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Synthesis and Characterization of Magnetite for Pollutant Remediation

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ABSTRACT

Phosphorus is one of the limiting nutrients for crop production, especially in developing countries where soil available P is low. To counter P deficiency, P has been applied at a rate above crop uptake which makes management of P fertilizer a challenge for the scientific community, as high input P can have environmental consequences like eutrophication of water bodies. Physico-chemical and biological methods are widely used for the removal of soluble P from wastewater. Adsorption of P onto a paramagnetic substance like magnetite holds a great promise for its removal and subsequent recovery of adsorbed P. The present study was carried out with the objective of synthesis of magnetite in different molar ratios and its characterization to select the best magnetite material for removal of P. Magnetite was synthesized using the co-precipitation method using ferrous and ferric ions at different molar ratios (1:1, 1:2, 2:1, 5:1) and characterized for Xray diffraction, Fourier transforms infrared spectroscopy, and Brunauer-Emmett-Teller method surface area. All the synthesized material resembled the Joint Committee on Powder Diffraction Standards XRD patterns of reference magnetite and showed strong peaks at 220, 311, 400, 511, and 440 cm^{-1}. FTIR analysis showed the presence of Fe-O bond at 580 cm^{-1} and characteristic peaks at 1633 and 3400 cm^{-1} suggesting the presence of a hydroxyl group. Highest surface area (93.001 (m^2/g) was observed for magnetite synthesized with a molar ratio of 1:2 (Fe^{2+}/ Fe^{3+}), whereas the surface area of the rest of the synthesized magnetite was close to 50 m^2/g. The smallest pore radius was also found in magnetite synthesized with a molar ratio of 1:2 (Fe^{2+}/ Fe^{3+}) which contributed to the highest pore volume.

***Key words:** Adsorption, Magnetite, XRD, BET, Phosphorus*

Introduction

Water quality is important in every aspect of the ecosystem and the well-being of humans. Rivers, lakes and other aquatic ecosystems, directly and indirectly influence human health and aquatic life (Maurya *et al.,* 2021, Kar, 2013). Meeting the water quality of aquatic bodies is also a major issue as these are the source for supplying water for various domestic, industrial, and agricultural use. The importance of P originating from agricultural sources as a nonpoint source of environmental pollution has been a challenging issue of the 21st century. To increase food production multi-fold and to cope with the rising food security, fertilizer are applied at a rate greater than crop uptake (Pradhan *et al.,* 2021). Continued application of P fertilizer and its subsequent movement to different water bodies triggers eutrophication (Zafar *et al.,* 2016). Therefore, removal of P from the contaminated water is a must for the safe use of water. Removal technologies of P are divided into three types, (i) physical-chemical (precipitation: primary, simultaneous, or final) (ii) biological (enhanced biological removal), or (iii) membrane purification techniques. Out of these physico-chemical techniques, adsorption and ion exchange, and magnetic separation are known to be more useful and economical. Adsorption is a surface phenomenon in which electrostatic attractionoccurs between positively charged surfaces of iron oxides and negatively charged phosphate ions, forming an outer-sphere complex. The main principle behind the use of magnetite for the separation of P is the use of a magnetic field to separate particles. To separate P from the wastewater P must be converted into insoluble form and the adsorbent must possess the magnetic property for its separation. Magnetite (Fe_3O_4) is a substance having paramagnetic properties. The present study was carried out with the objective of (i) synthesis of magnetite in different molar ratios (ii) Characterization of magnetite and evaluation of the best molar ratio for magnetite synthesis.

Materials and Methods

Magnetite was synthesized using the chemical co-precipitation method using ferrous sulphate ($FeSO_4.6H_2O$) and ferric chloride ($FeCl_3$) in a different ratio (Table 1). Fe (II) and Fe (III) salts were taken in four different ratios and dissolved separately in a beaker. Then, the $FeSO_4.7H_2O$ solution was poured into the $FeCl_3$ solution and the resulting mixture was placed on a magnetic stirrer and stirred at 60-700 C for 5 Min at 200 rpm. Nitrogen gas was supplied to eliminate oxygen from the working environment. The pH of the solution was then adjusted to pH 10-11 by adding 20% NaOH dropwise using a burette. The colour of the mixture changes from orange to brown at pH 6 and dark black at pH 10-11 indicating the formation of magnetite. The resultant suspension was kept for settling and washed with distilled water to attain neutrality. The precipitate was placed on a porcelain dish and dried at 50 ^{o}C in a hot air oven and finally ground to pass through a 100-mesh sieve.

Characterization of magnetite

The synthesized magnetite was characterized using X-ray diffraction technology for the identification of the crystal structure of the mineral and (FTIR) was used for the determination of the functional group. Before the FTIR analysis, the samples were prepared by mixing with KBr at a ratio of 1:100(w/w) for Fourier transform infrared spectroscopy and pressed into a film. The specific surface area was measured from the adsorption branch of the isotherm using the Brunauer-Emmett-Teller (BET) method.

Results and Discussion

X-ray diffraction (XRD)

The crystal structure of the magnetite was determined using X-ray diffraction technology (Fig. 1). The XRD peak of synthesized magnetite matched well with the Joint Committee on Powder Diffraction Standards (JCPDS) reference pattern of magnetite (JCPDS N0. 89-4319). Characteristics peak at 2 theta = 35.44 and 62.90 due to reflections from planes of (311) and (440) were observed for magnetite. The very broad peak of the magnetite in the XRD pattern suggests the ultra-fine nature and

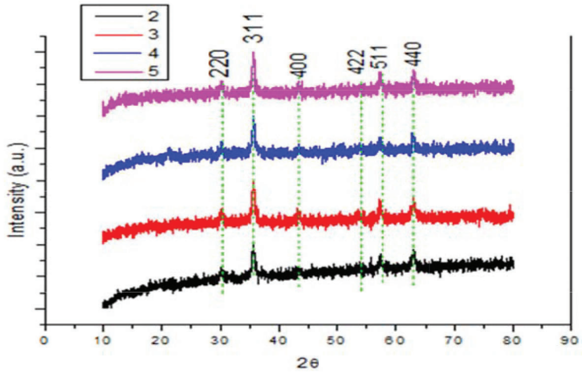


Fig. 1. XRD peak of synthesized magnetite of different molar ratio of Fe^{2+}/ Fe^{3+}. (2)- 1:1, (3)- 1:2, (4)- 2:1 and (5)- 5:1.

Table 1. BET and Barrett-Joyner-Halendra adsorption summary

Fe^{2+} / Fe^{3+}	Fe^{2+}(g)	Fe^{3+}(g)	Correlation coefficient	Surface Area (m^2g^{-1})	Pore Volume (cc g^{-1})	Pore Radius (A^{o})
1:1	1	1	0.99	51.56	0.13	17.01
1:2	0.5	0.66	0.99	93.00	0.19	15.29
2:1	2	1.33	0.99	50.40	0.11	17.03
5:1	5	1.83	0.99	49.76	0.14	17.12

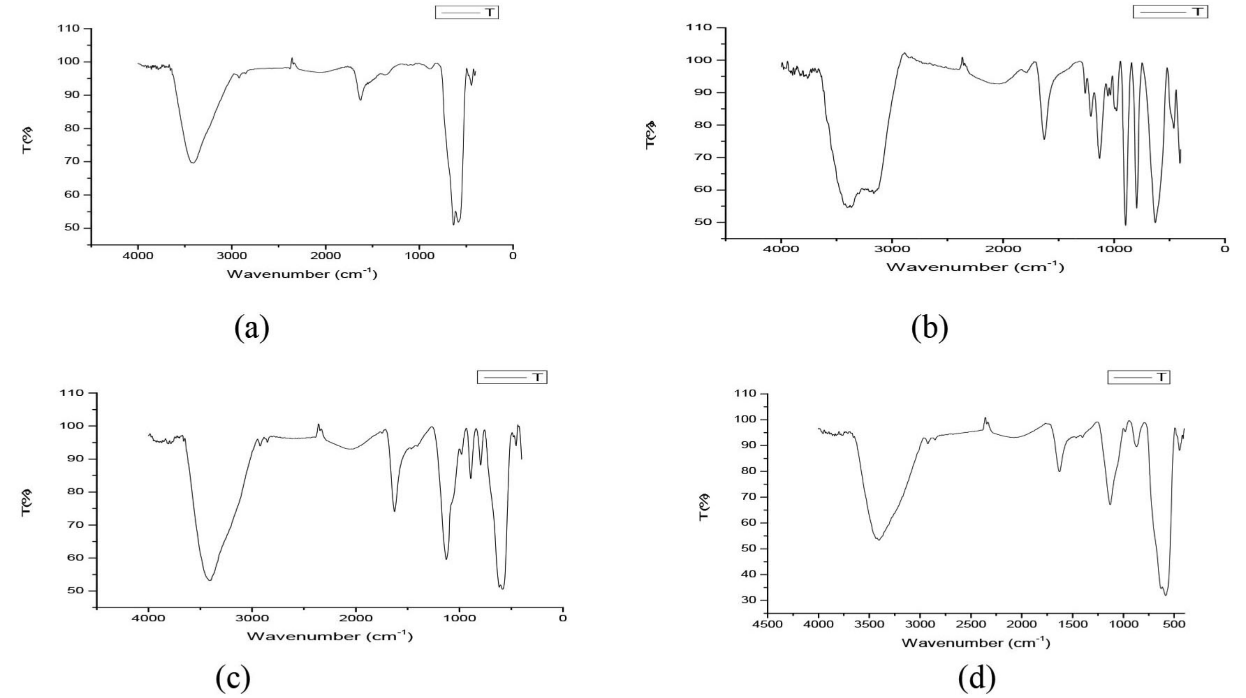
small crystalline structure of the magnetite. Kim *et al.* (2012) found a similar peak for synthesized magnetite. The size of the crystallite is determined using Debye Scherrer's formula, D= kλ / β cosθ, where k = 0.89, λ is the X-ray wavelength of Cu Kα radiation, β is the full width at half maximum (FWHM) of the peaks and θ is the glancing angle and the average crystallite size is 10 nm.

Fourier transform infrared spectroscopy (FTIR)

The functional group of the magnetite was determined using FTIR (MAKE: JASCO, Model 4700) analysis at 4000-400 cm^{-1} wave number and recording the corresponding Transmittance (%). The plot of wave number and percentage transmittance was presented in Fig. 2. The wave number associated with the different functional groupsis revealed by their characteristics peak. The vibration of the Fe-O bond was indicated by a band at 580 cm^{-1}. The vibration of the hydroxyl group on the surface of the magnetite was indicated by characteristics peaks at 1633 and 3400 cm^{-1}. Choi (2016) reported characteristics peak after phosphorus adsorption and observed major peaks at 1632, 1070, 619, and 469 cm^{-1}, which corresponded to the bending vibration of H_2O molecules and the stretching vibration of Fe–OH groups. In addition to this, four new bands appear at 1404, 1530, 2852, and 2923 cm^{-1} which suggest the presence of coating agents that are bonded to the surface of magnetite as esterification occurs between carboxyl and hydroxyl group. The bands at 1404 and 1530 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of the carboxyl group (COO$^-$), respectively (Saranya *et al.,* 2015).

Brunauer-Emmett-Teller Method (BET)

The surface area of the synthesized magnetite was presented in Table 1. A perusal of Table 1 suggests that magnetite synthesized at a molar ratio of 1:2 (Fe^{2+} / Fe^{3+}) has the highest surface area with a value of 93.001 m^{2}g^{-1} followed by magnetite synthesized at a molar ratio of 1:1 (Fe^{2+} / Fe^{3+}). The smallest surface area observed in magnetite synthesized at a molar ratio of 1:1, 2:1, and 5:1 ((Fe^{2+} / Fe^{3+}) could be attributed to a large amount of aggregation during synthesis. Nitrogen adsorption and desorption isotherm and the pore radius and pore volume were also shown in Table 1. Barrett–Joyner–Halenda (BJH) analysis confirmed the contribution of mesopore to the increased surface area of the magnetite. Adsorption isotherm of nitrogen gas suggests that magnetite (1:2) ratio has the highest specific surface area of



(a) (b) (c) (d)

Fig. 2. FTIR analysis showing characteristics peak corresponds to different functional group. (a) 1:1, (b) 1:2, (c) 2:1, (d) 5:1

62.484 m²/g, pore volume of 0.19 cc g^{-1}, and pore radius of 15.293 A°. The surface area of magnetite synthesized at other molar ratios (1:1, 2:1, and 5:1) was lower as compared to 1:2 molar ratio magnetite.

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Conflict of Interest

There is no potential conflict of interest.

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