Fe(OH)₃</td>
<td></td>
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<tr>
<td>- Fe(OH)₂</td>
<td></td>
</tr>
<tr>
<td>Schwertmannite Fe₅O₁₀(OH)</td>
<td></td>
</tr>
<tr>
<td>(SO₄)₃·nH₂O</td>
<td></td>
</tr>
<tr>
<td>Green Rusts Fe₅Fe₃(SO₄)·nH₂O</td>
<td></td>
</tr>
<tr>
<td>A⁺ =Cl⁺; ½SO₄²⁻</td>
<td></td>
</tr>
</tbody>
</table>
The formation of iron oxides in an aqueous system involves nucleation and crystal growth [4]. Nucleation is classified into homogeneous nucleation and heterogeneous nucleation. Homogeneous nucleation occurs spontaneously in bulk solution when the supersaturation (i.e., ion activity product of a certain compound exceeds its solubility product) exceeds a certain critical value. The formation of stable embryonic clusters of molecules or ions (nuclei) in solution is the essential requirement for precipitation to occur [1]. Heterogeneous nucleation thus occurs when the presence of a solid phase reduces the free energy of nucleation and thus leads to an increase in the rate of nucleation. The substrate may be minute particles of foreign phase or crystals (seeds) of the phase that is crystallizing. Heterogeneous nucleation can take place at a lower level of supersaturation than is required for homogeneous nucleation [1].

In crystal growth, a certain degree of supersaturation is required but it is much less than that needed for nucleation. Crystal growth may be controlled either by transport process or by surface chemical reaction. The mechanism by which a crystal grows may depend on some conditions. Changes in the degree of supersaturation or solution variables may lead to a change in mechanism during growth. The nature of a crystal is governed by the rate of growth of its different faces. Those faces that grow slowly tend to persist in the crystal, whereas fast-growing faces are eliminated. The crystal habit/nature is therefore determined primarily by the slow-growing faces. Adsorbing foreign ions may alter the rate at which different crystal faces grow and modify the habit of crystal [1].

Almost all the iron oxides and hydroxides can be prepared by a number of synthesis routes. The method of synthesis frequently influences the properties of the product, particularly crystal morphology, degree of crystallinity, sample surface area and water content. The synthesis methods proposed by Cornell and Schwertmann [1] are: hydrolysis of acidic solution of Fe(III) salts, transformation of ferrihydrite in alkaline media, transformation of ferrihydrite in alkaline media, oxidative hydrolysis, phase transformation, and decomposition of metal chelates.

![Fig. 1. a) Structure of Goethite α-FeOOH (1 0 0) – water interface. A schematic picture of the atomic layer model for CTR analysis: A – crystalline bulk structure, B – crystalline surface structure, and C – semi-ordered physisorbed water or sorbates (Ghose et al.) [15]; b) Structure of Hematite α-Fe2O3 (1102) – water interface. Layer Stacking Sequence Along c Axis for α-Fe2O3 (1 1 0 2); (i) ideal bulk stoichiometric termination and (ii) hydroxylated stoichiometric termination. The large spheres represent oxygen and small spheres represent iron atoms. The 'O and °O represent oxygen atoms coordinated to one and three iron atoms, respectively, and the °Fe and °Fe represent iron atoms coordinated to five and six oxygen atoms, respectively (Ghose et al.) [15]. c) Structure of magnetite Fe3O4 (1 1 1) – water interface. Layer stacking sequence along the c axis for the oxygen terminated Fe3O4 (1 1 1) (i) O4-Feoh-O4-Fetd1_oh_td2 and (ii) O4-Fetd1_oh_td2-O4-Feoh where the large spheres represent oxygen atoms and the small spheres represent iron atoms (Ghose et al. [15]).]
Hydrolysis of Acidic Solution of Fe(III) Salts

At very low pH (<1) Fe⁺ exists as a purple hexa-aquo ion, [Fe(H₂O)₆]³⁺. Hydrolysis involves the stepwise elimination of the proton from the six water molecules that surround the central Fe cation to form mono and bi nuclear species, which interact further to produce species of higher nuclearity [17]. The polymeric species eventually precipitate. The condition of crystallinity of the precipitate depends on the reaction conditions. Precipitation time may range from seconds to years.

Examples of hydrolysis reactions are:

\[
\begin{align*}
\text{Fe}^{3+} + \text{H}_2\text{O} & \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{H}^+ \quad (1) \\
\text{Fe}^{3+} + 2\text{H}_2\text{O} & \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2\text{H}^+ \quad (2) \\
\text{Fe}^{3+} + 2\text{H}_2\text{O} & \rightarrow \text{FeOOH} + 3\text{H}^+ \quad (3) \\
2\text{Fe}^{3+} + 3\text{H}_2\text{O} & \rightarrow \text{Fe}_2\text{O}_3 + \text{H}^+ \quad (4)
\end{align*}
\]

Heating of solution and the addition of base are the two principal methods used to induce hydrolysis in the laboratory.

As hydrolysis releases protons, pH of the system falls during the early stages of hydrolysis. pH may fall to a low enough value to inhibit further hydrolysis in cases where hydrolysis is induced by raising the temperature. The pH drop is important because incomplete hydrolysis reduces the yield of products [1].

Hematite, akaganeite, and ferrihydrite may be obtained by hydrolysis of Fe³⁺ solutions. The product formed is influenced by a variety of factors, including rate of hydrolysis, pH of the solution, temperature, concentration of Fe³⁺, and the nature of anion present. The reaction condition must be carefully controlled in order not to obtain mixtures, rather than a single product. Some researchers have investigated the synthesis method intensively and have shown the various ways in which the reaction product and also morphology may be influenced by reaction conditions [18, 19].

The most important application of the acidic hydrolysis method is in the production of hematite and akaganeite, but goethite can also be synthesized in this way [1]. Low product yield is the disadvantage of the method. Ramming et al. also reported the synthesis of nanosized super paramagnetic hematite using hydrolysis reaction [20]. A well-defined subrounded morphology hematite was obtained with an average diameter of 41 nm particle size. The synthesis of iron oxides by hydrolysis reaction using the hydrothermal method have been reported recently [21]. In this study single crystalline α-Fe₂O₃ nanocubes were successfully obtained in large quantities through a facile one-step hydrothermal synthesis route under mild conditions. The products were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), select-area electron diffraction (SAED), and Fourier transform infrared spectrometry (FTIR) [21].

Transformation of Ferrihydrite in Alkaline Media

Ferrihydrite is the initial product resulting from fast hydrolysis (by addition of alkali) of an Fe⁺ salt solution (2-line ferrihydrite). It is thermodynamically unstable and transforms into goethite, hematite or a mixture of the two with time. These compounds formed by different pathways. The formation of hematite, involves an internal dehydration/rearrangement process within the particles of ferrihydrite, whereas the formation of goethite proceeds via dissolution of ferrihydrite followed by nucleation and growth of crystalline phase [22, 23]. Both processes take place only in the presence of water. Hematite formation is promoted by factors that induce aggregation of ferrihydrite particles (pH near the PZC ferrihydrite, i.e pH 7-8) or dehydration (i.e increased temperature) [24]. The transformation to goethite is the dissolution/reprecipitation process in which the reaction rate is governed by the rate of dissolution of ferrihydrite or nucleation of crystal growth of goethite. The formation of goethite is favoured by raising or lowering the pH away from the PZC because this promotes dissolution of ferrihydrite [25]. A plot of transformation of ferrihydrite into goethite or hematite versus time displays an initial induction period to the nucleation of the product followed by a faster stage that is first-order with respect to the amount of precursor remaining in the system [23].

Oxidative Hydrolysis of Fe(II) Salts

This is a very versatile method capable of producing goethite, lepidocrocite, magnetite, ferrihydrite, and ferroxyhyte. The product formed depends on the reaction conditions, on particular pH, rate of oxidation, suspension concentration, temperature, and concentration of foreign species [26, 27]. An inert atmosphere of nitrogen must be provided for production [28]. The reaction can be carried out over the pH range 6-14. Between pH 6-7, goethite and lepidocrocite are formed; pure products of either can be obtained by adjusting the rate of oxidation and concentration of the carbonate in the system [27, 28]. Magnetite is obtained at pH >8 and pure goethite is produced at pH 14. Ferroxyhyte is obtained with very rapid oxidation (e.g. using H₂O₂).

The oxidation/hydrolysis reaction releases protons so that as the transformation proceeds, the pH drops to about 3 and the transformation rate falls to practically zero (if no extra base is added), hence oxidation is complete:

\[
2\text{Fe}^{2+} + 3\text{H}_2\text{O} + 1/2\text{O}_2 \rightarrow 2\text{FeOOH} + 4\text{H}^+ \quad (5)
\]

pH must be held constant by the continual addition of alkali to the system in order to obtain a higher yield of reasonable crystalline product. This is most conveniently achieved by using an automatic burette and pH-stat titration technique. The reaction is complete when the further addition of alkali is required [1]. An alternative method is the use of buffer (NaHCO₃ or imidazole), but the end product will be contaminated. A feature of the oxidation/hydrolysis of Fe⁺ systems is that a crystalline product can be obtained between a few hours at room temperature.
Phase Transformations

Phase transformation refers to conversion of one crystalline iron oxide or oxyhydroxide into another under suitable conditions. Every iron oxide can be converted into at least one other member of the groups [29]. The products frequently retain the crystal morphology of the starting material (pseudomorphosis) where a topotactic transformation mechanism is involved: for example, the formation of maghemite by thermal dehydration of lepidocrocite or by oxidation of magnetite and also the formation of hematite at moderate temperature (200°C) via thermal dehydration of goethite [1].

Decomposition of Metal Chelates

Decomposition of Fe (III) chelates is a suitable technique for the production of fairly monodispersed products (often with unusual morphologies) because it provides a constant and controlled supply of reactant [30]. The reaction is carried out at temperatures greater than 100°C and pH above 12. This method has been used to produce hematite and magnetite. The nature of the product in terms of the shape and size of the crystals are governed by the type of additives in the system. A disadvantage of this method is that the product may be contaminated by the ligand.

The sol gel method has also been reported for the synthesis of iron oxides. Duhan and Devi synthesized nanosized (20-42 nm) iron oxide powders using the solgel method at 700°C [31]. Gong et al. reported the synthesis of continuous hollow α-Fe2O3 fibers by sol gel method using ferric alkoxide and acetic acid as the starting materials and alcohol as the solvent [32]. Holland and Yamaura also reported the synthesis of nanoparticle magnetite by precipitation method [33]. The precipitation was carried out by heating the mixture in a boiling water bath and a domestic microwave oven. Their product was characterized by SEM, XRD, and FTIR. Parsons et al. synthesized iron oxide/oxyhydroxide using the microwave-assisted method [34]. The experiment was conducted by using iron (III) chloride titrated with sodium hydroxide at different temperatures from 100-250°C. The particles were characterized using TEM, XRD and XAS (x-ray absorption spectroscopy). The average particle sizes of the nanoparticles synthesized were in the range 17-33 nm [34]. A simple reduction-oxidation method also has been reported for the synthesizing plate-shaped γ-Fe2O3 nanocrystals at room temperature and under ambient pressure. The reaction was carried out in two steps: Fe (II) was reduced to Fe atoms by γ-ray irradiation in nitrogen atmosphere in the first step carried out in two steps: Fe (II) was reduced to Fe atoms by temperature and under ambient pressure. The reaction was carried out at temperatures greater than 100ºC and pH above 12. This method has been used to produce hematite and magnetite. The nature of the product in terms of the shape and size of the crystals are governed by the type of additives in the system. A disadvantage of this method is that the product may be contaminated by the ligand.

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Characterization of Iron Oxides

Iron oxides consist of crystals ranging in size from 0.01 nm to several µm; they are characterized and checked for purity by the techniques commonly used for submicroscopic particles. The most important techniques are x-ray powder diffraction and electron microscopy. In addition, Mossbauer spectroscopy, infrared absorption spectroscopy, and thermal analysis give complimentary useful information [36]. All iron oxides have vivid colors that can be used for their characterization.

X-ray powder diffraction is essential for identification and purity control of the product. In addition, it may provide information concerning crystal size and disorder, structural parameters (unit cell edge lengths), degree of Isomorphous substitution, and surface area. The minimum size required for a crystallite to diffract x-rays is in the range of a few cells (ca 2-3 nm) [1]. Usually the x-ray pattern is recorded as a diffractogram using a goniometer equipped with a proportional or scintillation counter and a registration unit. Occasionally, film cameras, such as the Guinier camera, may be used. The common type of x-ray radiation normally used for Fe oxides are CoK∞ or FeK∞ radiation with a wavelength of 0.178890 and 0.193604 nm, respectively.

Electron microscopy is also a technique that enables crystal dimensions and also morphology to be measured directly. It is also useful for indicating the presence of amorphous material or traces of iron oxides not detectable by XRD. For example, transmission electron microscopy revealed the presence of a few percent fine needles of goethite in a preparation that, according to XRD, consisted of hematite only.

Mossbauer spectroscopy is a very useful tool in studies of local interactions between nuclear probes contained in the material investigated and their nearest environment [37]. The sensitivity of Mossbauer spectroscopy is substantially higher than XRD; it allows phases invisible to XRD to be revealed [38]. Mossbauer spectroscopy can be used for quantitative analysis of mixtures of different phases.

Infra red spectroscopy provides a rapid method of identification if the iron oxide is crystalline. It is also useful for detecting traces (1-2%) of goethite in a hematite preparation [1]. This technique enables detection of low levels of impurities arising from the preparation procedure and not washed out of the product. Such impurities include nitrate (~1400 cm-1) and carbonate (~1300 and ~1500 cm -1) [4]. The most suitable procedure for examination involves the use of KBr tablets consisting of 0.5-2 mg iron oxide and 300 mg pure KBr. Too much iron oxide in the tablet leads to a poor spectrum.

Thermogravimetry analysis (TGA) is a technique that provides information about absorbed and structural water present in iron oxides and also about phase specific changes and transformations [1]. A sample is continuously heated at a constant rate (2-10°C/min) and its weight loss is measured using a balance. Fe-oxides containing structural OH, for example goethite and lepidocrocite, lose weight at between 250-400°C by the dehydroxylation reaction:

\[
2\text{OH}^- \rightarrow \text{O}_2^\rightarrow + \text{H}_2\text{O}
\]

All fine-grained material contains adsorbed water and additional weight loss stems from loss of adsorbed water at a characteristic temperature of between 100° and 200°C.
Pure oxides such as hematite may, if fine grained, contain some OH in the structure, and this is driven off over a wide temperature range.

In differential thermal analysis (DTA), a sample is continuously heated at a constant rate (~10ºC·min⁻¹) and the temperature difference between an inert compound and the sample is recorded. Differences in temperature occur if reactions are either exothermic or endothermic. These effects are recorded as peaks on a plot of temperature difference versus temperature for Fe oxides. Endothermic effects result from the release of adsorbed or structural water and exothermic effects come from phase transformations (e.g. Fe₂O₃ → Fe₃O₄) or from recrystallization processes involving the transformation of small crystals into larger ones. The latter process is often observed during the transformation of ferrihydrite to hematite [1, 25].

Point of zero charge is also another method of characterizing iron oxides. The pH where the net total particle charge is zero is called the point of zero charge (PZC), which is one of the most important parameters used to describe variable-charge surfaces [39, 40]. PZC is a very important parameter because it characterizes the protonation-deprotonation behavior of various types of solid, mainly that of (hydr) oxides in aqueous suspensions [41]. It is well known that positive or negative surface sites are developed on the surface of solids in aqueous suspensions. The position of the PZC defines the affinity of the surface to the ionic surfactants and polyelectrolytes, which are widely

<table>
<thead>
<tr>
<th>Material</th>
<th>Description</th>
<th>Electrolyte</th>
<th>TºC</th>
<th>Method</th>
<th>pH₀</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>Hematite, Alfa Aesar</td>
<td>0.03 mol·dm⁻³ NaCl</td>
<td>-</td>
<td>IEP</td>
<td>6.5</td>
<td>Pan et al. [44]</td>
</tr>
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<td>Fe₂O₃</td>
<td>Monodispersed hematite from FeCl₃</td>
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<td>IEP</td>
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<td>Hematite, natural, heated at 700°C, 0.68% SiO₂, 0.29% Al₂O₃</td>
<td>0-0.001 mol·dm⁻³</td>
<td>25</td>
<td>IEP</td>
<td>5.8</td>
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<tr>
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<td>0.001 mol·dm⁻³ KNO₃</td>
<td>22</td>
<td>Acousto</td>
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<td>Mensah and Ralston [47]</td>
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<td>8.8</td>
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<td>6.5</td>
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<td>Fe₂O₃·nH₂O</td>
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<td>-</td>
<td>IEP</td>
<td>8.1</td>
<td>Varanda et al. [56]</td>
</tr>
<tr>
<td>FeOOH</td>
<td>Goethite from nitrate 2 samples</td>
<td>0.1 mol·dm⁻³ NaNO₃</td>
<td>25</td>
<td>pH</td>
<td>9.2</td>
<td>Boily et al. [57]</td>
</tr>
<tr>
<td>FeOOH</td>
<td>Goethite from nitrate</td>
<td>0, 1 mol·dm⁻³ NaNO₃</td>
<td>25</td>
<td>IEP</td>
<td>7.8</td>
<td>Juang and Chung [58]</td>
</tr>
<tr>
<td>FeOOH</td>
<td>Goethite from nitrate</td>
<td>0.001-0.1 mol·dm⁻³ NaNO₃</td>
<td>25</td>
<td>Cip</td>
<td>9.3</td>
<td>Antelo et al. [60]</td>
</tr>
<tr>
<td>FeOOH</td>
<td>Goethite, from nitrate</td>
<td>0.005-0.1 mol·dm⁻³ KNO₃</td>
<td>25</td>
<td>Cip</td>
<td>9.3</td>
<td>Nielsen et al. [61]</td>
</tr>
</tbody>
</table>

CIP – common intersection point of potentiometric titration curves obtained at three or more ionic strengths
Intersection – intersection point of potentiometric titration curves obtained at two ionic strengths
Merge – the titration curves obtained at different ionic strengths merge below an above a certain pH
pH – natural pH of the dispersion
IEP – Isoelectric point obtained by means of electrophoresis or electroosmosis
Acousto – Isoelectric point obtained by means of the electroacoustic method
used to modify the surface properties. The knowledge of the PZC of the materials of interest facilitates the choice of surfactant for a specific purpose, e.g. in mineral processing (floatation) or the choice of an adsorbent for removal of certain solutes (e.g. from waste water) makes it possible to predict the pH effect on the phenomena and processes involving adsorption [42]. Table 2 presents the PZC of some iron (hydr)oxides.

**Synthesis and Characterization of Iron Oxides by Different Researchers**

Iron oxides such as hematite, goethite, ferrihydrite, and magnetite have been synthesized and characterized by researchers using different methods as earlier mentioned in the preceding discussion. Other reports by different researchers are discussed below.

Wang et al. synthesized well dispersed nanoparticles with a close cage structure hematite (α-Fe₂O₃) by a low temperature hydrothermal method. The final products were investigated by XRD, Raman spectrum, TEM, and field emission scanning electron microscopy [62].

Marek Kosmulski et al. in their study aged synthetic goethite at 140°C overnight, leading to composite material in which hematite is detectable by Mossbauer spectroscopy, but XRD does not reveal any hematite peaks [37]. Yu and Hui prepared uniform nano-needle hematite particles by forced hydrolysis, namely by reflux of Fe(NO₃)₃ solution in the presence of an organic chelating agent, 1-hydroxyethyl-1,1-diphosphonic acid (HEDP) and HNO₃. Nano-needle hematite particles with a length of 90-100 nm and axial ratio of 9-12 were obtained. The effects of concentration of HEDP and HNO₃ on the morphology of the hematite particle were investigated by TEM. They thought the amount of positive charges on the primary particle surface is crucial for the formation of nano-needle particles from the morphology of the particles extracted at different stages of hydrolysis [63].

Li et al. prepared ultrafine α-Fe₂O₃ and Fe₃O₄ particles through a hydrothermal process at 150°C from a (NH₄)₂SO₄ and FeSO₄·6H₂O solution in the presence of hydrazine. The products were characterized by XRD and TEM and the formation of pure ∞-Fe₂O₃ and Fe₃O₄ powders was strongly influenced by the pH values of the aqueous solution [64].

Sorescu et al. synthesized hematite particles of four different morphologies (polyhedral, platelike, needlelike, and diskshape) by hydrothermal method. The morphology and average particle diameter (1.4, 7.4, 0.2, and 0.12 μm, respectively) were determined by (TEM) combined with electron diffraction. The hematite samples were studied by Mossbauer spectroscopy in the temperature range 4.2-300 K. In all cases, a weak ferromagnetic phase (WF) was present above the Morin temperature (temperature for which the antiferomagnetic phase is reduced to 50% of the value) of 230 k and found to coexist with antiferromagnetic phase (AF) below this temperature. The populations of the two phases at 230 k were demonstrated to depend on the morphology of the particles. The weak ferromagnetic and anti-ferromagnetic phases exhibited a different dependence of the magnetic texture on temperature and particle morphology [65].

Schwertmann and Murad in their study stored ferrihydrite in aqueous suspension at 24°C and pH between 2.5 and 12 for as long as three years, resulting in the formation of goethite and hematite. The proportions and crystallinity of these products widely varied with pH. Maximum hematite was formed between pH 7 and 8, and maximum goethite at pH 4 and 12. The crystallinity of both products was indicated by X-ray powder diffraction line broadening and hyperfine field values and distribution widths. The lower the proportion of the corresponding product in the mixture, the poorer the distribution width. The existence of two competitive formation processes was suggested for the formation of goethite and hematite. Goethite is formed via solution, preferably from monovalent Fe(III), [Fe(OH)₂] and Fe(OH)₂, and hematite by internal rearrangement and dehydration within ferrihydrite aggregates. They stated that the conditions favourable for the formation of goethite are unfavourable for that of hematite and vice versa [66].

Yasuhiro et al. prepared submicrometer, crystalline hematite (α-Fe₂O₃) particles by hydrolysis of organic iron carboxylate solutions using water at 175°C for 30 minutes [67]. The particle size of hematite was significantly dependent on the liquid-phase stirring speed and the organic compositions. The precipitation rate of hematite from the organic solution followed first-order kinetics. The precipitation rate increased markedly with increasing temperature and the activation energy for the process was 94.6 kJ/mol. At 220°C, the hydrolysis of iron carboxylate solution leads to a mixture of hematite and magnetite (Fe₃O₄). The iron oxides prepared at 175°C-220°C were found to be free from organic contamination of the starting material. The precipitate of hematite was characterized by XRD, Infra-red and differential thermal analysis (DTA) and the particle size and morphology were obtained by using SEM [67].

Kandori et al. prepared hematite particles by forced hydrolysis reaction of acidic FeCl₃ solution and the effect of polyvinyl alcohol (PVA) on the formation of the spherical hematite particles was examined [68]. When the concentration of polyvinyl alcohol was increased, the shape of hematite particles varied from spherical to disk-like by reducing their thickness. The hematite particles formed with polyvinyl alcohol were hydrohematite with a crystal lattice distortion and exhibited a polycrystalline nature. These particles change from microporous to mesoporous after the elimination of residual polyvinyl alcohol molecules adsorbing on cluster particles by evacuating the samples above 300°C. This result supports the fact that hematite particles produced by the forced hydrolysis reaction are aggregates, as were further revealed by using simultaneous temperature programmed desorption, mass spectroscopy and thermogravimetric measurement. They characterized synthetic hematite particles by using TEM, SEM, XRD, mass spectroscopy, and thermogravimetric analysis in vacuo. TEM and SEM were performed under acceleration voltages of 100 and 15KV with JEOL-200B and JSL-5600 instruments.
were prepared by adding 1M KOH to 200 cm³ of a continuous crystal surface. Thirteen ferrihydrites with co-precipitated P other than phosphate adsorbed by ligand-exchange on the surface of phosphate that can incorporate phosphorus (P) in forms of iron at high temperature [71, 72].

Nanostructured hematite can be prepared by electrochemical synthesis [70] by decomposition of organic iron compounds in alkaline media (pH >12) or by oxidation of pure synthesis [71] by decomposition of organic iron compounds [69]. The produced sample was kept constant at about 98ºC through thermal wraps. With a feedback temperature controller, 0.04 mol of FeCl₃·6H₂O was added under continuous stirring to obtain an Fe solution and was left in the container for 48 hours. The resulting red precipitate was separated from the solution by centrifugation and washed with deionized water to remove cations and anion at pH 7 [69]. The produced sample was dried at 80ºC for 6 hours in a drier oven and had a fairly uniform size of 40 nm. The powder sample was characterized using XRD, TEM, and Mössbauer spectroscopy.

Gee et al. prepared hematite nanoparticles by forced hydrolysis of acidic Fe⁺. 0.02 mol of HCl was added to deionized water in a closed container and the temperature was increased until the water boiled. The temperature was kept constant at about 98ºC through thermal wraps. With a feedback temperature controller, 0.04 mol of FeCl₃·6H₂O was added under continuous stirring to obtain an Fe solution and was left in the container for 48 hours. The resulting red precipitate was separated from the solution by centrifugation and washed with deionized water to remove cations and anion at pH 7 [69].

Galvez et al. prepared synthetic hematite in the presence of phosphate that can incorporate phosphorus (P) in forms other than phosphate adsorbed by ligand-exchange on the crystal surface. Thirteen ferrihydrites with co-preipitated P were prepared by adding 1M KOH to 200 cm² of a continuously stirred 0.135 M Fe(NO₃)₃ solution containing KH₂PO₄ until the pH was 4 [73]. The resulting ferrihydrite suspension was centrifuged and 190 cm³ of the supernatant was discarded. Solid Mg(NO₃)₂·6H₂O and water were added to make the Mg concentration 2M to prevent the formation of goethite. After readjusting the pH to 4, the suspension was poured into a pyrex bottle and placed in an oven at 373±1 K. Crystallization of the hematite was complete when the volume occupied by the initial gelatinous precipitate was reduced to less than one-tenth of the original and the color of the sediment was bright red. After cooling, centrifugation, and decantation, the sediment was washed with 0.5M HNO₃ to dissolve any residual ferrihydrite, twice with 0.1M KNO₃ at pH 3 and twice with 0.1M KOH-0.5M KNO₃ to remove phosphate adsorbed on the surface of hematite. The substituted hematite was characterized by determining the surface area and the micropore surface area using N₂ adsorption (BET and t-plot methods, respectively) with a micrometrics ASAP 2010 surface area analyzer.

Oxyanion Removal by Adsorption on Iron Oxides

Oxyanion

Oxyanion (or oxoanion) is a chemical compound with the generic formula AₙOₙ⁺ (where A represents a chemical element and O represents an oxygen atom). Oxyanions are formed by a large majority of the chemical elements [74]. The formulae of simple oxyanions are determined by the octet rule. The structures of condensed oxyanions can be rationalized in terms of AOₙ polyhedral units with sharing of corners or edges between polyhedra. There are different types of oxyanions: the monomeric and the polymeric. The formula of monomeric oxyanions, AₙOₙ⁺, is dictated by the oxidation state of element A and its position in the periodic table. Elements of the first row are limited to a maximum coordination number of 4. However, none of the first row elements has a monomeric oxyanion with that coordination number. Carbonate (CO₃⁻) and nitrate (NO₃⁻) have a trigonal planar structure with π bonding between the central atom and the oxygen atoms. This π bonding is favoured by the similarity in size of the central atom and oxygen.

The oxyanions of second-row elements in the group oxidation state are tetrahedral. Tetrahedral SiO₄ units are found in olivine minerals (Mg,Fe)SiO₄ but the anion does not have a separate existence as the oxygen atoms are surrounded tetrahedrally by cations in the solid state. Phosphate (PO₄³⁻), sulphate (SO₄²⁻), and perchlorate (ClO₄⁻) ions can be found as such in various salts. Examples are borate (BO₃³⁻), carbonate (CO₃²⁻), nitrate (NO₃⁻), phosphate (PO₄³⁻), sulphate (SO₄²⁻), chromate (CrO₄²⁻), arsenate (AsO₄³⁻), nitrite (NO₂⁻), hypophosphite (PO₂⁻), hyposulphite (SO₂⁻), arsenite (AsO₃³⁻), etc.

A polyoxyanion is a polymeric oxyanion in which multiple oxyanion monomers, usually regarded as MOₙ polyhedra, are joined by sharing corners or edges [75] When two corners of a polyhedron are shared, the resulting structure may be a chain or a ring. Short chains occur, for example, in polyphosphates. Inosilicates, such as pyroxenes, have a long chain of SiO₄ tetrahedrals (each sharing two corners. The same structure occurs in meta-vanadates such as ammonium metavanadate (NH₄VO₃).

Examples of oxyanion contamination of groundwater include: perchlorate, borate, arsenate, selenate, chromate, and molybdate [76-79]. Other oxyanions found in ground water are nitrates, sulphates, carbonates, and phosphates.

Perchlorate salts are used in solid propellants (in rockets and missiles), munitions, commercial explosives, fireworks, and flares. Perchlorate compounds are also used in a number of other manufacturing operations (e.g. electroplating, pharmaceutical production, paints, and enamels) and agricultural uses [78, 80]. Perchlorate salts are highly soluble in water and the perchlorate anion has little affinity for most geologic materials except various oxides [80-82].
Sorptive Interaction of Oxyanions...

Removal of Oxyanions

The oxyanions of major concern today are arsenate, arsenite, chromate, phosphate, vanadate, and selenate. A few familiar methods in practice for the removal of these oxyanions are chemical precipitation, ion exchange, solvent extraction, reverse osmosis, and adsorption. Reverse osmosis, although very effective, is a cost-prohibitive process as membranes get easily spoiled, requiring frequent replacement. Chemical precipitation is not very suitable when the pollutants are present in trace amounts and sludge also is produced. Solvent extraction or electrolytic processes are also available, but they are considered to be cost-effective only for more concentrated solutions. Ion exchange is expensive and sophisticated. The process of adsorption has become one of the preferred methods for the removal of toxic contaminants from wastewater as it has been found to be very effective, economical, versatile, and simple [83]. Adsorption has the additional advantages of applicability at very low concentrations, suitability for using batch and continuous processes, ease of operation, little sludge generation, possibility of regeneration and re-use and low capital cost [84].

Adsorption of Some Oxyanions on Iron Oxides by Different Researchers

Gimenez et al. studied the sorption of As(III) and As (V) on different natural oxides (hematite, magnetite, and goethite) as a function of different parameters such as pH and adsorbate concentration. The sorption kinetics for the three iron oxides showed that equilibrium was reached in less than two (2) days and the kinetics of sorption was faster for goethite and magnetite than for hematite. The variation of the arsenic sorbed on the three different sorbents as a function of the equilibrium arsenic concentration in solution was fitted with a non-competitive Langmuir isotherm. The main trend observed in the variation of the arsenic sorbed with pH is a decrease of the sorption on the three sorbents at alkaline pH values. Highest As (III) sorption was observed on hematite surface in all the pH range compared to goethite and magnetite. Natural minerals studied in their work had similar sorption capacities for arsenic when compared with synthetic sorbents [85].

Ona-nguema et al. studied the modes of As (III) sorption onto two-line ferrihydrite, hematite, goethite, and lepidocrocite under anoxic conditions using XAS. X-ray absorption near edge structure spectroscopy (XANES) indicated that the absence of oxygen minimized As (III) oxidation due to Fenton reactions. Extended x-ray absorption fine structure spectroscopy (EXAFS) indicated that As (III) forms similar inner sphere complexes on two-line ferrihydrite and hematite that differ from those formed on goethite and lepidocrocite [86].

Fendorf et al. in their study observed that the molecular structure of ions retained on mineral surfaces is needed to accurately model their sorption process and to determine their stability. Extended x-ray absorption fine structure (EXAFS) spectroscopy was used in the study to deduce the local coordination environment of two environmental contaminants, arsenate and chromate on the mineral goethite ($\alpha$-FeOOH). Based on the oxyanion-Fe distances, it was concluded that three different surface complexes exist on goethite for both oxyanions, a monodentate complex, a bidentate binuclear complex, and a bidentate mononuclear complex. At low surface coverage, the bidentate complexes were more prevalent. They observed that the bidentate binuclear complex appears to be in the greatest proportion at the highest surface coverages [87].

Ding et al. also studied the adsorption of three anions (AsO$_3^-$, PO$_4^{3-}$, and CrO$_4^{2-}$) and two cations (Zn$^{2+}$ and Pb$^{2+}$) on a new form of amorphous black ferric oxyhydroxide that resembles in local structure $\beta$-FeOOH, akaganeite. The nature of the interaction between FeOOH substrate and the adsorbates was characterized with x-ray photoelectron spectroscopy on the core and valence band levels of trivalent iron and oxygen using frontier molecular orbital theory as a theoretical framework. Their findings indicated that substantial and variable charge transfer occurs in which the FeOOH substrate can function either as a Lewis acid or base in its interaction with different adsorbates. It was also suggested that the valence band spectra can be used to estimate qualitatively the energy level separation between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the surface complexes and to assess the chemical affinity between substrate and adsorbate [88].

Weerasooriya and Tobschall investigated the adsorption of CrO$_4^{2-}$ onto goethite as a function of pH, background electrolyte, and adsorbate loading. Experimental data were interpreted with a three-plane model (TPM) that accounts for spatial charge distribution of inner sphere surface complexes. In their study, the influence of co-anions such as Cl$^-$, NO$_3^-$, PO$_4^{3-}$, and SO$_4^{2-}$ and temperature were not considered. In accordance with EXAF spectroscopic data >FeO$_{5}^{3-}$CrO$_4^{2-}$ and >(FeO)$_{2}^{2-}$CrO$_4^{4+}$ surface species were selected for TPM calculations. TPM simulations replicate CrO$_4^{2-}$ adsorption data well when CrO$_4^{2-}$ coverage was <2x 10$^{-7}$ mol·m$^{-2}$ [89].

Foster-Mills et al. studied the sorption of chromate and phosphate onto hematite surface. They studied the thermodynamics and kinetics of the sorption of Cr(VI), a contaminant found in ground water at many United States of America Department of Energy Nuclear Sites and industrial sites on powdered hematite ($\alpha$-Fe$_2$O$_3$). Batch sorption experiments were performed to determine the maximum sorption capacities of Cr(VI), phosphate and sulphate oxyanion on hematite. Competitive sorption between Cr(VI), phosphate and sulphate oxyanions were examined using laser photoacoustic spectroscopy (LPAS) [90].

Smith and Ghiassi also studied chromate removal by an iron sorbent. In the study, a solution containing chromate was treated using waste shot-blast fines recovered from surface finishing operations in a cast-iron foundry as adsorbent in batch and fixed-bed modes. Equilibrium experiments for initial chromate concentration of 5 to 10
onto goethite (α-FeOOH) under oxic (i.e. pH 4), reduction to Cr(III) is assumed to contribute to oxy-hydroxide sites appears to be the primary mechanism of chromium removal at neutral pH. At lower pH values, reduction to Cr(III) is assumed to contribute to the increasing removal as a function of decrease in pH [91].

Peacock and Sherman studied the adsorption of V(V) onto goethite (α-FeOOH) under oxic (pO2 = 0.2bar) atmospheric conditions. EXAFS spectra showed that V(V) adsors by forming inner sphere complexes as VO2(O,OH)2 and VO3(OH). They predicted the relative energies and geometries of VO2(O,OH)2-FeOOH surface complexes using ab-initio calculations of the geometries and energetics of analogue Fe2(OH)2(H2O)6 and Fe2O2VO(OH)0 surface complexes. The bidentate corner-sharing complex was predicted to be substantially (57 kJ/mol) favored energetically over the hypothetical edge-sharing bidentate complex. Fitting the EXAFS spectra using multiple scattering showed that the only bidentate corner-sharing complex was present with Fe-V and V-O distances in good agreement with those predicted. They found it important to include multiple scatterings in the fits of their EXAFS data otherwise spurious V-Fe distances near 2.8 Å, which may be incorrectly attributed to edge-sharing complexes. No evidence for non-bidentate complexes was found, which agrees with predicted high energies of such complexes. Having identified the Fe2O2V(OH)2- and Fe2O2VO(OH)0 surface complexes, they were able to fit the experimental vanadium (V) adsorption data to the reaction [92]:

\begin{equation}
2\text{FeOH}^+ + \text{VO}_2^+ \rightleftharpoons \text{Fe}_2\text{O}_2\text{V(OH)}_2^+ + 2\text{H}^+ \tag{6}
\end{equation}

and

\begin{equation}
2\text{FeOH} + \text{HVO}_4^+ \rightleftharpoons \text{Fe}_2\text{O}_2\text{VO(OH)}_0^+ + 2\text{OH}^- \tag{7}
\end{equation}

The dissociation constant of the Fe2O2VOH2+ surface complex was also determined.

Naeem et al. summarized known vanadium occurrence in North American group water and assessed vanadium removal by three commercially available metal oxide adsorbents with different mineralogies. Preliminary vanadium adsorption kinetics onto GFH, E-33, and GTO had been studied and the homogeneous surface diffusion model (HSDM) was used to describe the adsorption kinetic data. The effects of pH, vanadium concentration, and volume/mass ratio were assessed. Vanadium adsorption decreases with increasing pH, with maximum adsorption capacities achieved at pH 3-4. Results indicated that all adsorbents removed vanadium, and that GTO has the highest adsorption capacity, followed by GTO and E-33. Data were best fitted with the Langmuir model rather than Freundlich isotherm. Both sorption maxima (Xm) and binding energy constant (b) followed the trend GFH> GTO> E-33. Naturally occurring vanadium was also removed from Arizona ground water in rapid small-scale column tests (RSCCT) [93].

O’Reilly et al. observed that sorption was initially rapid, with over 93% arsenate being sorbed in a 24-hr period at pH 6 onto goethite. Similar arsenate adsorption behavior was observed at pH 4. Analysis of the sample with extended x-ray absorption fine atomic shells surrounding the adsorbed As. The closest shell was identified as an O atom, the next shell out was identified as an Fe atom. The As-Fe bond distance of 3.30 Å, derived from XAFS data was indicative of a bidentate binuclear bond forming between the arsenate atoms and goethite surface. Their result was in agreement with the findings of a previous researchers. Analysis of the As EXAFS from samples incubated for various periods indicated that the molecular environment did not change over time. Complimentary desorption kinetics studies showed that when aging was increased, there was no significant change in the amount of arsenate desorbed from goethite by PO43- [94].

Researchers have shown that arsenate is specifically sorbed onto iron oxides such as goethite through an inner-sphere complex via a ligand exchange mechanism [87, 95, 96]. They found that using transmission-fourier transform infrared (T-FTIR) and attenuated total reflectance FTIR (ATR-FTIR) spectroscopy, arsenate replaced two singly coordinated surface OH groups to form binuclear bridging complexes.

Lumsdon et al. utilized infrared spectroscopy to discover that HASO42- ion participated in ligand exchange reactions displacing singly coordinated surface hydroxyl groups to adsorb as a binuclear species [95]. EXAFS studies by Fendorf [87], Waychunas et al. [97], and Manceau [98] found that bidentate binuclear complexation was the major bonding mechanism for arsenate adsorption on goethite. On the basis of pressure jump relaxation study and EXAFS, it was demonstrated that arsenate can form three types of surface complexes on goethite, depending on the surface coverage [87, 96].

The list of some oxyanions investigated for their adsorption characteristics with various iron oxides are shown in Table 3.

**Adsorption Isotherms and Adsorption Capacities**

Adsorption isotherm describes how adsorbates interact with adsorbents, and this information is essential in optimizing the use of adsorbent. Table 4 summarizes some literature values on adsorption capacities of various oxyanions on different iron oxides. The affinities of iron oxides for oxy-anion can generally be grouped into the ranges: 2.35×104 mol/g-0.607 mmol/g for (U(VI)); 3.13 µmol/g-6.0 mg/g for chromate (Cr(VI)); 0.69 to 9.4 mg/g for arsenite (As(III)); and 39.8 µmol/g-70.4 mg/g for arsenate (As(V)) on the various iron oxides. The adsorption isotherms employed include Langmuir, Freundlich, and Dubinin Radushkevich. For most of the adsorption data of
The surface complexation model used on some of the adsorption data include the constant capacitance model and these are illustrated in Table 5. It is evident from the tables that the level of interaction of oxyanions with iron oxides is strongly influenced by the method of preparation, surface area, and pH.

Conclusions

The particle sizes of the synthesized iron oxides depend on the method of synthesis, with sizes ranging from 17 nm to 7.4 micrometers. Acid hydrolysis of iron (II) and iron (III) nitrate, chloride, and sulphate is a common method of synthesis for the various iron oxides, but with modification by different authors. The pH of solution influences the product formation and particle size is also dependent on
Table 4. Adsorption characteristics of various oxyanions with iron oxides.

<table>
<thead>
<tr>
<th>Oxyanion</th>
<th>Iron oxide</th>
<th>Synthesis Method</th>
<th>Characterization Method</th>
<th>Surface Area (m²/g)</th>
<th>Adsorption Capacity (mol/g × 10⁻⁵)</th>
<th>Temp. K</th>
<th>Optimal pH</th>
<th>Kinetic Model</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>U(VI)</td>
<td>Hematite</td>
<td>Sol gel</td>
<td>FTIR, XRD, BET</td>
<td>398.5</td>
<td>2.35, 2.51, 2.76</td>
<td>298</td>
<td>&lt;6</td>
<td>Zhao et al. 2012 [107].</td>
<td></td>
</tr>
<tr>
<td>U(VI)</td>
<td>Goethite</td>
<td>Hydrolysis</td>
<td>XRD, SEM, BET</td>
<td>37.29</td>
<td>0.607, 1.7, 11.6</td>
<td>298</td>
<td>5</td>
<td>Yusan and Erenturk, 2011 [125]</td>
<td></td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>Hematite</td>
<td>Commercial</td>
<td>BET</td>
<td>1.7, 11.6</td>
<td>2.299, 1.955, 1.955</td>
<td>298</td>
<td>≤5</td>
<td>≤3</td>
<td>Ajouyed et al. 2010 [104].</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>Magnetite</td>
<td>Precipitation</td>
<td>FTIR, XRD, TEM</td>
<td></td>
<td>1.5260, 3.0693, 3.9572</td>
<td>303</td>
<td>313, 323</td>
<td>Namdeo and Bajpai, 2008 [103].</td>
<td></td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>Hematite</td>
<td>Natural</td>
<td>BET</td>
<td></td>
<td>3.13 µmol/g, 0.087</td>
<td>313</td>
<td></td>
<td>Singh et al, 1993 [104].</td>
<td></td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>Chitosan-magnetite nanocomposite</td>
<td>Precipitation</td>
<td>FTIR, TEM, TGA</td>
<td></td>
<td>1.515, 1.266, 1.006</td>
<td></td>
<td></td>
<td>Bajpai and Armo, 2009 [106].</td>
<td></td>
</tr>
<tr>
<td>Arsenate</td>
<td>Manganese oxide</td>
<td>Oxidation</td>
<td>XRD, FTIR, BET</td>
<td>101</td>
<td>5.72, 4.58</td>
<td></td>
<td>6-7</td>
<td>Lakshimpathiraj, 2006 [118].</td>
<td></td>
</tr>
<tr>
<td>Arsenate</td>
<td>Ce (VI) doped iron oxide</td>
<td>Precipitation</td>
<td>FTIR, BET</td>
<td></td>
<td>70.4 mg/g</td>
<td>293</td>
<td>5.0</td>
<td>Pseudo first order</td>
<td>Zhang et al, 2003 [129]</td>
</tr>
<tr>
<td>Arsenate</td>
<td>Akaganeite</td>
<td>Precipitation</td>
<td>XRD, FT-IR, SEM</td>
<td>330</td>
<td>1.79, 2.24, 2.89</td>
<td>298</td>
<td>7.5</td>
<td>Deliymann et al, 2003 [114].</td>
<td></td>
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<tr>
<td>Arsenate</td>
<td>Ferrihydrite</td>
<td>Hydrolysis</td>
<td>XRD, FT-IR</td>
<td></td>
<td></td>
<td>348</td>
<td>3</td>
<td>Jia et al, 2007 [119].</td>
<td></td>
</tr>
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</table>
Table 4. Continued.

<table>
<thead>
<tr>
<th>Oxyanion</th>
<th>Iron oxide</th>
<th>Synthesis Method</th>
<th>Characterization Method</th>
<th>Surface Area (m²/g)</th>
<th>Adsorption Capacity</th>
<th>Temp. K</th>
<th>Optimal pH</th>
<th>Kinetic Model</th>
<th>References</th>
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<tbody>
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<td>Arsenate</td>
<td>Arsenite</td>
<td>Goethite</td>
<td>Hydrolysis</td>
<td>XRD, FTIR, BET</td>
<td>39</td>
<td>&lt;4</td>
<td>4&lt;pH&lt;9</td>
<td></td>
<td>Lenoble et al. 2002 [111]</td>
</tr>
<tr>
<td>Arsenate</td>
<td>Arsenite</td>
<td>Goethite</td>
<td>Oxidation</td>
<td>FTIR, BET</td>
<td>103</td>
<td>1941 mol⁻¹</td>
<td>302</td>
<td>5.0</td>
<td>Lakshmipathiraj, 2006 [117]</td>
</tr>
<tr>
<td>Arsenite</td>
<td>Arsenite</td>
<td>Iron oxide coated cement</td>
<td>Precipitation</td>
<td>XRD, EDX, PZC</td>
<td>0.69</td>
<td>0.22</td>
<td>300</td>
<td>Pseudo second order</td>
<td>Kundu and Gupta, 2007 [131]</td>
</tr>
<tr>
<td>Arsenate</td>
<td>Arsenite</td>
<td>Iron hydroxide based sorbent</td>
<td>Commercial</td>
<td>XRD, XRF, XPS, BET</td>
<td>236</td>
<td>22.2</td>
<td>293</td>
<td></td>
<td>Zeng et al, 2008 [121]</td>
</tr>
<tr>
<td>Arsenate</td>
<td>Arsenite</td>
<td>Magnetite</td>
<td>Commercial</td>
<td>BET, SEM, XPS</td>
<td>49</td>
<td>10.6</td>
<td>298</td>
<td>5</td>
<td>4.5</td>
</tr>
<tr>
<td>Arsenate</td>
<td>Arsenite</td>
<td>Cr(VI)</td>
<td>Commercial</td>
<td>BET, SEM, XPS, FT-IR</td>
<td>35.4</td>
<td>9.3</td>
<td>298</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

stirring speed, and organic composition. The methods of synthesis also affect the points of zero charge of the iron oxides according to Marek Kosmulski PZC compilation.

Sorptive interactions between oxyanions and mineral surface have received considerable attention due to their important nutrient and contaminant roles and the ubiquitous distribution of minerals in aquatic, sedimentary, and terrestrial environments. Mineral surfaces, particularly metal (hydr) oxides, concentrate oxyanions through both specific and non-specific complexation mechanisms. Specifically adsorbed oxyanions are strongly surface associated through covalent bonds formed by ligand exchange with surface hydroxyl groups (inner-sphere complexed), whereas non-specifically adsorbed oxyanions are weakly surface associated due to electrostatic interaction through an intervening water molecule (outer-sphere complexed). It is therefore evident that further research needs to be carried out so as to have a better understanding of the mechanism of sorption of oxyanions on iron oxides. More efforts also need to be directed at defining optimal conditions for oxyanion removal from aqueous solution in column experiments and for ultimate industrial application.

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**References**


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