Original Article

Synthesis and characterization of molecularly imprinted ferrite (SiO₂@Fe₂O₃) nanomaterials for the removal of nickel (Ni²⁺ ions) from aqueous solution

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The study for the extraction of nickel (Ni²⁺ ions) from aqueous solution by applying surface modified molecularly imprinted ferrite nanomaterials as an adsorbent. Molecularly imprinted ferrite nanoparticles were synthesized by co-precipitation method, using ferrous and ferric salts in basic medium. Silica coating was done by the Stober method followed sol-gel hydrolysis, using precursor TEOS. Use of Trinitrotoluene (TNT) as a catalyst establishes to be necessary to obtain a proper coating. The particle sizes reveal in the range of 20–24 nm calculated by X-ray diffraction method, which shows the spinal nature of ferrite nanoparticles. Monodispersity of the nanoparticles was also confirmed due to the size distribution of the particles by SEM analysis. Silica coating functionalization with TEOS and adsorbed peak of Ni(II) ion on the surface of ferrite nanocomposites were confirmed by Energy dispersive X-ray (EDX) spectroscopy. The metal adsorption behavior (Ni²⁺ ion adsorbed on the surface of silica-coated ferrite nanocomposites) characterized by Fourier Transform Infrared spectroscopy (FT-IR). Magnetic property was studied by VSM and the nanocomposites are found to be superparamagnetic at room temperature. Batch experiment conduced to study the adsorption kinetics and the adsorbent stability in the acidic and basic medium was an accessible mechanism of nickel adsorption by ferrite nanocomposites. Adsorption isotherms were well described by Langmuir equations with maximum adsorption capacity (qₑ) = 2.64 mol/g. The adsorption process establishes to be pH dependent (7.6), adsorbent dose (0.2 g) and equilibrium could be attained within 15 min. All the reaction parameters were considered to complete the adsorption process; it conceded that 94% nickel adsorbed under different optimization conditions. In the study, desorption study, as well as its reusability and recyclability, were accessible indicates that ferrite nanocomposite succeeding adsorption and desorption cycle and retains metal removal capacity until more cycles happened adequately.

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1. Introduction

There is a basic need for all properly functioning societies to provide safe drinking water to its people. Contamination of water with toxic metals included mercury (Hg), nickel (Ni), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), lead (Pb) copper (Cu), cobalt (Co), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), selenium (Se), zinc (Zn), and aluminum (Al) in ground water are of major concern for its hazardous effect on the environment [1]. Heavy metal pollution in water is very high in areas where mining, smelters, metal processing refineries, wood preservation, and paper processing facilities are located. Human exposure to heavy metals as well as public concern for the associated health risks have both risen dramatically as a result of an exponential increase of their use in these various applications. Major pollutants are heavy metals, inorganic and organic compounds. For heavy metals, major sources – industries such as – electroplating, metal processing, mining, tanneries, pharmaceuticals, pesticides, organic chemicals, rubber and plastic lumber and wood products are responsible [2]. Heavy metals which are generally released by industries are Cu, Co, Ni, Cr, Cd, As, Hg, Pb, Ag, Au, U, etc. Some heavy metals including cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se) and zinc (Zn) are essential minerals that are necessary for various biochemical and physiological functions. They serve as components of several key enzymes and play important roles in various oxidation–reduction reactions in our bodies. For example, anemia (red blood cell deficiency) can result from low iron. Supplements can prevent or treat diseases resulting from mineral deficiency. An excess amount of any particular heavy metal produces cellular and tissue damage leading to a variety of adverse effects and human diseases. For some metal including chromium and copper, there is a very narrow range of concentrations between beneficial and toxic effects, so be careful when taking supplements. Other metals such as aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), bismuth (Bi), cadmium (Cd), gallium (Ga), germanium (Ge), gold (Au), indium (In), lead (Pb), lithium (Li), mercury (Hg), nickel (Ni), platinum (Pt), silver (Ag), strontium (Sr), tellurium (Te), thallium (Tl), tin (Sn), titanium (Ti), vanadium (V) and uranium (U) have no established biological functions and are considered nonessential metals in our diet. Even in very low quantities, lead, cadmium, chromium, mercury, and arsenic are known to induce cardiovascular diseases, developmental abnormalities, neurologic and neurobehavioral disorders, diabetes, hearing loss, hematologic and immunologic disorders. These heavy metals are also classified as human carcinogens (known or probable) according to the U.S. Environmental Protection Agency, and the International Agency for Research on Cancer. Although the acute and chronic effects are known for some heavy metals, Studies have shown that toxic heavy metals can interfere with absorption and use of nutritionally essential metals such as iron, calcium, copper, nickel and zinc. Each metal differs in how it behaves in our bodies, and exposure alone does not always cause disease or harm. The human body's natural response to heavy metal exposure is to store them and slowly excrete them over time to minimize organ damage. Most of the heavy metals discharge into the water are found to be toxic, carcinogenic and causes a serious threat to the human health. Elemental density and toxicity are inter-related. Arsenic, which is technically categorized as a metalloid (like metal), is quite dense and is extremely toxic in very small quantities. People can be exposed to heavy metals through ingestion, inhalation, or contact with skin. The severity of health effects of heavy metals is related to the type and chemical form of each particular contaminant and is also depends on the exposure time and dose. Nickel is an essential trace element that is vital to the health of all living things [3]. Generally, heavy metal toxicity causes chronic degenerative diseases such as muscles-joint pain, mental and gastrointestinal disorders, chronic fatigue, kidney and liver damage in human beings [4]. Sometimes symptoms are vague and difficult to diagnose the diseases at the early stage. Infact oxidation state of metals and the degree of the solubility of its different forms of salts defines its level of toxicity in water [5]. Acute heavy metal poisoning usually occurs when people are exposed to large amounts of one particular metal at a time. For example, a child swallowing a lead bullet can cause a large amount of lead exposure all at once. Acute exposures can quickly cause serious health effects or death. Chronic or long-term exposure to lower levels of heavy metals can also cause health problems. The symptoms of chronic heavy metal poisoning can be severe, but are often less obvious and develop much more slowly over time than the symptoms caused by acute exposure. This is a topic of growing scientific evidence that needs to be better researched to clarify all the possible health implications [6]. True chronic heavy metal poisoning is rare but also difficult to diagnose.

Many kinds of adsorbent have been vitalized since a long time for the removal of toxic metals from wastewater. Generally, these adsorbents are made from highly porous materials and thus providing a high surface area for better adsorption. But intraparticle diffusion causes low adsorption rate and capacity, especially for macromolecules. Thus developing an adsorbent with the large surface area and small diffusion resistance is of great importance in environmental remediation. The advent of nanotechnology has solved this problem to a large extent by synthesizing various kinds of nanomaterials for the treatment of waste water. So far magnetic nanomaterials have been explored extensively in water remediation pastures. Various researches [7,8] have proved that magnetic nanomaterials especially ferrite, magnetite, and maghemite are widely used in removal of organic, inorganic and heavy metal impurities from water. Magnetic nanomaterials apart from having the high surface area to volume ratio, also having sole properties which make remediation process economical, efficient and eco-friendly, such as – least toxic, biodegradable and magnetically removal of pollutants [9,10]. The present study investigates that the application of modified ferrite nanomaterials for the removal of Ni(II) from aqueous solution. It establishes that bare ferrite nanoparticles adsorb negligible amount of metal compared to modified magnetite. Modification of the surface dramatically enhanced the adsorption capacity due to the presence of multifunctional groups which are helpful in making chelates or complexes with metal ions [11-14]. Nickel has no known biological function and is of medium toxicity to humans. The organic form
of nickel is much more toxic than its inorganic forms. It is highly irritant to the skin and is toxic to the cardiovascular system, as well as being carcinogenic. Most nickel is often released into the atmosphere from burning fossil fuels, mining, industrial settings, landfills, refining operations and incineration of municipal waste. Nickel compounds will settle and be bound to either water sediment or soil treated with sewage sludge, and in cigarettes, which contain between 0 and 0.51 µg per cigarette. Soil generally contains about 4–80 ppm. Usually water-soluble nickel compounds occur in the environment after release through application in agriculture [15]. Soluble nickel compounds form the largest threat to human health. Skin exposure may occur when jewelry which contains nickel is worn. Once in the body, nickel can replace metals in metalloenzymes and cause disruption of metabolic pathways required to sustain life. For example, enzymes are indispensable in cellular activity for signal transduction and cell regulation [16]. The most toxic of nickel compounds is nickel carbonyl, a very volatile liquid at room temperature, which is known to be a lung carcinogen when inhaled. Generally and unknowingly we ingest a daily average of 170 µg of nickel [17,18]. This may come from the air we breathe, the water we drink and the food we eat. Most of the nickel absorbed goes to the kidneys. Nickels consumed are usually disposed off in the feces quickly while those that get into the bloodstream are eliminated through the urine. Water contaminated with high levels of nickel (250 ppm) had stomach aches and suffered adverse effects to the blood and kidneys. A child who ate 5700 mg of nickel as crystals of nickel sulfate died of heart failure. The average concentration of nickel in the air in the US is about 1–86 ng/m³ (1 ng/m³ is equivalent to 1 billionth of a gram in a cubic meter of air) [19]. The average daily adsorption of nickel is minimal – no more than 200 µg. The average concentration of nickel in drinking water is around 2 ppb. People who are not sensitive to nickel must ingest very large amounts to show adverse health effects. Ideally concentration levels of organic and inorganic nickel should be 0 [20]. Hence, there is an awful inevitability to remove nickel from water by using cost-effective and environmentally friendly techniques [21].

Till now various processes are available to remove heavy metals from wastewater including thermal, biological and chemical methods such as chemical precipitation, solvent extraction, ultra-filtration, electro-dialysis, adsorption, ion-exchange, etc. [22,23]. Among numerous techniques adsorption is the most promising technique used in the removal of toxic metals from water [24]. Adsorption is a surface phenomenon driven by physico-sorption and chemisorptions processes for the bonding of contaminants on the surface. Now a day’s application of ferrite nanomaterials as a nanosorbents is an attractive and efficient method for the removal of nickel and other toxic metals from polluted water [25,26]. The distinctive physicochemical properties of ferrite nanomaterials such as size, larger surface area to volume ratio, high mechanical strength, easy surface functionalizations with different chemical groups, etc., makes them as an efficient and selective for water purification. Several research groups are exploiting the sole possessions of ferrite nanoparticles to develop high capacity and selective sorbents for metal ions and anions [27–29]. Ferrites are usually ferrimagnetic ceramic compounds derived from iron oxides [30]. Among nanosorbents, Ferrite nano-materials, such as α-Fe₂O₃ and γ-Fe₂O₃ and its composites Fe₃O₄ (magnetite) have special advantage in water purification technology due to their tremendous magnetic property, adsorptive property, less toxicity, biodegradable, eco-friendly, easy and facile synthesis, etc. [31–33].

Various research studies on molecularly imprinted nanomaterials [34], such as silica-coated ferrite (SiO₂@Fe₂O₃) and (SiO₂@CoDGO) and its composites silica-coated magnetite (SiO₂@Fe₃O₄) as the best adsorbents for the removal of heavy metal ions from water with a variety of inorganic and organic compounds [35,36]. The determination of heavy metals in water is also an integral part of separation methods [37–39]. Various instrumental techniques such as – UV–Vis spectrophotometer [40], ion exchange [41], atomic absorption spectrometry (AAS) [42], inductively coupled plasma (ICP), chromatography [43], etc., have been used for the analysis and determination of traces toxic metals from water.

Ferrites that are used in transformer or electromagnetic cores contain nickel, zinc, and manganese compounds [44]. They have a low coercivity and are called soft ferrites. Example of soft ferrites-nickel-zinc ferrite (NiZn, with the formula Ni₆Zn₁₋₉Fe₂O₄) [45]. NiZn ferrites exhibit higher resistivity than MnZn, and are therefore more suitable for frequencies above 1 MHz. Manganese-zinc ferrite (MnZn, with the formula Mn₆Zn₁₋₉Fe₂O₄). MnZn have higher permeability and saturation induction than NiZn [46]. Cobalt ferrite, CoFe₂O₄ (CoO-Fe₂O₃), is in between soft and hard magnetic material and is usually classified as a semi-hard material [47]. It is mainly used for its magnetostriuctive applications like sensors and actuators [48]. In contrast, permanent ferrite magnets are made of hard ferrites, which have a high coercivity and high remanence after magnetization. Iron oxide and barium or strontium carbonate are used in the manufacturing of hard ferrite magnets [49]. The high coercivity means the materials are very resistant to becoming demagnetized, an essential characteristic for a permanent magnet. They also have high magnetic permeability. Example of hard ferrite strontium ferrite, SrFe₁₂O₁₉ (SrO-6Fe₂O₃), used in small electric motors, micro-wave devices, recording media, magneto-optic media, telecommunication and electronic industry [50].

Barium ferrite, BaFe₁₂O₁₉ (BaO-6Fe₂O₃), a common material for permanent magnet applications. Barium ferrites are robust ceramics that are generally stable to moisture and corrosion-resistant [51]. They are used in, e.g. loudspeaker magnets and as a medium for magnetic recording, e.g. on magnetic stripe cards. Uses-ferrite particles are also used as a component of radar-absorbing materials or coatings used in stealth aircraft. Most common radio magnets, including those used in loudspeakers, are ferrite magnets. Ferrite magnets have largely displaced Alnico magnets in these applications. It is a common magnetic material for electromagnetic instrument pickups [52]. Ferrite nanoparticles exhibit superparamagnetic properties [53].

Barium hexaferrite (BaFe₁₂O₁₉) as both a high coercivity (170 kA/m) and low raw material costs [54]. In the 1960s Philips developed strontium hexaferrite (SrFe₁₂O₁₉), with better properties than barium hexaferrite [55]. Barium and strontium hexaferrite dominate the market due to their low costs.
In present study silica-coated ferrite nanoparticles with its surface functionalized by tetra ethoxy silanes (TEOS) was experienced as a nano sorbents for the capturing of toxic metals from water. It has been found that it (SiO₂@Fe₂O₃) is an excellent adsorbent for toxic metals [56]. Its removing capacity is far better than conventional sorbents. UV–Vis spectrophotometer technique is also applied to the determination of equilibrium Ni²⁺ metal ions concentration in the solutions with the help of a calibration graph. This will help in the calculation of percentage recovery of toxic metal ions [57].

The novelty of the present research work to synthesized the MI silica coated iron oxide (SiO₂@Fe₂O₃) nanomaterials and its application in removal and adsorption of heavy metals from aqueous solution under the influence of various operational parameters such as the effect of concentration, contact time, adsorbent dose and solution pH. These parameters are useful in the calculation of percentage recovery of heavy metal ions. It was reported that the experimental data were fitted in the adsorption isotherms to Langmuir model and compare results with Freundlich model [58]. In order to understand the rate and mechanism of the adsorption processes, the adsorption kinetics was also carried with its relation to the adsorption mechanism [59]. Therefore, MI (ferrite) nanomaterials may be the future materials for the removal of heavy metals from water.

2. Experimental

2.1. Materials and reagents

The chemicals used in the experiment were of high purity (99.99%) purchased from Sigma Aldrich (Merck) Bangalore, India. The company name details as ©2015 Sigma-Aldrich Co. LLC. All rights reserved. SIGMA and SIGMA-ALDRICH are trademarks of Sigma-Aldrich Co. LLC, registered in the US and other countries. But I have purchased these chemicals from Bangalore, India namely such as – ferrous chloride (FeCl₂) and ferric chloride (FeCl₃), sodium hydroxide (NaOH), tetra ethoxy silane (TEOS), glacial acetic acid (CH₃CO₂H), trinitrotoluene – TNT (C₆H₂(NO₂)₃CH₃), ethanol (C₂H₅OH) were of analytical grade reagents. Distilled water (18.2 MΩ cm at 25 °C) was used throughout the experiment. The stock solution 0.1 M (NiCl₂·6H₂O) for adsorption study was prepared, by dissolving calculated amount of nickel (II) chloride hexahydrate in deionized water and different concentration of solution were obtained by diluting the stock solution.

2.2. Instrumentation

The test instruments used in this experiment, viz. namely – Magnetic Stirrer, Centrifuge, UV–Visible Spectrophotometer, XRD, SEM, EDX, FT-IR, VSM. The Magnetic Stirrer and Centrifuge instruments were performed by REMI 2MLH. But the UV-Visible double beam Spectrophotometer analysis was performed using a Shimadzu UV-2600/2700 spectrophotometer (Japan). The instrument was controlled by UV-2600/2700 operation software. The as-obtained samples were characterized using X-ray diffraction (XRD), which was carried out on a Siemens D 500S powder X-ray diffractometer equipped with a Cu Kα (λ = 0.1542 nm) radiation tube operating at 40 kV and 25 mA. Scanning electron microscopy (SEM) images were obtained on a JSM-6700F field emission scanning electron microscope (Japan). Energy dispersive X-ray (EDX) spectroscopy was performed on an Omnisorp 100CX (Coulter, USA) apparatus. Fourier transform infrared (FT-IR) spectra (4000–400 cm⁻¹) in KBr were recorded using a Magna-560 spectrometer (Nicolet, USA). All the measurements were performed at room temperature. And the VSM was performed using a Shimadzu AA6300 magnetometer (Coulter, USA) apparatus.

2.3. Preparation of molecularly imprinted ferrite nanomaterials

The monodisperse uniform size molecularly imprinted ferrite nanomaterials were prepared by co-precipitation method followed by a silica coating based on the Stober method through sol-gel hydrolysis using precursor TEOS, was carried out. Use of Trinitrotoluene (TNT) as a catalyst was found to be necessary to obtain a proper coating [60]. The spinel structure of iron oxide nanoparticles was prepared by adding an aqueous solution of ferrous and ferric salts were taken in 1:2 molar ratio co-precipitated in the presence of base (1 M-NaOH) kept on stirrer (@400 rpm) at the fixed temperature (90 °C). The reaction medium was continued until complete precipitation occurs. After stirring for 6 h, the precipitated solution was centrifuged; brown precipitate obtained dried for 24 h at temp of 100 °C in oven. The dried precipitate was powdered by grinding and then kept into an automatic furnace for 6 h at temp 450°C (with heating rate – 250 °C and cooling rate – 100 °C). In this synthesis process, the striking point was to synthesize ferrite in the absence of an inert atmosphere by maintaining the high temperature of the reaction medium. Though silica coating based on the Stober method through sol-gel hydrolysis, polycondensation of precursor TEOS, followed by functionalization of Trinitrotoluene in slightly acidic reaction medium (via sol–gel process) [61,62]. The ferrite hydrolyzes in ethanol medium by the addition of tetra ethyl oxysilane (TEOS) followed by 30 min stirrer, further functionalization with TNT solution (2–3 ml) and kept on stirring for 2 h [63]. A crude suspension was obtained on sonication for 50 min, which was centrifuged washed with ethanol and kept in an automatic furnace for 6 h at 400 °C (with heating rate – 250 °C and cooling rate – 100 °C). The mass obtained was powdered by grinding [64].

The distinct approach of molecularly imprinting as shown in Fig. 1 “the synthesis route for Silica coated iron oxide (SiO₂@Fe₂O₃) nanoparticles”.

2.4. Static adsorption test

Adsorption experiment was conceded by stirring fixed amount of nanocomposite as a nanosorbent (0.1 g) with 10 ml of 0.1 M solution of NiCl₂·6H₂O for 15 min at room temperature [65]. Metal loaded adsorbent was separated magnetically. The concentration of unadsorbed metal ions was found out with the help of a calibration graph of nickel solution at a fixed wavelength – λmax (550 nm) with varying initial metal concentration. After the equilibration, the pH was stabilized to
The spectrophotometer concentration monolayer tions were optimized following the reaction and separation, the residual metal concentration was determined with the help of UV-Vis spectrophotometer.

2.4.1. Adsorption experiment
Adsorption isotherm was determined by mixing 0.1 g adsorbent with 10 ml of a metal solution with varying initial metal concentration ranging from 0.01 M to 0.1 M, followed by stirring for 15 min at room temperature to attain equilibrium [67]. The pH of the reaction medium was set at 7.6 as an optimized value. After adsorption, the metal loaded sorbent was magnetically separated and final metal concentration in the supernatant was determined with the help of UV-Vis spectrophotometer at a fixed Wavelength of 550 nm [68]. The calibration graph is shown in Fig. 7, assumes that the monolayer sorption occurs on a homogenous surface of the adsorbent with varying initial concentration of metal solutions carried out no lateral interaction between adsorbate molecules. A number of metal ions adsorbed at time t, qt in mg/g were calculated as a mass balance Eq. (1).

\[ qt = (C_0 - C_t) \frac{V}{m} \]  

(1)

where \( C_0 \), \( C_t \), \( V \), \( m \) are initial concentration of metal ions, the concentration of metal ions after time t, the volume of the solution and the mass of the adsorbent used. Langmuir adsorption isotherm as shown in Fig. 8, assumes that the monolayer adsorption occurs on a homogenous surface of the adsorbent with no lateral interaction between adsorbate molecules. The adsorption process was examined by using Langmuir adsorption isotherm as described in Eq. (2).

\[ \frac{1}{q_e} = \frac{1}{q_m B C_e} + \frac{1}{q} \]  

(2)

where \( q_e \) is the equilibrium adsorption capacity of adsorbent toward Ni(II) (mg/g), \( C_e \) is the equilibrium Ni(II) concentration in solution (mg/L), \( q_m \) is the maximum capacity of adsorbent (mg/g), and \( b \) is the Langmuir adsorption constant pertaining to the energy of adsorption [69].

2.4.2. Dynamic adsorption
To detect the effect of adsorbent dosage on the adsorption capacity, 10 ml of 0.1 M metal NiCl₂·6H₂O (nickel salts) solution was taken and pH of the solution was adjusted at 7.6. Then the various amounts of adsorbents were added to the solutions on the ultrasonic stirrer at room temperature for 15 min [70]. After the reaction and separation, the residual metal concentration was determined with the help of UV-Vis spectrophotometer.

2.4.3. Effect of sample pH
The effect of pH on adsorption capacity was experienced by taking 0.1 g of the adsorbent with 10 ml of 0.1 M NiCl₂·6H₂O metal solution with varying pH values from 2 to 8, at room temperature, followed by stirring for 15 min. After adsorption and separation, the residual metal concentrations were determined by UV–Vis spectrophotometer [71].

2.4.4. Effect of contact time
To study the effect of time on adsorption capacity, 0.1 g of adsorbent was mixed with 10 ml of 0.1 M NiCl₂·6H₂O metal solutions, followed by stirring at room temperature for various time intervals ranging from 5 to 20 min [72].

2.5. Regeneration and reusability
The desorption study was conceded by using 0.1 M HCl solution as an eluent for eluting the adsorbed metal ions from the adsorbent. For this fixed amount of metal loaded adsorbent was mixed with 10 ml of HCl, followed by ultrasonic stirring at room temperature for 15 min for desorption of metal ions. After complete elution, the unloaded adsorbent was separated magnetically and metal concentration in the supernatant was determined. The recovered adsorbent was reused till more recycling process happened [73].

3. Results and discussion
The characterizations of the prepared molecularly imprinted nanomaterials were carried out by XRD, SEM-EDX, and adsorption–desorption studies have been discussed with reference to these techniques.

3.1. XRD analysis
It indicates that a high percentage of particles as a spinel structure but few of them were crystalline. Fig. 2a and b show the XRD pattern of ferrite and functionalized silica-coated ferrite
Monodispersity of the nanoparticles was also confirmed by the size distribution of the particles. The EDX spectra of Ni(II) metal loaded on the nano sorbent before and after are shown in Fig. 4a and b [88]. Results showed that the observable peak of Ni(II) clearly seen in Fig. 4b which was adsorbed on the surface of ferrite nanocomposites.

Further chemical analysis by FT-IR spectra as shown in Fig. 5b shows the Ni<sup>2+</sup>-ions adsorbed on the surface of silica-coated ferrite nanocomposites and the metal adsorption behavior. The spectra of bare ferrite nanoparticles have been shown with characteristic peak of Fe–O–bond stretching vibration at 595 cm<sup>-1</sup>. A new peak at 1095.9 cm<sup>-1</sup> for Si–OH bond indicating that the silica has been coated on the surface of ferrite nanoparticles is shown in Fig. 5a. Fe–O–Si peak could not be seen due to the overlapping with Fe–O peak. In Fig. 5b a new peak has been observed at 1680 cm<sup>-1</sup> for C–O–stretching vibration in –Ni<sup>2+</sup>–metal complex clearly suggests the complexation or chelation of nickel metal ions with carboxyl functional groups [89].

Hence, confirming the binding of Ni<sup>2+</sup>-metals on the surface of silica-coated ferrite composites. The redshift of the peak of –C–O bond is clearly shown in Fig. 5b, thus attesting the binding of metal ions with –Ni<sup>2+</sup> by substituting the hydrogen ions (H<sup>+</sup>) to form a –Ni<sup>2+</sup>–metal complex. It also revealed that the binding of metal ions with –Ni<sup>2+</sup>–metal was guided by ion exchange and electrostatic interaction mechanism.

### 3.3. Vibrating sample magnetometer (VSM) analysis

The relation between the applied magnetic field (H) and saturation magnetization (M<sub>s</sub>) of the prepared ferrite (Fe<sub>2</sub>O<sub>3</sub>), silica coated ferrite (SiO<sub>2</sub>@Fe<sub>2</sub>O<sub>3</sub>) nanoparticles functionalized by TNT were measured and compared by the vibrating sample magnetometer at room temperature [90]. Here, VSM study are shown in Fig. 6 reveals the superparamagnetic property of ferrite nanocomposite also known that the saturation magnetization curves for ferrite, silica coated ferrite and functionalized ferrite nanocomposites. Saturation magnetization values were observed as 51 emu/g, 46 emu/g and 44 emu/g respectively at room temperature. Although saturation magnetization value for the nanocomposite is less than the bare ferrite but enough to carry out magnetic separation from aqueous solution. Although modification of ferrite nanocomposites decreases the magnetic property but enough to separate metal
Fig. 4 – (a) EDX spectra of molecular imprinted silica coated ferrite (SiO$_2$@Fe$_2$O$_3$) nanomaterials. (b) Ni$^{2+}$-adsorbed on the surface of molecular imprinted ferrite nanocomposites [83].

Fig. 5 – (a) FT-IR spectra molecular imprinted silica coated ferrite (SiO$_2$@Fe$_2$O$_3$) nanomaterials. (b) Ni$^{2+}$-adsorbed on the surface of molecular imprinted ferrite nanocomposites.
loaded adsorbent magnetically by applying external magnetic field [91].

3.4. Adsorption isotherm measurement

To determine the sorption capacity of the nano sorbent, sorption studies were carried out with varying initial concentration of metal solutions ranging from 0.02 to 0.1 mol/l at a constant temperature is shown in the calibration graph (Fig. 7) [92]. The equilibrium adsorption isotherms for Ni\textsuperscript{2+} on the nano sorbent and the adsorption behavior are described by Langmuir model as shown in Fig. 8 [93]. The value of q\textsubscript{m} (maximum absorption coefficient) was calculated as 2.64 mol/g for 0.2 g adsorbent. The %R value is calculated as 94% for 0.2 g adsorbent.

3.5. Dynamic adsorption and its optimization

The adsorption process is dependent upon the amount of adsorbent as shown in Fig. 9. The adsorption was negligible in the beginning as the adsorbent was very low (0.04–0.09) g in quantity, as soon as the amount of adsorbent was increased (0.1–0.2) g the more metals happened to be adsorbed hence adsorption capacity increased very fast. It also showed that there was no further increase in recovery of metal ions when the numbers of nano sorbent were above 0.2 g [94]. The reason is that for the decrease in adsorption capacity beyond the optimize quantity has been full of occupied reaction sites and no more sites were available for further chelation or complexation. Therefore, 0.2 g was taken as an optimized amount for the maximum adsorption.

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**Fig. 6** – VSM study of molecular imprinted iron oxide nanomaterials.

**Fig. 7** – Calibration graph for Ni(II) at 550 nm wavelength [84].

**Fig. 8** – Langmuir adsorption isotherm for Ni(II) [85].

**Fig. 9** – Effect of adsorbent on the adsorption of nickel (Ni\textsuperscript{2+}) ions [86].
3.6. Effect of sample pH

The effect of pH of Ni$^{2+}$ ion on adsorption mechanism found to be ion exchange and electrostatic attraction during the process of at room temperature by varying the reaction pH of medium from 2 to 10 while keeping other parameters constant to reach the equilibrium of the reaction or completion of the phenomenon [95]. It was observed that surface adsorption phenomenon has been highly pH dependent, as in beginning pH range 2–4; adsorption found to be negligible. As pH increases from 4 to 6, adsorption also increased, it was continued (6–8) to increase pH, till reaches 7.6 after that decreases (Fig. 10). This suggests that at lower pH, the concentration of H$^+$ ions is higher which competes for complexation with metal ions on the reaction sites. At higher pH, OH$^-$ may dominate in the reaction medium and metal ions would have a tendency to get precipitated in the form of metal hydroxides; some of them would escape binding with reaction sites [96]. Hence, the diagram shown the higher the adsorption value with increasing pH because of hydroxy species could strongly contribute with Ni(II). Hence, optimization of pH (7.6) has been necessary action for the quantitative recovery of metals.

3.7. Adsorption capability

The adsorption capability of Ni$^{2+}$ ion on adsorption mechanism has been found to be time-dependent as shown in Fig. 11. In this regard, the effect of time on adsorption was tested through a range of 5–20 min. In the beginning adsorption of metal ions was almost negligible between time intervals of 5–9 min. After that when the time was increased from 10 to 15 min adsorption process increases and maximum adsorption was reported at 15 min. After further increase in time (15–20) adsorption starts decreasing. The reason behind this was no available reaction sites for further complexation with metal ions [97]. Hence, the maximum recoveries of Ni$^{2+}$ was found 94% at pH = 7.6 at time interval of 15 min.

3.8. Adsorption specificity

To investigate the adsorption specificity of metal ion on molecularly imprinted nanosorbents, static adsorption experiment was carried for the binding of Ni$^{2+}$ ion in a buffered solution. The adsorption specificity was conceded by mixing 10 ml of 0.1 M HCl with 0.2 g of adsorbent in a beaker followed by stirring on an ultrasonic stirrer for 15 min at room temperature. After that magnetic nanosorbent was separated by applying external magnetic field and the concentration of the eluted metal ions in the filtrate was measured with the help of a calibration graph of nickel metal ions by measuring the absorbance using UV–Visible Spectrophotometer [98]. It was observed that the desorption of Ni$^{2+}$ metal ions, in the beginning, was 94–95%. Elution of metal ions was quite satisfactory till more cycles happened as shown in Fig. 12.

4. Conclusions

A new synthetic approach for the preparation of nonporous molecularly imprinted ferrite nanomaterials was developed by a surface imprinting technique. It has been proved that the imprinted sorbent showed a good selectivity for the imprinted molecule by both functional groups and dimensional structure of specific binding site. Furthermore, Spinel structure ferrite nanoparticles with regular spherical structure were obtained successfully. It was found that the maximum diameter of the nanopore particle size approximately 24 nm by XRD analysis while the uptake of Ni$^{2+}$ ions from aqueous solution with the nanosorbent make sure by EDX analysis correspondingly. The adsorption process was found to be pH and time dependent but also adsorption mechanism noted as ion exchange. Each method has its advantages and limitations. Comparing with these methods, the method developed in this paper was sufficiently accurate. The precise adsorption with 0.2 g of adsorbent was enough to extract 94% Ni(II) at pH 7.6 within 15 min and performed better characteristics such as
selectivity and cleanliness of the extracts. Adsorption isotherms were described by Langmuir equations with maximum adsorption capacity of \( q_m = 2.64 \text{mol/g} \). Hence, molecularly imprinted nanomaterials as an adsorbent would be a better option in remediation technology of wastewater especially polluted with heavy metals due to its high adsorption capacity and easy separation ability.

**Conflicts of interest**

The authors declare no conflicts of interest.

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