Efficient removal of Pb (II) from water solution using CaFe_{2−x−y}Gd_{x}Sm_{y}O_{4} ferrite nanoparticles

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Abstract
Rare-earth doped calcium nano ferrites (CaFe_{2−x−y}Gd_{x}Sm_{y}O_{4}; x = y = 0.0; x = 0.025, y = 0.05) are synthesized by citrate nitrate auto combustion method. The prepared samples are characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), high-resolution transmission electron microscope (HRTEM), and vibrating sample magnetometer (VSM) analyses. After that, the samples were examined for Pb (II) ions removal from the water solution. The orthorhombic structure with space group Pnma is ratified from XRD. The average crystallite size of the synthesized powders is estimated from the broadening of the XRD lines in the range of 18–21 nm. FTIR confirms the molecular signature of the samples. The magnetic property is discussed based on super exchange interactions. The hysteresis loop shows two different magnetic behaviors of the investigated sample as well as increasing the coercivity from 14 to 240 G due to the doping. The electrical parameters are discussed in the basic hopping charge model, while the conduction mechanism of the samples will be discussed based on de-Boer and Verwey. The experimental results are subjected to kinetic and isotherm analyses. The Langmuir and Freundlich isotherms describe the adsorption of heavy metal ions as designated by the high correlation coefficient (R^2). The use only 4 mg of the doped sample with low price ferrite nanoparticles has been utilized for 99.31% removal of Pb (II) from wastewater at a contact time of 10 min at room temperature.

Keywords CaFe_{2}O_{4} · Hexagonal perovskite · Magnetic particles · Antiferromagnetic · Lead removal

1 Introduction
Innovative designs of nanocrystalline spinel ferrites have received much attention because of their exclusive properties related to their remarkable structure and outstanding electrical and magnetic properties. Furthermore, magnetic ferrites are of great interest due to their wide range of applications, such as the magnetically controlled transport of anti-cancer drugs [1, 2] and as contrast agents in magnetic resonant imaging (MRI) to detect cancer or other diseases [3]. Generally, magnetic nanostructures research has tremendously increased due to their specific applications in high-density magnetic storage, hyperthermia treatment and protein separation [4–9]. Magnetic nano ferrites are a group of ferrites with unique physical characteristics that make them competitive candidates for many biomedical applications such as detecting and diagnosing precancerous lesions; In addition, they are presently used for heavy metal removal from wastewater and soil [7–13].

It was thought that magnetic ferrite composites can be frequently utilized to form cheap and highly controllable materials used in various applications of communications, radiofrequency devices, electronic appliances, solar cells, biosensors and microwave devices [14–16]. The development of such magnetic ferrite composites could conduce to the creation of a multi-functional devices promising for nano Opto-electromechanical systems, catalysts, memory storage, logic operations, and especially for multiple functional electronic devices that can be actively exchanged among transistor, inductor, capacitor and resistor to achieve multifunctions inside the same system [17, 18].

Nanocrystalline calcium ferrite (CaFe_{2}O_{4}) has a wide range of applicability, such as an anode material for the fabrication of electrodes in Lithium-ion batteries, p-type photocathode material, photo catalyst, drug delivery agent
and gadolinium (Gd) have been widely studied due to their excellent mechanical hardness, chemical stability, and high magnetocrystalline anisotropy [44]. The substitution of Sm$^{3+}$ and Gd$^{3+}$ ions into the spinel ferrite would eventually bring structural distortion. Larger ionic radii of RE ions compared with Fe ions implies larger strain and as a result, the magnetic and electrical properties will be modified. Additionally, the interaction between the unpaired electrons in the 4f subshell of RE ions and that of the 3d subshell of Fe ions turns out the structural, magnetic and electrical properties [34]. Spinel ferrites substituted with rare-earth ions have been reported by numerous research groups as Almessiere et al. [45] and Slimani et al. [46].

In this work, we are doping CaFe$_2$O$_4$ with tiny amounts of rare earth RE elements, namely Sm and Gd, to enhance the physical properties of calcium ferrite nanoparticles. Boosting these structures properties will improve their qualifications and may open new areas of application. The chosen concentration was selected according to the previous work [47]. Moreover, if the concentration percentage of the doped RE ions increases over 3.75% in the B site of spinel nano ferrite, it will be indexed as a secondary phase. Additionally, the ad-sorption characteristics of Pb (II) ions on the CaFe$_{2-x-y}$Gd$_x$Sm$_y$O$_4$ were testified in a batch experiment at different ad-sorption parameters, the ad-sorption kinetics and ad-sorption isotherm for lead ions were determined. The obtained information will be useful for application in the treatment of wastewater containing lead ions.

2 Experimental

2.1 Sample preparation

Using the citrate auto-combustion method to achieve a relatively small particle size distribution of nanocrystalline calcium ferrite [47]. A schematic diagram of the citrate auto-combustion preparation method is shown in (Fig. 1), in this method, the stoichiometric quantities of calcium nitrate Ca(NO$_3$)$_2$.4H$_2$O, ferric nitrate Fe(NO$_3$)$_3$.9H$_2$O, gadolinium nitrate Gd(NO$_3$)$_3$.6H$_2$O, and samarium nitrate Sm(NO$_3$)$_3$.6H$_2$O were well mixed and dissolved in 20 ml of double distilled water with citric acid as a chelating agent. The solution was continuously stirred well with a magnetic stirrer until a homogenous solution is obtained. Then, the solution was stirred vigorously and heated for one hour till the solution turned into gel. Subsequently, the sample is heated until the gel is burned out and the sample is transformed into gray ash. Then, the gray ash is collected and grounded into fine powder. The powder is then calcined at 950 °C for 4 h in a furnace.
2.2 Characterization techniques

The structure and crystallite size were tested by X-rays diffractometer (XRD), Diaon corporation with target Cu-Kα (λ = 1.5424 Å). The average nanoparticle size was estimated using Scherer's relationship. The surface composition and the chemical states of the elements in the prepared nano powders were studied by K-Alpha X-ray Photoelectron Spectrometer (XPS) System (Thermo Fisher Scientific, USA) using CASAXPS software.

The surface morphology or the microstructure was identified by a high-resolution tunneling electron microscope (model JEM-100S). The molecular signature of the samples was confirmed by Fourier transform infra-red spectrometer FTIR (IR-Affinity-1 FT-IR spectrometer) studies.

The saturation magnetization, the remanence and the coercive fields were measured by tracing M-H hysteresis loops for the powder samples at room temperature and in a varying magnetic field up to 20 kOe, using the LDJ model 9600, vibrating sample magnetometer (VSM). The surface area and pore volume were carried out using N2 adsorption/desorption isotherms at 77 K acquired with NOVA 2200 BET surface area analyzer.

2.3 Adsorption of heavy metals

The addition of 0.01 g of an adsorbent for 10 ml of a typical solution containing on lead ion with contraction 25 ppm and stirred at 200 rpm on electric shaker after adjusting pH at certain values for 1 h at room temperature. The concentration of heavy metal (HM) ions was measured by ICP for lead ions at pH extended from 2 to 8 [49].

3 Results and discussion

3.1 Structural analyses

3.1.1 X-ray analysis (XRD)

The nano ferrites $\text{CaFe}_{(2-x-y)}\text{Gd}_x\text{Sm}_y\text{O}_4$, $x = y = 0$; $x = 0.025$, $y = 0.05$, symbolized CaFeO and CaFeREO, respectively, are successfully obtained without any secondary phase even after the substitution of small amounts of soluble rare-earth (Gd-Sm) ions. The X-ray diffraction pattern of CaFeO and CaFeREO samples are recorded in the 20 range 20–80° with a step size of 0.04°, as illustrated in (Fig. 2). The broadness of the peaks is a characteristic of nanoparticles and is indexed to the orthorhombic structure diffraction orthorhombic peaks with space group Pnma (No.62).

Noticeably, all peaks are well-matched with the standard CaFe$_2$O$_4$ spectrum (ICDD 00-008-0100), which has
been allocated to the typical crystallographic planes of the high-purity calcium ferrite [50].

Generally, the calcium ferrite with the general formula \( \text{CaFeO} \) is described as a cubic spinel structure at low calcination temperature. The transformation from spinel structure to orthorhombic phase is due to the high calcination temperature (950 °C), and no spherical nanoparticles are formed at this temperature.

The Williamson–Hall (W–H) plot method is utilized to define both the average crystallite size (\( D \)) and the micro strain (\( \varepsilon \)) for the synthesized samples [9, 51]. The average crystallite size and the strain can be calculated from XRD data using the following equation:

\[
\beta \cos \theta = \frac{K \times \lambda}{D} + 4\varepsilon \sin \theta,
\]

where \( \beta \) is the full-width half maximum in radian, \( \theta \) is the Bragg’s angle in radian, \( \lambda \) is the wavelength of X-ray source, \( K \) is the shape factor approximately equals to 0.94. Consequently, the gradient (slope) of the fitted straight line and the \( y \)-intercept (\( \frac{\beta \cos \theta}{D} \)) provide \( \varepsilon \), and \( D \) respectively. The obtained data is shown in (Fig. 3) and tabulated in Table (1).

The experimental lattice parameters (\( a_{\text{exp.}} \)) are computed based on orthorhombic unit cells, and tabulated in (Table 1). The large difference of ionic radius of \( \text{Gd}^{3+} \) (0.938 Å), \( \text{Sm}^{3+} \) (0.958 Å) and \( \text{Fe}^{3+} \) (0.645 Å) [54] lead to the increase in the lattice parameters.

The theoretical density \( D_x \) is determined and reported in (Table 1) using the following equation \( D_x = \frac{ZM}{NAV} \) [31, 55], where \( Z \) is the number of molecules per orthorhombic unit cell, \( M \) is the molecular weight, \( N_A \) is the Avogadro’s number, and \( V \) is the unit cell volume. The data shows that the density \( D_x \) increases as a result of RE ions doping, which is directly explained by the dissimilarity of the average atomic mass numbers of Fe (55.847), with that of Gd (157.25), and Sm (150.36) [56].

The tolerance factor (T), for the orthorhombic structured materials, is calculated as mentioned in the previous work [31] and the results are displayed in (Table 1). Generally, the BO\(_6\) octahedra tilt cooperatively causes orthorhombic structure in such case the “T” can be written as 0.75 < T < 0.90. Whilst for 0.90 < T < 1.0, instead of buckling of BO\(_6\) a small distortion leads to a lower symmetry structure may be expected.

However, the perovskite oxides can be crystallized not only in orthorhombic but in hexagonal, rhombohedral, and monoclinic structures [57]. In the present case \( T > 1 \) indicates a hexagonal perovskite structure forming by neighboring hexagonal close-packed in the layers of Fe cations and O anions. The hexagonal structure is a variable of the oxygen packing in perovskite oxides leading to a structure with chains of face sharing BO\(_6\) octahedra. This can may be due to the increase of the A cation (Ca) size favors sharing its edges octahedrally, in addition to the B-site (Fe) distortion [58].

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**Table 1** Average crystalline size (\( D \)), Micro strain, Experimental lattice parameters (\( a, b, c \)), theoretical density (\( D_x \)) and tolerance factor (T) for the prepared samples

| Sample   | Average crystallite size D (nm) | \( \varepsilon \times 10^{-4} \) | Lattice parameters | \( D_x \) (gm/cm\(^3\)) | T   |
|----------|---------------------------------|----------------------------------|--------------------|--------------------------|-----|
|          | W–H plot Scherrer formula       |                                  |                    |                          |     |
| CaFeO    | 22.35 21.00                     | 3.234                            | 9.05 10.64 2.99    | 4.86                     | 1.276|
| CaFeREO  | 18.06 18.00                     | 3.419                            | 9.45 10.69 3.04    | 5.02                     | 1.272|

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![Fig. 3](image-url) The Williamson–Hall plot for CaFeO and CaFeREO
3.1.2 XPS spectroscopy

XPS spectroscopy is used to identify the valence states of the elements in the CaFeO and CaFeREO nano powders. The broad scanning of the XPS spectrum in (Fig. 4a) indicates the existence of Ca, Fe, Gd, Sm and O elements, which confirm the elemental surface composition for each of the two samples. The observed peak of C 1s is attributed to the attaching of nano powder to an adhesive tape of carbon during measurement [59, 60].

XPS spectra of Ca 2p for CaFeO and CaFeREO samples are shown in (Fig. 4b). Calcium 2p peak is split into two components of 2p1/2 and 3p3/2 in addition to variable weak satellite loss peak. The split of Ca 2p peak is caused by the spin-orbital coupling while the shift in satellite peak of CaFeREO to lower binding energy is attributed to the change in the Plasmon energy loss [61, 62]. The peak of Ca 2p3/2 at

![XPS spectra](image)

Fig. 4 (a–e) XPS analysis for the CaFeO and CaFeREO samples
Fe$^2+$ destabilizes the orthorhombic structure of the samples at 710.58 and 724.18 eV, respectively [62]. The Fe 2p$_{3/2}$ peak is divided into two peaks revealing the existence of Fe$^{2+}$ and Fe$^{3+}$ ions of binding energies 710.08 and 711.78 eV, respectively [64]. Similarly, the Fe 2p$_{1/2}$ peak is also divided into two peaks of Fe$^{2+}$ at 727.08 eV and Fe$^{3+}$ at 724.08 eV. The other two peaks located at 719.48 eV and 716.48 eV, are named the satellite peaks of Fe 2p$_{3/2}$ for Fe$^{3+}$ and Fe$^{2+}$ ions, respectively. The absence of the corresponding satellite peak of the Fe 2p$_{3/2}$ chemical state because it does not have satellite peaks [65]. Therefore, the existence of multivalent Fe ions together with the oxygen vacancies can be one of the primary factors to enhance the conduction process. On the other hand, as theionic radius of Fe$^{3+}$ is greater than that of Fe$^{2+}$, then the partial substitution of Fe$^{3+}$ destabilizes the orthorhombic structure of the samples through the oxygen deficiency and hence, the existence of Fe$^{3+}$ instead of Fe$^{2+}$ leading to the formation of hexagonal (metastable) phases under ambient conditions as will be discussed in XPS analyses of the Fe species [70].

3.1.3 High resolution transmission electron microscope (HRTEM)

The HRTEM micrographs of the solution of the samples are shown in (Fig. 5). The micrographs reveal a uniform distribution of the particles of varying shapes, and well-defined boundaries. The corresponding particle size histograms of the samples are depicted in (Fig. 5c, f), which are obtained from the frequency sizes from the measurement of different particle sizes using ImageJ software [60]. The histogram depicts the size distribution of the nanoparticles in the range of 33–65 nm. The grains of the two samples are hexagonal, with a relatively lower agglomeration for the CaFeREO sample. Generally, the grains of the samples have a homogeneous distribution indicating a good physical mixing. There are three factors that led to the appearance of the hexagonal structure of the samples, the larger ionic radius of calcium ion in the B-site, the existence of Fe$^{2+}$ instead of Fe$^{3+}$ under ambient conditions as discussed in XPS analyses of the Fe 2p spectrum and the view plane of the crystal structure.

The HRTEM micrographs depend on the view plane of crystallography. For most cases, the features of orthorhombic structure can be identified by considering only hkl planes with small values of indices such as zero and one. Scarcely, the equilibrium structure shaping is contained faces with higher values of indices [71]. Figure 5g shows three prospective shapes of the crystal structure in different plane views which drew online using the SMORF crystal model depending on the calculated values of h, k and l from XRD [72]. The HRTEM micrographs of CaFeO and CaFeREO matched well with the view of the structure in the “bc” plane.

The high crystallinity of the samples is ratified from the typical lattice fringes as detected in (Fig. 5a). Moreover, the polycrystalline nature of the samples is identified through the selected area electron diffraction (SAED) pattern (Fig. 5e). The bright rings signify various diffraction planes in the unit cell.

3.1.4 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the parent and doped samples are tested in the 400–4000 cm$^{-1}$ range as revealed in (Fig. 6). The bands in the wavenumber regions 580–440 cm$^{-1}$ and 580–650 cm$^{-1}$ are due to the deformation of FeO$_6$ octahedral and the asymmetric stretching vibrations of Ca–O and Fe–O bonds respectively. The higher frequency band in the wavenumber region 650–745 cm$^{-1}$ is assigned to a strong Fe–O bond.
stretching vibration mode, which involves internal motion of a change in Fe–O bond length. While, the lower band around 440 cm⁻¹ corresponds to the bending mode, which is indicative of any changes in the Fe–O–Fe bond angle [73]. These findings confirm the formation of the calcium ferrite orthorhombic structure in accordance with the XRD data.

In the parent and doped samples, as shown in (Fig. 6), small bands at 3430 cm⁻¹, matched to O–H stretching vibration. In addition, the bands at ≈ 1635 cm⁻¹ correspond to the asymmetrical stretching of C–O [27]. These may be initiated from surface-adsorbed carbonate group species [74]. Since all the measurements are performed in ambient conditions, the existence of OH and CO functional groups in the spectra is predicted.

3.1.5 Energy dispersive X-ray analysis (EDAX)

EDAX analysis is employed to examine the configuration and stoichiometry of the CaFeO and CaFeREO nanoparticles (Fig. 7). Intense O, Ca,Fe, Sm and Gd peaks are observed,
and the atomic ratio between Ca to Fe equals 2.01 (see inset in Fig. 7c. The successful synthesizing of the CaFeO and CaFeREO is confirmed.

### 3.1.6 Brunauer–Emmett–Teller (BET) surface area analysis

BET analysis includes the specific surface area, the pore size and the pore volume of the studied samples. The nature of the porous affects the crystallinity and the magnetic properties of the nanoparticles. (Fig. 8a, b) shows the variation of relative pressure (P/Po) with the volume for CaFeO and CaFeREO samples. The inset figures show the distribution

![Fig. 6 FTIR spectra the CaFeO, and CaFeREO samples](image)

![Fig. 7 The energy dispersive X-ray spectroscopy for CaFeO and CaFeREO samples](image)

| Element | CaFeO | CaFeREO |
|---------|-------|---------|
| Ca      | Weight percentage (Wt %) | Expected EDAX analysis | Atomic percentage (At %) | Expected EDAX analysis |
| Ca      | 18.41 | 19.03   | 13.82 | 15.62 |
| Fe      | 54.13 | 55.79   | 28.02 | 29.43 |
| O       | 27.46 | 25.18   | 58.16 | 54.95 |

| Element | CaFeO | CaFeREO |
|---------|-------|---------|
| Ca      | Weight percentage (Wt %) | Expected EDAX analysis | Atomic percentage (At %) | Expected EDAX analysis |
| Ca      | 17.97 | 16.42   | 14.29 | 13.03 |
| Fe      | 48.21 | 50.47   | 27.5  | 28.81 |
| Gd      | 1.76  | 1.79    | 0.36  | 0.36 |
| Sm      | 3.37  | 4.17    | 0.71  | 0.88 |
| O       | 28.69 | 27.15   | 57.14 | 56.92 |

![Fig. 8 a, b The adsorption/desorption isotherm of nitrogen at 77 K for a CaFeO and b CaFeREO samples](image)
of pore size versus pore volume of the synthesized samples. The investigated samples have a hysteresis loop characteristic, which is related to the capillary condensation/evaporation process in the mesopores [75].

Generally, the characteristic shape and size of the hysteresis loop are utilized to extrapolate the kind of pores encountered by the gas during a sorption technique. Therefore, the isotherm of ad-sorption/de-sorption of the samples in (Fig. 8) exhibits type IV behavior with H3-type hysteresis loop according to the IUPAC classifications [76]. The IV hysteresis is the characteristic of mesopores structures that have pore width intermediate between 2 and 50 nm [77].

The specific surface area, the pore volume and the pore width are calculated and tabulated in (Table 2). The surface area of CaFeREO are found to be significantly higher than CaFeO, which means that reactive sites increase inside the pores to adsorb organic pollutants of the waste water and hence increasing the photo/Fenton activity [9].

### 3.2 Magnetic properties

The magnetic hysteresis loop (M-H) allows us to accurately determine the magnetization behavior as well as the values of magnetic parameters like the saturation magnetization (Ms), the remnant magnetization (Mr) and the coercive field (Hc) [31]. The M-H curves for the prepared nanoparticles CaFeO and CaFeREO are recorded and plotted in (Fig. 9) at room temperature.

It is clear from the figure that the CaFeO sample shows a paramagnetic trend due to the weak super exchange interaction between Fe ions inside the orthorhombic structure. It should be noted that the magnetic behavior of nano ferrite mainly depends on the microstructure so the transformation of the structure that occurs in the sample leads to a lack of the magnetization indicated by the paramagnetic phase [78].

The CaFeREO sample exhibits antiferromagnetic behavior, which is characterized by a lack of saturation S-shaped hysteresis loop. This shape can be attributed to the small loop area and the small values of magnetization. The substitution of various rare-earth ions (Gd$^{3+}$, and Sm$^{3+}$) at A and/ or B sites in place of Fe$^{3+}$ ions interrupts the A–O–B super exchange interactions and causes an increase of the coercive field as well as reduction of saturation magnetization.

![Fig. 9 Hysteresis loops for the samples](image)

The antiferromagnetic character of CaFeREO originates from the single-ion anisotropy and the mutual interactions between two magnetic sublattices (electrons in a 4f subshell of rare earth ions and electrons in a 3d subshell of Fe ions) [79]. Furthermore, the antiferromagnetic alignment results from the coupling of iron and rare-earth cations via the $\pi^*$ orbitals of the oxygen ion. The magnetic moments of Gd and Sm are arranged not completely antiparallel but with a small angle to that of the nearest Fe as a result of the Dzyaloshinskii and Moriya antisymmetric exchange interaction [31]. However, this study shows that magnetization of RE doped calcium nanoparticles cannot be clarified on the basis of the magnetic moment of the individual ions. Additionally, the 3d–4f interaction along with the 3d–3d interaction in the ferrite will play an important to manipulating the magnetic properties of investigated samples.

The mixed-valence (Fe$^{3+}$ and Fe$^{2+}$) and the existence of Gd$^{3+}$, Sm$^{3+}$ can exhibit magnetic ordering, charge ordering, and orbital ordering. Some of the simplest magnetic orderings for B-site cation are shown in (Fig. 10) which represents one FM and four AFM (A-, C-, G-, and CE-type) ordering. The Sm$^{3+}$ and Gd$^{3+}$ RE ions also exhibit the Van Vleck effect due to the presence of multiplicity in both its first excited and ground spin states [13].

### Table 2 The calculated surface area, pore size and pore volume for the investigated samples

| Sample    | Surface area (m²/g) | Pore volume (cc/g) | Pore width (nm) |
|-----------|---------------------|--------------------|-----------------|
| CaFeO     | 34.22               | 0.143              | 13.76           |
| CaFeREO   | 77.16               | 0.0163             | 7.065           |

![Fig. 10 The ordering of ferromagnetic and four types of antiferromagnetic](image)
the Gd$^{3+}$(8.9 $\mu$B) ion, although the magnetic moment is high compared to the Fe$^{3+}$ (5.9 $\mu$B) ion, numerous surface effects as spin pinning, spin canting, and disordered surface spins may be the main reason for the reduction of $M_s$ as shown in (Table 3). The squareness ratio (Mr/Ms) is considered as a very significant parameter for determining the dimensional homogeneity of the nanoparticles. Its values for the loop of CaFeO is equal to 0.0007. This value is smaller than the super paramagnetic limit of 0.001 indicating the presence of multidomain and single-domain magnetic nanoparticles.

The variation of the Hc with particle size can be analyzed based on the anisotropy (K) of the crystal and domain structure as mentioned in the previous work [28]. From (Table 3), Hc increases from 14.323 G to 239.98 G for CaFeO and CaFeREO respectively which can be explained by the particle size and increasing magnetic anisotropy of CaFeREO. The increase in magnetocrystalline anisotropy resulted from the coupling of the spins of the Gd$^{3+}$, Sm$^{3+}$ and Fe$^{3+}$ ions in the multi-domain regions of CaFeREO [80]. The coercivity Hc is seen to increase with the addition of Gd-Sm ions which specifies a stronger alignment of magnetic dipoles in define direction [81]. In other words, the reason for the highest coercivity has been explained in terms of the transition from paramagnetic to antiferromagnetic with magnetic multidomain as elucidated by Morrish and Yu [82, 83]. A recommended application is to achieve the high core loss which is desirable in some electrical appliances [84].

### 3.3 Electrical properties

Figure 11a, b shows the relation between the AC conductivity ($\ln\sigma$) and the reciprocal of the temperature (1000/T) as a function of the applied frequencies. The samples exhibit a semiconducting nature, and the data obey the well-known Arrhenius equation [85]. The conduction mechanism of the samples will be elucidated by the de-Boer and Verwey models [86] mechanism, which includes electron exchange between the cations of the same element on the B site that exists randomly distributed in more than one valence state through the crystalline lattice. As cations are densely packed in the orthorhombic structure compared to cubic spinel structure, the distance between sequential Fe$^{3+}$ ions is extremely small, leading to efficient electrons exchange [27]. Thus, the conduction in the samples is ascribed to electron hopping from Fe$^{2+}$ to Fe$^{3+}$ ions.

The activation energies ($E_I$ $E_{II}$) are calculated using the Arrhenius equation and tabulated in (Table 4) [85]. Obviously, for the prepared samples, the $E_{II}$ at a high temperature is greater than the $E_I$ at a low temperature. That means more energy is needed to liberate the confined charges in the paramagnetic region to contribute to the conduction process.

The total conductivity $\sigma_{total}$ at a given frequency can be written as the sum of DC conductivity $\sigma_0$ due to band to band conduction and AC conductivity $\sigma_{ac}(\omega)$ due to hopping conduction. Moreover, the $\sigma_{ac}(\omega)$ obeys the universal power-law

$$\sigma_{ac}(\omega) = A\omega^\beta$$  

(2)

### Table 3

| ABO₃ | Hc(G) | Ms(emu/g) | Mr(emu/g) | Squareness Mr / Ms |
|------|------|-----------|-----------|-------------------|
| CaFeO | 14.323 | 0.657 | 0.0005 | 0.0007 |
| CaFeREO | 239.98 | 0.652 | 0.0512 | 0.0786 |

Fig. 11 Correlation between ln ($\sigma$) and reciprocal of absolute temperature as a function of applied frequency for the samples a CaFeO, and b CaFeREO
where ω is the angular frequency, A is a temperature-dependent constant, and s is an exponent whose value is in the range 0.0 ≤ s ≤ 1.0.

Figure 12a, b illustrates the dependence of ln σ ac versus frequency ln ω at numerous temperatures for the examined samples. The general characteristic of semiconductors is frequency-dependent. Their conductivity increases linearly with increasing frequency due to the increase in the hopping rate of the cation’s charge [87].

As the applied frequency increases, the net pumping force pushes the charge carrier between Fe2+ and Fe3+ ions to hop between the two different conduction states leading to improve the ion conduction process [88, 89].

Figure 13 shows the dependence of “s” exponent on absolute temperature (T) for the considered samples. For the CaFeO sample, the value of “s” initially increases slowly and then fluctuates at higher temperatures, whereas the CaFeREO sample shows an initial monotonic increase followed by a decrease of s value. The degree of correlation between AC conductivity and frequency is given by the exponents. The value of s defines the type of conduction mechanism that might change over the temperature range, as is evident for the investigated samples. Random hopping occurs when “s” equals zero; this means that AC conductivity is frequency independent. Small polaron (SP) and correlated barrier hopping (CBH) (Fe2+ → Fe3+ + e) is usually related to an increase and decrease in “s” with temperature, respectively.

### 3.4 The removal of heavy metals

The removal of heavy metal (Pb2+) from an aqueous solution is detected using CaFeO and CaFeREO as adsorbent through a batch adsorption experiment. Various analytical parameters, including pH, the dosage of adsorbate and adsorption capacity are optimized. The removal efficiency [90] and the sorption capacity are calculated according to the following equations:

\[
\text{Removal efficiency} \% = \frac{C_0 - C_f}{C_0} \times 100 \quad (3) 
\]

\[
\text{Sorption capacity} = \frac{C_0 - C_f}{m} \times V \quad (4)
\]

where \(C_0\) and \(C_f\) are the initial and final concentration (mg/L) of lead ion solution, respectively. \(V\) is the volume of the aqueous phase (L) and \(m\) (g) is adsorbent’s mass.
3.4.1 Effect of pH for removal of Pb II ions

The removal efficiency of Pb II ions for CaFeO as a function of pH is illustrated in (Fig. 14). The investigational data designates that the adsorption of Pb (II) increases with changing pH from 2 to 8 at 30 ºC as illustrated in the graph. The maximum removal efficiency % η of Pb (II) at pH ≅ 7 is nearly 99.59%. The obtained results reveal that CaFeO can be considered an active adsorbent for Pb (II) removal in practical applications, where the Pb (II) concentration in wastewater is usually lower than 30 mg/L.

The minimum adsorption of Pb ions is detected at pH 2. This can be ascribed to the mobility, as well as the high content of hydrogen ions existent at lower pH, prefer the adsorption of H⁺ rather than Pb II ions. Consequently, with increasing pH, the available proton number decreases. This is due to the active sites turning more negatively and/or neutral charged. Though, the sorption of the metal ions that have a positive charge is increased through the electrostatic attraction force [91].

At pH > 7, the formation of hydroxyl complexes increases the adsorption activity as testified by Ali et al. [92]. Subsequently, the increase of participating metal ions in the adsorption process is detected which is not favorable for the efficiency of the process.

3.4.2 Effect of adsorbent dosage for removal efficiency η of heavy metals

The effect of magnetic CaFeO and CaFeREO dose on the η of Pb (II) is determined using concentrations of 0.01 g to 0.06 g. The experiment is carried out under definite parameters (contact time ≅ 10 min, shaking speed ≅ 200 rpm, T ≅ 30 C° and pH ≅ 7). The heavy metal removal efficiency η as a function of adsorbent dosage is illustrated in (Fig. 15a).

The η at optimum adsorbent dosage (40 mg) of CaFeO, and CaFeREO are 96.32, and 99.31% respectively. The increase of the adsorbent dosage also increases the η of metal ions until an optimal dosage of 40 mg, after which the removal is more or less the same as detected from the obtained results. Increasing the percentage of adsorption with adsorbent dose is due to the increase in adsorbent surface area and the availability of more adsorption sites. The decrease of η for CaFeO after the optimal adsorbent dosage is due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles [93].

On other side, the adsorbent dose studies after the addition of the rare-earth ions display an increase in η increasing the adsorbent dose compared to CaFeO. This is due to the presence of a tiny amount of rare-earth ions in the sample significantly reducing the agglomeration of the nano particles and providing greater surface area for adsorption. The accessibility of more adsorption sites with an increase in dosage results in more interactions occurring between CaFeREO with the negatively charged surface, and Pb (II) ions with + Ve charged [94].
3.4.3 Adsorption isotherms

Several isotherm models can be utilized to designate the distribution of Pb^{2+} ions between the solid phase and liquid phase as well as the efficiency of the adsorbent. The Langmuir and Freundlich models are the most testified models to investigate the sorption isotherm of Pb (II) ions as presented in (Fig. 16a, b) respectively. The adsorption process of Pb (II) on CaFeO and CaFeREO is clarified by the previous models [22]. The Freundlich and Langmuir equations can be expressed as [95]:

**Langmuir isotherm**

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

**Freundlich isotherm:**

\[
\log q_e = \log K_f + \frac{1}{n} \log (C_e)
\]

where \(q_e\) represents the amount of heavy metal ion (Pb^{2+}) adsorbed by the adsorbent at equilibrium (mg/g); \(C_e\) is the equilibrium concentration of heavy metal ion (Pb^{2+}) in the solution (mg/L); \(q_{\text{max}}\) denotes the maximum adsorption capacity corresponding to complete monolayer coverage on the whole adsorbent surface (mg/g); \(K_L\) is the Langmuir adsorption equilibrium constant for the relative energy of adsorption (L/mg) and \(K_f\) and \(n\) are Freundlich constants associated with adsorption capacity and intensity of adsorption, respectively.

The Langmuir model is applied at particular binding sites on the homogenous adsorbent surface where a monolayer of adsorbed Pb^{2+} ions is wrapped completely on the surface of the adsorbent. Additionally, no interaction can occur between the adsorbed Pb^{2+} molecules on the adsorbent surface [96, 97]. This model describes the adsorption of heavy metal ions as designated by the high correlation coefficient \((R^2)\) of 0.981 and 0.999 for CaFeO and CaFeREO respectively.

The Langmuir constants, \(q_{\text{max}}\) and \(K_L\) values are attained from the slope and the intercept of the linear scheme of \(Ce/qe\) against \(Ce\) as shown in (Fig. 16a). The obtained values are 22.49 mg/g, 0.148 L/mg for CaFeO, and 27.47 mg/g, 0.079 L/mg for CaFeREO respectively. The higher value of \(q_{\text{max}}\) signifies the higher Langmuir monolayer adsorption capacity of CaFeREO. While a lower \(K_L\) value for CaFeREO implies the lower surface energy in the process.

Freundlich model is designated the process of chemical adsorption on multilayer physisorption in the heterogeneous surfaces [98, 99] by the high correlation coefficient \((R^2)\) of 0.998 and 0.999 for CaFeO and CaFeREO respectively.

Freundlich constants, \(K_f\) and \(n\) values are obtained from the slope and the intercept of the linear plot of \(\log q_e\) versus \(\log C_e\) as illustrated in (Fig. 16b) and found to be 35.69 mg/g, 1.059 for CaFeO and 36.06 mg/g, 0.996 for CaFeREO, respectively. The great adsorption capacity of the adsorbent towards Pb^{2+} is ratified from the obtained results.

The High value of \(K_f\) and the low value of \(n\) for CaFeREO indicate the higher Freundlich multilayer adsorption capacity and the higher intensity of adsorption respectively. The preference of adsorption and heterogeneity degree on the surface of the adsorbent can be identified by the magnitude of \(1/n\). The increase of \(1/n\) for CaFeREO ratifies the high sorption capacity and the formation of new adsorption sites [100].

The obtained results show that the CaFeO and CaFeREO have a good fit with the Freundlich and Langmuir models. The high correlation coefficients of the samples indicate that the entire isotherm models agree well with the results and hence a combination of homogenous monolayer and multilayer is convenient for the two samples. The obtained data indicate that the CaFeREO is a promising and better adsorbent for Pb (II) ions. The use of only 4 mg of CaFeREO with low price ferrite nanoparticles has been utilized for...

Fig. 16 The fitting of the obtained data with isotherm models a Langmuir model and b Freundlich model. The inset tables contain the obtained isotherm parameters
99.31% removal of Pb (II) from wastewater at a contact time of 10 min at room temperature. This is the prime novelty of the investigation.

4 Conclusion

CaFe$_2$–$_{x}$Gd$_{x}$Sm$_{y}$O$_4$ (with $x = y = 0.0; x = 0.025, y = 0.05$) nanoparticles were successfully synthesized in orthorhombic structure using citrate auto combustion method. The preparation of the samples in a single phase is ratified from XRD data. HRTEM micrographs show that the particle size is in the range of 33–65 nm. The parent nanoparticles exhibit paramagnetic nature at room temperature with low remanence while antiferromagnetic nature is manifest after doping by the rare-earth ions. The obtained data indicate that the CaFeREO is a promising and better ad-sorbent for Pb (II) ions. The use of only 4 mg of CaFeREO with low price ferroite nanoparticles has been utilized for 99.31% removal of Pb (II) from wastewater at a contact time of 10 min.

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