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Efcient adsorption and photocatalytic degradation of textile dye from metal ion‑substituted ferrite for environmental remediation

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Abstract

A fuel-based solution combustion method was used to synthesize Sr-substituted copper ferrites $\left[\text{Cu}_{1-x}\text{Sr}_{x}\text{Fe}_{2}\text{O}_{4}\left(x=0.00\right)\right]$ 0.25, 0.50, 0.75, 1.00)]. X-ray diffraction (XRD) pattern demonstrates that CuFe₂O₄ has a tetragonal structure and SrFe₂O₄ a cubic structure and the formation of particles of spherical and needle-like structures was observed using scanning electron microscopy (SEM). The magnetic behavior was investigated through a vibrating sample magnetometer (VSM) at room temperature under an applied magnetic feld ranging from −20 kOe to+20 kOe. Based on the M–H hysteresis loop, the soft-ferrite nature of the samples was observed. The synthesized samples were investigated for adsorption and photocatalysis in the degradation of textile dyes malachite green, crystal violet, and congo red. Compared to other compositions, $SrFe₂O₄$ demonstrated comparatively better adsorption and photocatalytic efficiency.

Keywords Spinel ferrites · Dyes · Photocatalysis · Adsorption · Magnetic properties

Introduction

Dyes are frequently used in textile, pulp and paper, paint, food, and other industries (Affat [2021](#page-15-0)). Dyes and other industrial pollutants are highly toxic, carcinogenic, and cause environmental degradation due to their non-degradable nature (Fatima et al. [2022](#page-16-0); Lellis et al. [2019\)](#page-16-1). Pollutant reduces the reoxygenation capacity of the receiving wavelength in waterbodies due to the cutoff of sunlight that negatively infuences the environment (Berradi et al. [2019](#page-15-1)). Water pollution caused by textile dyes and heavy metal ions is one of the major concerns (Ali and Gupta [2006](#page-15-2)) because they are the prime cause of dreadful diseases, and dysfunctioning of organs such as liver, brain, and kidney failure. The need for the degradation of toxic dyes from polluted water

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has gained appreciable attention (Jiad and Abbar [2023](#page-16-2)), particularly to develop materials that could degrade pollutants into harmless substances (Akarslan et al. [2015;](#page-15-3) Pereira et al. [2012](#page-17-0)). Depending on the nature of the contaminant, diferent methods are used for detoxifcation (Slama et al. [2021](#page-17-1)). Converting organic pollutants into harmless end products such as $CO₂$, water and inorganic ions through heterogeneous semiconductor oxide has become a promising technology (Rafq et al. [2021\)](#page-17-2). Several methods are used to eliminate these pollutants, e.g., adsorption, solar photo fenton method (Khaleel et al. [2023](#page-16-3)), ultrafltration, chlorination and photocatalysis (Sharma and Kaur [2018](#page-17-3)). Every method has pros and cons; therefore, a balanced approach is needed to select a material for degrading organic pollutants. Among all, photocatalysis appears to be the most suitable method for degrading textile dyes because it is eco-friendly, provides complete degradation of pollutants, is highly efficient, and leftover products have a very low level of toxicity (Rueda-Marquez et al. [2020](#page-17-4)).

In photocatalysis, semiconducting materials are used as catalysts for dye degradation in the presence of sun-light (Mills et al. [1997](#page-17-5)). However, commonly used photocatalysts, such as TiO₂, ZnO, ZnS and MoS₂ (Khan et al. [2023](#page-16-4)), are expansive and can't be separated from the water after degradation (Jacinto et al. [2020](#page-16-5)). Filtration and centrifugation processes are commonly used to separate the photocatalyst after

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the reaction. Nevertheless, these are expensive, less efficient, and time-consuming methods for separating the photocatalyst. Meanwhile, the industrial application of photocatalysts is highly restricted due to the above-mentioned problems. Therefore, photocatalyst, which possesses magnetic and photocatalytic properties, has gained signifcant attention (Das [2019](#page-15-4)). Consequently, spinel ferrite nanoparticles (SFNPs) have been considered a potential candidate as a photocatalyst in dye degradation to overcome the above-mentioned limitations (Ma and Liu [2021\)](#page-16-6). Along with excellent photodegradation properties, these materials can easily be separated from the solution after the completion of the reaction with the help of an external magnet. Diferent types of SFNPs (MFe₂O₄ where M—transition metal, e.g., Co, Ni, Cu, Mn) have been extensively used as a photocatalyst due to their unique magnetic, optical, and electric properties along with thermal and chemical stability (Nie et al. [2019](#page-17-6)).

In the family of spinel ferrites, copper ferrites are extensively used in sensors, catalysis, electronics, gas sensing, hydrogen production, ceramics, and memory devices (Amiri et al. [2019\)](#page-15-5). Copper ferrites possess phase transitions, interesting magnetic and electrical properties, and are non-toxic in nature (Roman et al. [2019\)](#page-17-7) and it has significant potential and possesses promising outcomes in photocatalysis, reported in the previous literature (Masunga et al. [2019](#page-16-7)). The photodegradation of rhodamine B was studied using pure and Ce-doped copper ferrites (Keerthana et al. [2021](#page-16-8)). $CuFe₂O₄@biochar composite prepared by one-step sol–gel$ pyrolysis method to degrade malachite green dye (Huang et al. [2021](#page-16-9)). Hydrothermally synthesized copper ferrites nanocomposite with graphene oxide was used for the malachite green degradation (Yadav et al. [2021\)](#page-17-8). Photodegradation activity of $TiO₂$ -doped copper ferrites studied toward the degradation of azo dyes (Masoumi et al. [2016](#page-16-10)). Green engineered synthesis of Ag doped copper ferrites and its catalytic activity toward malachite green degradation were investigated (Surendra [2018](#page-17-9)).

 $CuFe₂O₄$ has an inverse spinel structure in which 8 $Cu⁺²$ ions occupy the octahedral B-site, and 16Fe^{+3} ions occupy equal tetrahedral A-site and octahedral B-site in the unit cell (Sharma et al. [2020\)](#page-17-10). This confguration can be written as $(Fe^{3+})_A [Cu^{2+}Fe^{3+}]_B O_4^{2-}$. Copper ferrites exist in two phases; cubic (stable at higher temperatures) and tetragonal (due to the Jahn–Teller distortion) (Calvo-De La Rosa and Segarra Rubí [2020](#page-15-6)). Diferent synthetic routes are employed to synthesize copper ferrites, such as co-precipitation, hydrothermal, solid-state, mechanical milling, electrochemical advance oxidation methods, (Jiad and Abbar [2023\)](#page-16-2) thermal decomposition, microwave-assisted, and sol–gel auto combustion (Dippong et al. [2021](#page-16-11)). In the present study, the synthetic chemical route (self-propagating-combustion) was adopted due to its ease, scalability and viability in synthesizing Cu(1−*^x*) Sr*x*Fe2O4 nanoparticles. Citric acid monohydrate

was used as a chelating agent. Furthermore, this method provides other merits, such as no post-annealing is required, high yield and good chemical homogeneity of the samples.

To the best of our knowledge, no studies till now have been carried out on the application of Sr-substituted copper ferrites for photocatalytic dye degradation and adsorption. The large ionic radius of Sr^{+2} ions as compared to Cu^{+2} ions leads to lattice distortion and hence signifcant alteration in material's characteristics. In a prior investigation, the addition of Sr^{+2} to cobalt ferrites resulted in a comparable effect. The study also investigates the sample's structural, optical, morphological, and magnetic characteristics and then this synthesized samples are used for the photocatalytic activity on cationic and ionic dyes as well as adsorption study are also carried out.

Materials and methods

The sol–gel auto combustion method synthesizes $Cu_{1-x}Sr_xFe_2O_4$ with x varies to 0, 0.25, 0.50, 0.75, and 1.00. $Cu(NO₃)₂·6H₂O$, $Sr(NO₃)₂·6H₂O$ and $Fe(NO₃)₂·6H₂O$ of high purity (99.5%), purchased from Sigma-Aldrich, were used for sample preparation. Citric acid monohydrate was used as fuel to prepare the nanopowder. Metal nitrates and citric acid ($C_6H_8O_7·H_2O$) were used without any further purifcation. Nitrate precursors were weighed stoichiometrically and mixed in 50 mL of distilled water. Subsequently, 5 g citric acid was added into the precursor's solution under continuous stirring for 15 min to mix the solution and the temperature was increased up to 90 °C, the ratio of fuel to oxidizer was 1:1. The pH of the solution was adjusted to 7 by using an ammonia solution after that solution color turns green. The ignition temperature was raised to 150 °C, and the solution covert into slurry gel under vigorous and constant stirring. The gel afterwards formed powder after the auto combustion process, and it was calcined at 700 °C, as shown in Fig. [1](#page-2-0).

Adsorption and photocatalytic test on malachite green, crystal violet dye and congo red

Adsorption studies were carried out before the photocatalysis experiment. 20 mg of catalyst is mixed with 100 ml of dye solution. At fxed time intervals (0, 5, 10, 15, 20, 30, and 60 min), the adsorption kinetics were examined by taking 2.0 mL of the sample solution and observing for 1 h. Pseudo-frst- and pseudo-second-order adsorption models were employed to study the degradation of textile dyes via adsorption. The linearized form of the kinetic model (Huang and Shih 2021) is shown in Eqs. ([1](#page-2-1) and [2](#page-2-2)).

Fig. 1 Schematic of synthetic procedure for the copper strontium ferrites preparation by solution auto combustion method

$$
\log\left(Q_e - Q_t\right) = \log\left(Q_e\right) - \frac{K_1}{2.303}t\tag{1}
$$

$$
\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \tag{2}
$$

where K_1 and K_2 are the reaction rate constant for the first order and second order, respectively. The adsorption capacity (Q_t) can be determined from Eq. ([3\)](#page-2-3).

$$
Q_t = \frac{(C_0 - C_t)V}{m} \tag{3}
$$

where Q_t and Q_e represent adsorption capacity at time (*t*) and equilibrium adsorption capacity, respectively, whereas C_0 and C_t denote the initial dye concentration and dye concentration at time (*t*), respectively; *V* denotes the volume of dye solution; *m* stands for the mass of adsorbent.

Adsorption and photocatalysis efficiency were evaluated from Eq. (4) (4)

Degradation efficiency(
$$
\% = \left(\frac{C_0 - C_t}{c_0}\right) \times 100
$$
 (4)

The photocatalytic and adsorption experiment was performed at room temperature that was around 45 °C for all the prepared samples however, we reported here for the best three catalysts (CuFe₂O₄, Cu_{0.5}Sr_{0.5}Fe₂O₄ and SrFe₂O₄). The adsorption and photocatalytic experiment performed individually. Initially, the adsorption experiment was performed for 60 min. Only MG was degraded in adsorption phenomenon whereas other dyes' degradation efficiency was quite less. The photocatalytic performance of $CuFe₂O₄$, $Cu_{0.5}Sr_{0.5}Fe₂O₄$ and SrFe₂O₄ was evaluated separately for 30 min in the degradation of textile dyes (MG, CV, and CR). The stock solution of dye was prepared, and an aliquot of stock solution was taken for photocatalysis reaction. Catalyst $(CuFe₂O₄, Cu_{0.5}Sr_{0.5}Fe₂O₄$ and SrFe₂O₄), 20 mg, was added to 100 mL of aqueous solution of dye. All the prepared solutions were exposed to sunlight for 30 min in photocatalytic reaction. At fxed time intervals, 5 ml of dye solution was pipetted out until a complete degradation of dyes. This procedure is the same for both adsorption and photocatalysis. Finally, the degradation spectra of the pollutant were observed using a UV–Vis spectrophotometer by using Eq. [4.](#page-2-4)

Characterizations

Powder XRD patterns were recorded using Rigaku Ultima IV X-ray diffractometer with a Cu $K\alpha$ source ($\lambda = 1.54$ Å) in the 2θ range $10^{\circ} - 80^{\circ}$ at a rate of $2^{\circ}/$ min). The surface morphology was examined using a high-resolution (SEM; Quanta 3D FEG). UV–Visible spectrophotometer (Agilent Technologies) was used to measure the absorption spectra at room temperature in the 200–450 nm range. The functional group of the samples has been studied from Fourier Transform infrared radiation (FTIR), Bruker tensor 37 in the range (500–4000) cm⁻¹ and the Raman spectroscopy of the prepared was measured by using Invia Renishaw at 532 nm. Zeta potential measurements were done using a Malvern Zetasizer Nano ZS90, Mott–Schottky measurements were performed using potentiostat/galvanostat Autolab PGSTAT 204 (Metrohm, The Netherlands). The charge carriers' recombination times were examined by recording time-resolved photoluminescence (TRPL) using a Horiba (DeltaFlex01-DD) spectrophotometer at 280 nm excitation wavelength. The magnetic measurements were carried out at room temperature in the range of applied feld −20 kOe to+20 kOe from Cryogenic Limited UK VSM.

Results and discussion

Phase analysis using X‑ray difraction

The powder XRD was used to examine the crystallinity, phase purity and crystallite size. XRD patterns of $Cu_xSr_(1-x)Fe₂O₄$ (*x* = 0.00, 0.25, 0.50, 0.75, and 1.00) are shown in Fig. [2](#page-3-0). We observed the tetragonal phase of $CuFe₂O₄$ (JCPDS No. 34-0425) and cubic phase of SrFe₂O₄ (JCPDS No. (001-1027) in Cu_(1-*x*)Sr_xFe₂O₄ when *x* = 0.00 and 1.00, respectively. $SrFe₂O₄$ secondary phase was observed in Cu_(1-*x*)Sr_{*x*}Fe₂O₄ for *x* = 0.25, 0.50, and 0.75. It confirms the substitution of Sr atoms in $CuFe₂O₄$ systems.

The presence of the $SrFe₂O₄$ phase is possibly due to phase segregation. Since the excess amount of Sr atoms occupy both substitutional and interstitial sites (tetrahedral and octahedral) in the host lattice and increases the Sr concentrations; consequently, the interaction probability increases with other atoms of the host lattice and forces them

Fig. 2 XRD pattern of $Cu_{(1-x)}Sr_xFe_2O_4$ for all compositions

to leave their sites. With the higher temperature treatment given to the samples and increased Sr atoms incorporation, Gibb's free energy stabilizes and produces the secondary phase (Jelonek et al. [2020\)](#page-16-13). The sharp XRD peaks indicate a high crystallinity of the as-synthesized nanocomposites.

The lattice parameters ('a' $\&$ 'c') are calculated using the interplanar spacing (d_{hkl}) given in Eq. [5](#page-3-1).

$$
\frac{1}{d_{\text{hkl}}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}
$$
\n(5)

The compositional variation of the lattice parameters is shown in Fig. [3](#page-3-2)A. Lattice parameters ('a' $\&$ 'c') are calculated taking the 2*θ* (hkl): 35.86° (211) and 2*θ* (hkl): 62.15° (224) miller plane values. The nonlinear behavior of lattice parameters indicates the contribution of both compositional and structural disorder, where the structural disorder can be attributed due to point defects. Crystallite size and the lattice strain were calculated from the line broadening of difraction peaks of XRD using the Williamson–Hall method (Vishwaroop and Mathad [2020](#page-17-11)) and also shown in Fig. [3](#page-3-2)B. Crystallite size is also calculated using the Debye–Scherrer formula given by $D(nm) = 0.9\lambda/\beta\cos(\theta)$, where λ represents X-ray wavelength (1.5406 Å), θ is diffraction angle, and β is full-width half maximum (FWHM) (broadening of the peak) (Rabiei et al. [2020\)](#page-17-12).

According to the W–H method:

$$
\beta \cos \theta = \frac{k\lambda}{D} + 4\varepsilon \sin \theta \tag{6}
$$

 ϵ is the strain produced in the lattice.

A plot between $\beta \cos\theta$ and [4](#page-4-0) sin θ is shown in Fig. 4A–E. From the linear fit to the data, the strain (ε) was calculated from the slope, and the crystalline size was calculated from the y-intercept of the plot. The negative slope signifes the compressive strain in the lattice (Dey et al. [2020](#page-16-14)). The crystallite size decreases with increasing Sr concentration due to the produced lattice strain by the lattice mismatch (as given in Table [1\)](#page-4-1).

Morphology study

The morphology of the synthesized Cu_{1−*x*}Sr_{*x*}Fe₂O₄ nanoparticles for the selected composition was explored using SEM analysis and is shown in Fig. [5A](#page-4-2)–E. A mixed morphology, i.e., needle-like structure and spherical shape of the particles, were observed along with the large number of agglomerations suggesting the inhomogeneous synthesis process. The reason behind agglomeration is magnetic nature and primary particles union apprehended together via feeble surface interface such as van der Waals forces (Dhir et al. [2014](#page-16-15)). The uneven distribution of particles size could be due to the synthesis method.

Fig. 4 Williamson–Hall (W–H) plot for Cu_xSr_(1−*x*)Fe₂O₄, **A** $x=0.00$, **B** $x=0.25$, **C** $x=0.50$, **D** $x=0.75$, **E** $x=1.00$

Fig. 5 SEM images of synthesized Cu_{1-x}Sr_xFe₂O₄ for compositions at 1 µm. A $x=0.00$, B $x=0.25$, C $x=0.50$, D $x=0.75$, E $x=1.00$ and F EDAX pattern for $Cu_{0.5}Sr_{0.5}Fe₂O₄$

UV–visible study

The absorbance spectra of undoped and Sr-doped CuFe₂O₄ are illustrated in Fig. [6A](#page-5-0). The optical bandgap was estimated using Tauc's equation given by $(\alpha h v) = A(hv - E_g)^n$ where α is absorption coefficient, *h*^{*i*} is incident photon energy in eV, E_g is optical bandgap (eV), and n indicates the type of transition. For direct transition (direct bandgap), *n*=2 is used, and for indirect transition (indirect bandgap), *n*=1/2 is used for the bandgap estimation (Arifin et al. 2019). The E_g was estimated through the intercept, and its relationship with the compositional variation is shown in Fig. [6](#page-5-0)B. The band gap of Cu(1−*^x*) Sr*x*Fe2O4 was found to be decreased from 3.7 to 2.3 eV for increasing *x* from 0 to 1. The E_g shows a linear dependence on Sr composition *x* given by $E_g = 2.59 + 1.51x$ and follows ideal Vegard's law (Kempter [1966\)](#page-16-16). A red shift is observed in the bandgap as the Sr composition increases, where additional sub-energy levels are introduced in the band structure due to lattice strain or point defects (Manikandan et al. [2013](#page-16-17); Liu et al. [2004\)](#page-16-18). Therefore, Sr-substituted copper ferrites can absorb more photons and generate more electrons and holes, which favors enhancing photocatalytic efficiency.

Raman and FTIR spectroscopy

According to the factor group analysis, cubic spinel has 5 Raman active mode that can be represented by $(A_{1g} + 3T_{2g} + E_g)$ and in tetragonal spinel there are 10 Raman active mode represented by $(2A_{1g} + 3B_{1g} + B_{2g} + 4E_g)$ (shown in Fig. [7A](#page-6-0)). According to the literature, the modes beyond 600 cm⁻¹ (A_{1g)} frequently indicates the symmetric stretching of an oxygen atom with the metal ion at A-site. The presence of metal ions in the B-sites is responsible for the other low frequency symmetric and asymmetric bending and stretching modes $(T_{2g}, B_{1g}, B_{2g}, \text{and } E_g)$. (Channagoudra et al. [2021\)](#page-15-8).

The FTIR spectra recorded in the range (500–4000) cm⁻¹ to investigate the functional group and to determine the bonding between the atoms shown in Fig. [7B](#page-6-0), C. Two metal

oxygen bonds obtained in the range (200–800) cm−1 one is observed at 790 cm−1 for metal–oxygen bond. The other one in the range (200–400) cm⁻¹ was not observed because of instrument limit. The wavenumber at 3386 cm^{-1} due to the bonding of O–H. The peak that are observed in the range $(3200-3700)$ cm⁻¹ appears due to the stretching vibrations of O–H (Dhyani et al. [2022](#page-16-19)).

VSM (Vibrating sample magnetometer) measurement

The Magnetic properties of undoped and Sr-doped copper ferrites were investigated from vibrating sample magnetometer (VSM) in a magnetic feld of 20 kOe. The M–H curve (Hysteresis loop) describes the material's magnetic behavior as shown in Fig. [8A](#page-7-0)–C. We calculated the saturation magnetization (M_s) , Remanent magnetization (M_r) , coercivity (H_c) and the squareness ratio (M_t/M_s) from the S-shaped hysteresis loop. The calculated values of M_s , M_r , H_c and squareness ratio are reported in Table [2.](#page-7-1) The value of magnetic parameters obtained from the hysteresis loop was observed to decrease with an increase in Sr-doping concentrations.

The magnetic response of the spinel ferrites depends on various parameters such as crystallite size, cation distribution in tetrahedral sites (A) and octahedral sites (B), oxygen deficiency, exchange interactions and ionic radii of alkaline earth metal (Ateia et al. [2020\)](#page-15-9). In principle, there are three types of interactions in spinel ferrites, namely AOA, BOB and AOB. Interaction corresponding to the coupling of electrons with metal ions, AOB, is the strongest among them (Odio et al. [2017](#page-17-13)). CuFe₂O₄ belongs to the inverse spinel category, therefore, the divalent ion occupies the octahedral site, and trivalent is distributed in tetrahedral as well as octahedral sites, similar to the strontium ferrites (Ghahfarokhi and Shobegar 2020). The ionic radius of Sr^{+2} ion is larger than the Fe^{+2} ion; therefore, due to the incorporation of rare earth metals, Fe^{+2} ions migrate from the octahedral to the tetrahedral site. Consequently, AOB super exchange interaction decreases, which leads to the lower

Fig. 6 A Tauc's plot for $CuFe₂O₄$, inserted image shows the absorption spectra of the Cu1−*x*Sr*x*Fe2O4, B Variation in bandgap with Sr composition variation (inserted Tauc's plot for $SrFe₂O₄$)

Fig. 7 A Raman spectra for CuFe₂O₄, Cu_{0.5}Sr_{0.5}Fe₂O₄ and SrFe₂O₄ and FTIR spectra for CuFe₂O₄, Cu_{0.5}Sr_{0.5}Fe₂O₄ and SrFe₂O₄. **C** Enlarged portion of the FTIR spectra in the range of (500–2000) cm−1

value of the saturation magnetization (Abdel Maksoud et al. [2020](#page-15-10)). Another possibility for the decrement in saturation magnetization is the non-magnetic nature of Sr^{+2} ions. The synthesized samples were found to be soft ferrites due to low coercivity (see Table [2\)](#page-7-1). The squareness ratio (SQR) value was observed in the range of 0.53–0.21. The materials with squareness less than 0.5 belong to the single-domain category, and those with squareness greater than 0.5 belong to the multi-domain class (Gore et al. [2022](#page-16-21)). VSM results indicate durability and easy magnetic material recovery in the applied external magnetic feld.

Adsorption study

An adsorption study was performed for MG, CV and CR dyes; however, only MG was degraded signifcantly and the rest of the dyes degraded below 55%. The possible reason for the difference in efficiencies is due to the small structural change in MG and CV. There are diferent factors such as charge density, electron distribution, substitutions present or steric factors which may responsible for this diference in efficiencies in cationic and anionic dyes (Liu et al. [2004](#page-16-18); Zhuo et al. [2011\)](#page-17-14). The adsorption experiment was done in the dark for one hour, and MG was observed to be degraded maximum from the Uv–Vis spectrometer. $C/C₀$ vs time plot-ted for dark degradation as shown in Fig. [9A](#page-8-0). Efficiency was calculated and obtained to be 68% in copper ferrites (SF1), 82% in copper strontium ferrites (SF2) and 92% in strontium ferrites (SF3) (shown in Fig. [9B](#page-8-0)).

Adsorption kinetics

To investigate the reaction mechanism of the adsorption of dye on the surface of the catalyst, two kinetic models, frst and second order, were considered. Adsorption plots for frst- and second-order kinetics are shown in Fig. [10](#page-9-0)A, B. The values of rate constants K_1 and K_2 , corresponding linear regression coefficient (R^2) , were calculated and shown in Table [3](#page-9-1). A lower R^2 value for first-order reaction, reveals that the frst-order model does not predict the rate kinetics of adsorption of MG dye on the nanocomposite surface. However, the R^2 value corresponding to second-order kinetics is close to 1 and indicates that second-order model is suitable for the adsorption of MG onto the catalyst surface.

Therefore, we conclude that the adsorption of MG follows pseudo-second-order kinetic model and chemisorption is paramount in the adsorption reaction (Sahoo et al. [2018](#page-17-15); Vergis et al. [2018\)](#page-17-16).

Adsorption mechanism

In principle, the adsorption mechanism contains three main steps (Alaqarbeh [2021\)](#page-15-11).

- 1. Film difusion, where adsorbate ions or molecules transfer from the bulk solution to the external surface of the adsorbent's particles due to the boundary layer.
- 2. Intraparticle difusion, where the adsorbate transports into adsorbent either due to the internal pores (pore diffusion) or through the internal surface (surface difusion).
- 3. Energetic interaction between the fnal adsorbate and internal adsorption active sites (Worch [2012](#page-17-17); Han et al. [2017](#page-16-22)).

The adsorption process rate, in general, is controlled by the second and third steps, whereas the frst step occurs rapidly.

The adsorbent initially encounters the solution of adsorbate material then the pores of the adsorbent's material are flled with water (pores water). In the frst step of adsorption process, the metal ion transforms from a bulk solution to a thin flm solution and surrounds the adsorbent by a layer which is known as the boundary layer. The concentration of the adsorbate (dye molecules) in the solution decreases because the adsorbent ion (catalyst) ensnared into the boundary layer. This flm difusion process is the rate-governing mechanism in the adsorption process until the adsorbate concentration equilibrates in the bulk and boundary layer solutions.

More reduction of the adsorbate concentration in the bulk solution depends on intraparticle difusion of adsorbate ions/molecules through pore difusion and/or surface difusion (Han et al. [2017](#page-16-22)). This reduction in concentration

can be explained by Weber-Morris intraparticle difusion model.

$$
q_t = kt^{0.5} + c \tag{7}
$$

where *q* refers to the solid phase concentration (mg/g), i.e., quantity of adsorbate on the adsorbent, *t* is the adsorption time (minutes), *k* is the rate constant (mg/g–h^{0.5}) for film or intraparticle difusion, and *c* is a proportionality constant for the boundary layer thickness (mg/g). If the intraparticle difusion is the solitary rate-controlling mechanism, then the q versus $t^{0.5}$ gives a straight line that passes through the origin. A non-zero intercept means another mechanism is also involved in the adsorption process (Singh et al. [2012](#page-17-18)).

Two intraparticle difusion rate constants have been calculated from the linear ft data. The adsorption mechanism can be explained based on the above explanation. The steep slope K_1 represents the rapid adsorption process due to the electrostatic interaction between the adsorbate and adsorbent. K_1 was found to be maximum for SrFe_2O_4 and correlated with maximum degradation efficiency. The value of the frst slope is larger than the second one, see Fig. [10C](#page-9-0). The second slope K_2 is more gradual, representing a slow difusing process (Mortazavian et al. [2019](#page-17-19)).

The adsorption efficiency is maximum for $SrFe₂O₄$, and adsorption isotherms at different concentrations (1 mg/100 ml, 2 mg/100 ml, 3 mg/100 ml and 4 mg/100 ml) were studied for $SrFe₂O₄$. The Langmuir and Freundlich adsorption isotherms were used to investigate the adsorption capability of MG at diferent equilibrium concentrations.

Table 2 Magnetic parameters obtained from VSM measurements

23.18	12.5	1520	0.53
18.22	8.92	820	0.48
8.78	1.86	260	0.21
			M_s (emu/g) M_r (emu/g) H_c (Oe) SQR (M_r/M_s)

Fig. 8 VSM plot of \mathbf{A} CuFe₂O₄, \mathbf{B} Cu_{0.5}Sr_{0.5}Fe₂O₄ and \mathbf{C} SrFe₂O₄

$$
\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{k_{\rm L}Q_{\rm m}} + \frac{C_{\rm e}}{Q_{\rm m}}\tag{8}
$$

$$
\log\left(q_e\right) = \log\left(k_f\right) + \frac{1}{n}\log\left(C_e\right) \tag{9}
$$

The amount of dye adsorbed at the equilibrium concentration is q_e , C_e is the concentration of solute at equilibrium, maximum adsorption capacity is Q_m and K_L is the equilibrium constant of Langmuir isotherms. K_f and $1/n$ are the Freundlich constants related to adsorption intensity and adsorption capacity, respectively (Edet and Ifelebuegu [2020](#page-16-23); Chen [2015](#page-15-12)). Figure [10D](#page-9-0), E shows the ftting results for the isotherms Langmuir and Freundlich adsorption model. Isotherm constants obtained from the ftted data are given in Table [4.](#page-10-0) We obtained Langmuir isotherm adsorption model is better ft for adsorption equilibrium of Malachite Green on CuFe₂O₄, Cu_{0.5}Sr_{0.5}Fe₂O₄ and SrFe₂O₄. In Langmuir model, one dye molecule is adsorbed on an individual (one) adsorption site, and a monolayer is formed on the surface of the adsorbent, resulting decrease in the adsorption sites for further layer (Alaqarbeh [2021](#page-15-11)). The half life of the photocatalyst was also calculated from the below expression (Mahmoud et al. [2009](#page-16-24))

$$
t_{1/2} = \frac{0.693}{k} \tag{10}
$$

We have calculated the half life of the photocatalyst from rate constant. The minimum decrement in half life is obtained in difusion model and second-order rate kinetics. We have calculated the half life of the photocatalyst from rate constant. The minimum decrement in half life is obtained in difusion model and second-order rate kinetics (as given in Table [3](#page-9-1)).

The feasibility and favorability of adsorption are determined by Langmuir dimensionless separation factor R_L shown in Eq. (10) (10) .

$$
R_{\rm L} = \frac{1}{1 + k_{\rm L} C_0} \tag{11}
$$

 R_L value lies in the range (0–1) favors the adsorption process, whereas $R_L > 1$ indicates the unfavorable adsorp-tion (Ayawei et al. [2017](#page-15-13)). R_L value obtained from Langmuir isotherms is 0.92 and confrms the favorable adsorption (as given in Table [5](#page-11-0)).

Adsorption isotherms was studied for $Cu_{0.5}Sr_{0.5}Fe₂O₄$ and found that it is also follows Langmuir isotherms model as the $SrFe₂O₄$ followed.

Efect of pH and temperature on degradation of dye

The effect of temperature has been studied at three different temperature 30 °C, 50 °C and 70 °C from SrFe₂O₄ (SF3) for 30 min in case of adsorption. Increase in temperature leads to improved dye adhesion on catalyst surfaces compared to lower temperatures. As indicated in Fig. [11A](#page-11-1), the adsorption efficiency varies with temperature. When the temperature increased from 303 to 343 K, there was an initial increase in adsorption efficiency from 75 to 95% for a 1 mg/100 ml concentration at pH 7.0. This observation suggests that the adsorption reaction is endothermic in nature. (Karthikeyan et al. 2005) The enhanced adsorption efficiency at higher temperatures may be attributed to chemical interactions between adsorbates and the adsorbent, potentially resulting in the creation of additional adsorption sites or an accelerated rate of pollutant ion difusion into the pores of the adsorbent.

Fig. 9 A C/Co plot for dark degradation. **B** Efficiency plot in case of malachite green, crystal violet and congo red for CuFe₂O₄ (SF1), $Cu_{0.5}Sr_{0.5}Fe_2O_4$ (SF2) and SrFe₂O₄ (SF3)

Fig. 10 The adsorption mechanism model for malachite green **A** the frst-order kinetics model; **B** the second-order kinetics model; **C** difusion model langmuir isotherm model; **D** langmuir isotherm model; **E** Freundlich isotherm model

 K_1 : first-order slope, K_2 : second-order slope, R^2 : correlation coefficient

Efect of pH Usually, the pH of the solution plays a very crucial role in wastewater treatment, and it is a very important factor that infuence the photocatalytic degradation process of organic compounds. The efect of pH on the degradation of MG was studied at pH values of 4, 7 and 9 and it was found that efficiency increases as pH vary from $(4-9)$, i.e., the photodegradation efficiency increases from acidic to alkaline medium (Rahman et al. [2021\)](#page-17-20) (shown in Fig. [11](#page-11-1) B. This result indicates that the photodegradation process occurs at the catalyst surface and not in bulk solution. In addition, one would expect that the interaction between the photogenerated holes and hydroxide ions (OH) to generate hydroxyl radicals (OH) is enhanced in alkaline pH, which in turn would facilitate the photocatalytic degradation of MG. The maximum degradation efficiency was obtained 95.04% at pH 9. The increased proton concentration in

acidic solutions slows down the dye's photodegradation, which lowers the degradation efficiency. In a basic Conversely, the existence of the acidic end products are neutralized by hydroxyl ions once they are generated by the process of photodegradation.

Photocatalytic degradation of textile dyes (malachite green, crystal violet, congo red)

The photocatalytic activities of CuFe₂O₄, Cu_{0.5}Sr_{0.5}Fe₂O₄ and $SrFe₂O₄$ nanocomposite were evaluated by degrading malachite green, crystal violet and congo red dyes. We found that complete degradation of MG occurred in 30 min. The catalyst $SrFe₂O₄$ displayed the highest photodegradation efficiency due to uniform structure and negative surface charge. The photo-decolorization of MG was found to 93.20% for copper ferrite, 94.50% for Cu–Sr ferrites and 97.00% for strontium ferrites. For CV, 16.92% efficiency was observed in the presence of $CuFe₂O₄$ and 26.15% dye was degraded by $Cu_{0.5}Sr_{0.5}Fe_{2}O_{4}$ photocatalyst, while 41.67% degradation was observed for $SrFe₂O₄$. Notably, the surface charge of $SrFe₂O₄$ is negative and supports cation dye degradation. Therefore, from Fig. [12A](#page-11-1), B, it can be concluded that $SrFe₂O₄$ exhibits relatively better photocatalytic activity compared to pure copper ferrites and their composites.

The photocatalytic degradation efficiency of CR in the presence of CuFe₂O4, Cu_{0.5}Sr_{0.5}Fe₂O₄ and SrFe₂O₄ nanocomposite is shown in Fig. [12B](#page-11-2). It was observed that after 30 min, about 83.64% of CR was degraded in the presence of CuFe₂O₄ and 73.03% was degraded by Cu_{0.5}Sr_{0.5}Fe₂O₄ photocatalyst, while 72.98% degradation was observed for $SrFe₂O₄$. Photocatalysis efficiency is minimal for $SrFe₂O₄$ due to the interaction between the anionic dye and the negatively charged surface of SrFe_2O_4 Moreover, photocatalytic efficiency was enhanced in light compared to dark in half time.

Zeta potential and TRPL (time‑resolved photoluminescence) studies

Zeta potential study was performed to investigate the surface charge of $CuFe₂O₄$, $Cu_{0.5}Sr_{0.5}Fe₂O₄$ and $SrFe₂O₄$. The $CuFe₂O₄$ and $Cu_{0.5}Sr_{0.5}Fe₂O₄$ exhibited a positive zeta potential of +5.49 mV and +3.08 mV, respectively, while S rFe₂O₄ showed a negative zeta potential of −13.8 mV (see Fig. [13A](#page-12-0). These results are in good agreement with the previous literature (Kamel et al. [2020](#page-16-26)). We calculated the surface charge for $Cu_{0.75}Sr_{0.25}Fe_2O_4$ and $Cu_{0.25}Sr_{0.75}Fe_2O_4$ nanocomposites, and their values were obtained to be $+4.42$ mV and -1.21 mV, respectively. Sr-doped CuFe₂O₄ samples suggest the higher dispersion stability of nanoparticles in the solution. The opposite surface charge favors the adsorption of cationic dye (malachite green and crystal violet) on the $SrFe₂O₄$ photocatalyst due to the electrostatic force of attraction. Degradation efficiency is observed less for anionic dye (congo red) because of the opposite surface charge.

The enlarged portion of decay-associated spectra of Srsubstituted Cu ferrites is shown in Fig. [13](#page-12-0)B. However, the complete decay spectra of the samples are shown in the inset Fig. [13B](#page-11-1). The calculation and ftting of the experimental data were implemented by triexponential function using Eq. [12](#page-10-1) (Chen et al. [2012\)](#page-15-14).

$$
y = A_1 + B_1 e\left(-\frac{1}{\tau_1}\right) + B_2 e\left(\frac{-i}{\tau_2}\right) + B_3 e\left(\frac{-i}{\tau_3}\right) \tag{12}
$$

where B_1 , B_2 and B_3 are amplitudes, τ_1 , τ_2 , and τ_3 correspond to the lifetime of components 1, 2 and 3, respectively. The average lifetime of the samples $CuFe₂O₄$, $Cu_{0.5}Sr_{0.5}Fe₂O₄$ and SrFe_2O_4 were found to be 2.07 ns, 3.62 ns and 3.90 ns,

Table 4 Isotherms model constants describing the adsorption of Malachite green on $SrFe₂O₄$

Langmuir isotherms	SrFe ₂ O ₄	Freundlich isotherms	SrFe ₂ O ₄
$Q_{\rm m}$ (mg/g)	1000	K_f (mg ^{1-1/n} ·L ^{1/n} ·g ⁻¹)	280
K_{I} (L/g)	0.082	n	3.98
$R^{}_{\rm L}$	0.92	R^2	0.78
R^2	0.98		

 Q_m : maximum adsorption capacity, K_L : Langmuir equilibrium constant, R_L : separation factor, R_2 : correlation coefficient, K_f and *n*: Freundlich constants

respectively. The recombination time was obtained maximum for SrFe_2O_4 , which can be correlated with the higher degradation efficiency. The χ^2 value was obtained in the good fit data range. The TRPL results (see Table [7\)](#page-13-0) of undoped and Sr-doped copper ferrites indicated high charge carrier recombination in Sr ferrite, which correlates with better photocatalytic performance (Table [6](#page-12-1)).

Mott Schottky measurement

Mott Schottky measurements were conducted in 0.1 M solution of Na₂SO₄ with Ag/AgCl electrode for CuFe₂O₄, $Cu_{0.5}Sr_{0.5}Fe₂O₄$ and SrFe₂O₄ nanocomposites. We calculated the fat band potential and the positions of the valance band (VB) and conduction band (CB) (see Fig. [14A](#page-13-1)-C). The negative slope demonstrates that $CuFe₂O₄, Cu_{0.5}Sr_{0.5}Fe₂O₄$ and $SrFe₂O₄$ possess a p-type conductivity. These results are in good agreement with the previous literature (Fedai-laine et al. [2016](#page-16-27)). The flat band potential value for $CuFe₂O₄$, $Cu_{0.5}Sr_{0.5}Fe₂O₄$ and SrFe₂O₄ nanocomposites are −0.28 V, −0.09 V and −0.84 V, respectively (see Table [8](#page-13-2)).

Reported degradation efficiencies of textile dyes on photocatalysts

Here, we collected the reported degradation efficiencies of the textile dyes due to photocatalysts in Table [9.](#page-13-3) We compare our results with the reported data on the degradation of textile dyes using copper ferrites and their composites in Table [9](#page-13-3). The comparison is made on the basis of the degradation efficiency and performance of the synthesized samples. The present work shows better degradation efficiency of MG, CV and CR dyes using Sr-substituted copper ferrites (97%, 41.67% and 72.98%, respectively) and consumed relatively lesser time to degrade the dyes (see Table [9](#page-13-3)).

Mechanism of textile dye de‑colorization

The photocatalytic degradation mechanism of textile dyes is shown in Fig. [15](#page-14-0). When the surface of photocatalyst

 $(CuFe₂O₄, Cu_{0.5}Sr_{0.5}Fe₂O₄$ and SrFe₂O₄) is irradiated by UV–vis light, electrons in the valance band get excited, as shown in Eq. [13](#page-11-3). Furthermore, the complete mechanisms of photodegradation are shown in Eqs. [13–](#page-11-3)[21.](#page-12-2) Electrons jump to the conduction band and create an equal number of holes in the valance band (Ajormal et al. [2020](#page-15-15)). The holes in the VB can directly react with dye or interact with water and form hydroxyl radicals (·OH), a powerful oxidant for the mineralization of dyes. Meanwhile, the photogenerated electron can be captured by absorbed reactive oxygen molecules to yield O_2^- . The generated O_2^- reacts with H^+ to produce $H₂O₂$, which further reacts with the excited electrons and generates OH− radicals. All the reactive radicals react with the dye and lead to the formation of degradation products. Sr-substituted copper ferrites have a lower band gap than pure copper ferrites. $CuFe₂O₄$ band gap was determined

from Tauc's plot as 3.7 eV, which lies in the UV–Vis region, i.e., \sim 5% of the solar spectrum. However, the modified bandgap of Sr-substituted copper ferrites (2.3 eV) lies in the visible region (which is approx. 46% of the spectrum) that enhances the photocatalytic degradation efficiency of the synthesized material.

$$
SeFe2O4 + h\nu \rightarrow SrFe2O4(e-) + SrFe2O4(h+)
$$
 (13)

$$
SrFe_2O_4(e^-) + O_2 \to .O_2^-
$$
 (14)

$$
H_2O \rightleftharpoons H^+ + OH^-
$$
 (15)

$$
\text{OH}^- + h_{\text{VB}}^+ \rightarrow .\text{OH}
$$
 (16)

Cu_0 , Sr_0 , Fe_2O_4	Freundlich isotherms	Cu_0 $5Sr_0$ $5Fe_2O_4$
700	K_f (mg ^{1-1/n} ·L ^{1/n} ·g ⁻¹)	250
0.078	n	3.16
0.92	R^2	0.77
0.96		

Fig. 11 A Efect of temperature

on MG dye degradation, **B** efect of pH on degradation of dye MG from $SrFe₂O₄ (SF3)$

Table 5 Isotherms model constants describing the adsorption of Malachite green

on $SrFe₂O₄$

Fig. 12 Photocatalysis degradation of textile dyes (MG, CV, and CR) for CuFe₂O₄ (SF1), $Cu_{0.5}Sr_{0.5}Fe_2O_4$ (SF2) and $SrFe₂O₄ (SF3), A C/Co plot B$ efficiency with time (min)

$$
SeFe2O4(e-) + .O2- + 2H+ \to H2O2
$$
 (17)

$$
SeFe2O4(e-) + H2O2 \rightarrow .OH + OH-
$$
 (18)

$$
SrFe2O4(h+) + H2O \rightarrow .OH + H+
$$
 (19)

 $MG + .OH \rightarrow Degradation$ Products (20)

$$
MG + .O_2^- \rightarrow Degradation\ Products
$$
 (21)

Scavenger test for malachite green (MG)

To investigate the role of the active species, including holes $(h⁺)$, hydroxyl radicals (\cdot OH) and superoxide radicals $(·O₂)$ which are responsible for the degradation of dyes, trapping experiments were performed in the representative dye MG. Diferent types of scavengers were used for trapping active species. Radicals benzoquinone (BQ) was used for the superoxide, KI for holes and hydroxyl radicals trapping; however, t-BuOH for hydroxyl radicals (Janani et al. [2021](#page-16-28)). As expected, it was observed that maximum photodegradation efficiency was obtained without a scavenger. However, photodegradation efficiency with the scavenger decreased due to the trapping of produced active species by the scavenger (see Fig. [16\)](#page-14-1). The photocatalytic degradation efficiency for malachite green is reduced to 73.8% from 98.8% (blank, i.e., without scavenger) after the addition of BQ, implying that superoxide radicals are mainly responsible for the degradation of MG. The degradation efficiency was reduced to 96.8% with KI; however, the degradation efficiency remains unchanged for t-BuOH (see Fig. [16](#page-14-1)). Based on the scavenger test, it is observed that superoxide radicals $(O₂)$ and hydroxyl radicals (·OH) are the major and minor active species for the degradation of MG, respectively. Similarly, the scavenger test can be performed for the other dyes as well. In addition, H_2O_2 was also used as scavenger in scavenger test. H_2O_2 generates super oxide and hydroxyl radical that are responsible to degrade the pollutant. The degradation efficiency is 91% in case of H_2O_2 .

The reusability of the magnetic photocatalyst

The reusability of a catalyst plays a crucial role in using it for industrial applications. We tested reusability for the strontium ferrites, and 20 mg of the photocatalyst was used in 100 ml of dye solution. After the photodegradation process, the photocatalyst was magnetically extracted using a magnet. To remove the remnant dye molecule on strontium ferrite, the used strontium ferrites were washed thrice with 10 ml of ethanol followed by 10 ml of deionized water. The diference in colour of MG dye is shown in Fig [17A](#page-14-2). The recyclability was tested fve times to verify the reusability of strontium ferrite, and obtained efficiencies were 97%, 96%, 95%, 93% and 92%, respectively, shown in Fig. [17](#page-14-2)B. There is a slight change in degradation efficiency, which confirms the reusability of the photocatalyst.

Table 6 The degradation efficiency of all synthesized samples

Samples		Degradation efficiency (η)			
	MG (cationic dye $(\%)$	CV (cationic dye) $(\%)$	CR (ani- onic dye) (%)		
CuFe ₂ O ₄	93.20	16.92	83.64		
Cu_0 , Sr_0 , Fe_2O_4	94.50	26.15	73.03		
SrFe ₂ O ₄	97.00	41.67	72.98		

Fig. 13 A Zeta potential and **B** time-resolved photoluminescence (TRPL) for samples CuFe₂O₄, Cu_{0.5}Sr_{0.5}Fe₂O₄ and SrFe₂O₄

Table 7 TRPL data of undoped and Sr-doped copper ferrites

Fig. 14 A Mott Schottky plot for $CuFe₂O₄$, **B** $Cu_{0.5}Sr_{0.5}Fe₂O₄$ and **C** SrFe₂O₄

Table 8 Mott-Schottky measurements of synthesized samples	Sample	Position of conduc- tion band	Position of valance band	Flat band position [V	Bandgap (eV)
	CuFe ₂ O ₄	-0.377	$+3.32$	-0.28	3.7
	Cu_0 5 Sr_0 5 Fe_2O_4	-0.187	$+3.01$	-0.09	3.2
	SrFe ₂ O ₄	-0.70	$+1.36$	-0.84	2.3

Table 9 Reports on copper ferrites and their composites for degradation of diferent dyes

Fig. 16 Scavenger test using S rFe₂O₄ for Malachite green

Conclusion

 $Cu_{1-x}Sr_xFe_2O_4$ (where *x* varies from 0 to 1) were synthesized using a fuel-based sol–gel auto-combustion method. The X-ray difraction pattern indicated the formation of different structures, including a single-phase tetragonal spinel for CuFe₂O₄ ($x=0$), a cubic spinel for SrFe₂O₄ ($x=1$). The particles exhibited mixed morphologies, with both spherical and needle-like shapes observed. The optical bandgap decreased from 3.7 eV $(x=0)$ to 2.3 eV $(x=1)$. The adsorption and photocatalytic properties of the prepared samples were studied for dye degradation. Maximum adsorption was observed for MG, and the highest decolorization efficiency, reaching 97%, was achieved for S rFe₂O₄. Photocatalytic degradation efficiency improved under light compared to dark conditions in half time. The adsorption mechanism followed

Fig. 17 A Color diference in MG dye in the presence of photocatalyst with a digital photograph of recovery of magnetic photocatalyst from dye solution **B** degradation efficiency for five cycles

the second-order kinetic model and intra-particle difusion model, consistent with Langmuir isotherms. For various dyes, the highest photocatalytic efficiency was achieved with strontium ferrites (97% for MG, 41.67% for CV, and 72.98% for CR), except for copper ferrites, which achieved 83.64% efficiency in CR degradation. The magnetic study showed that samples exhibited a ferromagnetic nature. This property allowed for easy recovery and magnetic separation of the nanocatalysts from the reaction mixture. Consequently, these highly efficient and reusable photocatalysts offer a promising solution for the degradation of industrial pollutants. The photocatalyst was found to be reusable for up to five cycles, especially in the case of $SrFe₂O₄$.

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Author contributions MS: data curation, formal analysis, methodology, software, writing—original draft, conceptualization, investigation, validation, visualization, writing—review & editing. NM: conceptualization, validation, visualization, writing—review & editing. SB: validation. AMS: supervision, validation, writing—review & editing. MK: funding acquisition, project administration, resources, supervision, conceptualization, writing—review & editing.

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Data availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest Authors declare no conficts of interest.

Ethical approval This is an observational study, and the research ethics committee has confrmed that no ethical approval is required.

Consent to participate All individual participants are included in the study. Please keep this consent form in the patient's case fles. The manuscript reporting this patient's details should state that 'Written informed consent for publication of their clinical details and/or clinical images' was obtained from the patient/parent/guardian/ relative of the patient. A copy of the consent form is available for review by the Editor of this journal.

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