

Characterization of Magnetite (Fe₃O₄) Nanoparticles: Specific Surface Area, Size Distribution, Structure and Composition, and Surface Charge Density

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Abstract— Characterization of magnetite nanoparticles (MNPs) was carried out to assess the structure, composition, particle size distribution, specific surface area, and surface charge density. The X-ray Diffraction (XRD) analysis confirmed structure of the magnetite nanoparticles and the average particle diameter was found to be 22.9 nm. The specific surface area of the nanoparticles was found by the BET (Brunauer-Emmett-Teller) analysis. Potentiometric titration revealed nanoparticles surface charge density at different pH values, which was an important surface characteristic for assessment in different adsorption techniques. An important finding of the DLS (Dynamic Light Scattering) test was that the hydrodynamic radius (R_h) of the MNPs in aqueous suspension was about eight times the actual diameter of the particle.

Keywords – Magnetite Nanoparticles; XRD (X-ray Diffraction); BET (Brunauer-Emmett-Teller); Potentiometric titration; DLS (Dynamic Light Scattering)

1. Introduction

Nanomaterials (typically 1~100nm in diameter) have been of considerable environmental attention due to their small particle size and large surface area. They exhibit different physical, chemical, and biological properties that may not be predictable from observations on larger-sized materials, such as monodisperse sizing, freedom from surface defects, and special magnetic and optical properties. Nanomaterials are applicable in the areas of reduction of environmental burden, reduction/treatment of industrial and agricultural wastes, and nonpoint source pollution control [1]. Presently, nanomaterials are also used as adsorbents in many environmental remediations such as adsorption techniques in water treatment systems. Among the nanomaterials MNP is one of the most promising adsorbents which can be applicable in environmental remediation. Because of their miniscale size, MNPs cannot be directly used in removal systems. Common options are either to use nanoparticle-water slurry or anchor nanoparticle in a solid matrix [2]. The surface properties of iron oxides are key factors in adsorption technique. Adsorbent particles are widely used in separations in some remediation of developing environmental technologies [3], [4], [5], [6] summarized many of the application and theoretical advantages of using nanoparticles for separations, particularly as applied to biomolecular

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separations. Some of the advantages are directly related to the large and controllable surface areas, but many of the potential advantages are linked to the fundamental nature of a dispersed adsorbent versus a conventional column of fixed packed particles or of a rigid membrane [6]. This dispersed separation avoids many of the classical problems related to plugging and fouling of packed columns and membranes. In a water treatment application, dispersed adsorbents also remove the need for high pressure treatment streams. Moeser [7] showed potential advantages of MNPs in separation of the extremely small size (i.e., ~10 nm) particles and a large surface area without a high mass transfer resistance. Application of nanomaterials could help improve the environment and control pollution, which further progresses environmental science and engineering [8]. Nanomaterials have enhanced structural, magnetic, electrical, and optical properties and could be used to replace existing materials for environmentally friendly applications in future [9]. Their enhanced properties could also potentially reduce the amount of nanomaterials needed. Therefore, specific characteristics of nanomaterials are needed in order to know the behavior of such particles in aqueous system for environmental remediation. This paper represents a detailed characterization of commercially available MNPs including specific surface area (SSA), particle size distribution, structure and composition of MNPs, and measurement of particle surface charge density. The detail of magnetite nanoparticles is listed in Table 1 which is provided by the manufacturer. A TEM (Transmission Electron Microscope) image is also shown in Fig. 1.

Table 1. Details of Commercially Procured Magnetite Nanoparticles

Iron Oxide (Fe ₃ O ₄)	
Purity:	98+ %
Apparent Particle Size (APS) :	20 - 30 nm
Specific Surface Area (SSA):	~ 60 m ² /g
Color:	black
Morphology:	spherical
Bulk density:	0.84 g/cm ³
True density:	4.8-5.1g/cm ³

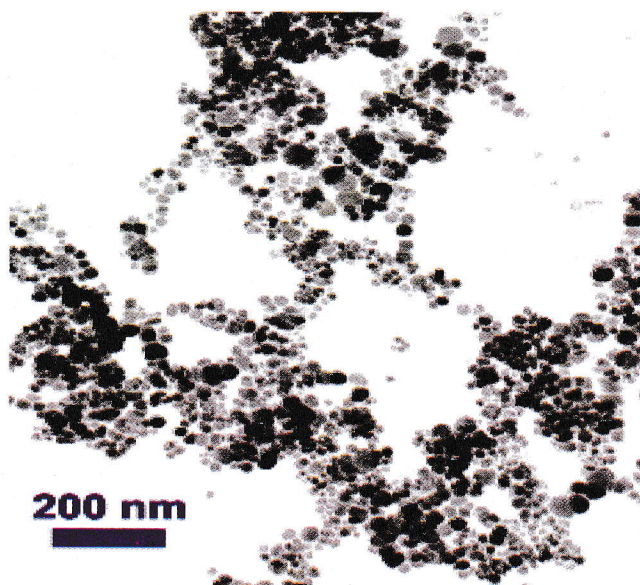


Fig. 1. TEM image of 20-30 nm MNPs

(Source: Nanostructured & Amorphous Materials, Inc.

www.nanoamor.com/products)

2. Materials and Methods

2.1. *Materials*

The commercially manufactured MNP was purchased for characterization from Nanostructured & Amorphous Materials, Inc. 16840, Clay Road, Suite113, Houston, TX 77084, USA.

2.2. *Methodology for Characterization of Magnetite Nanoparticles*

I. *Surface area measurement by BET method*

Physical gas adsorption is applied to study the pore characteristics of solid materials. The isotherm obtained from these adsorption measurements provides information on the Surface Area and Particle Size Distribution (PSD). Different probe gases including N₂, Ar, and CO₂ are frequently used as adsorptives, depending on the nature of the material (adsorbent) and the information required [10]. N₂ adsorption at 77 K (-196 °C) and at sub-atmospheric pressures has remained universally pre-eminent and can be used for routine quality control, as well as for investigation of new materials. If it is applied over a wide range of partial pressures (p/p_0), N₂ adsorption isotherms provide information on size distributions in the micro, meso and macro-porosity range (approximately

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0.5~200 nm). On the other hand, the classical pore size model was developed by Barrett, Joyner and Halenda (BJH) in 1951 which was based on the Kelvin equation and corrected for multilayer adsorption [11].

BET (Brunauer-Emmett-Teller) method is based on physical adsorption of gas molecules on a solid surface. Effective surface area of the iron nanoparticles was estimated using Brunauer-Emmett-Teller (BET) physisorption method [12]. Nitrogen adsorption-desorption isotherms were measured at -196 °C (77K) using a static volumetric instrument Autosorb-1C (Quanta Chrome, Boynton Beach, FL). Prior to the measurement, the samples were out-gassed at 300 °C to a residual pressure of 5×10^{-3} Torr (5 millitorr). The pore size distributions were estimated from the desorption isotherms using the BJH model [11].

II. Dynamic light scattering (DLS) analysis

For DLS Analysis stock solution of the MNP suspension was prepared in de-ionized water. Three test runs were made on magnetite samples. These consist of the following;

- 1) At first the particle size of magnetite was observed in de-ionized water after sonicating for 10 minutes.
- 2) Aggregation of the nanoparticles was observed after adding 10mM NaNO₃ in the solution as background electrolyte to commence aggregation.
- 3) Aggregation of the nanoparticles was observed after adding 10mM NaNO₃ and 50mM MES or HEPES in the solution to commence aggregation.

The aggregation experiments were performed using a multi-angle light scattering unit (ALV-5000, Langen, Germany) equipped with a solid-state Nd:vanadate (Nd:YVO₄) laser (Verdi V2, Coherent, Santa Clara, CA) providing a single-frequency output of 532 nm. Further details of the instrument are described elsewhere [13]. The iron nanoparticle samples were placed in new glass vials (Supelco, Bellefonte, PA) that were previously soaked in a cleaning solution (Extran MA 01, Merck KGaA, Darmstadt, Germany) overnight, thoroughly rinsed in deionized water, and oven-dried under dust-free conditions [14]. Electrolyte solutions, pH adjusting reagents, and biological buffers were added prior to the aggregation experiments following the protocol described by Chen and Elimelech [15], [16].

The dynamic light scattering measurements were conducted by positioning the detector at 90° with the incident laser beam and the autocorrelation function having been allowed to accumulate for over 15 sec. The measurements were performed for a time period ranging from 20 mins to 3 hours to obtain an approximately 30% increase in the original hydrodynamic radius of the iron nanoparticles while these experiments were carried out at room temperature (23°C).

III. X-ray diffraction analysis

X-ray Diffraction (XRD) is an efficient analytical technique used to identify and

characterize unknown crystalline materials. In this research work the XRD analysis of the procured magnetite nanoparticle was performed at the Laboratory of Bangladesh Atomic Energy Commission (BAEC) to analyze the composition of the magnetite nanoparticles. The XRD analysis was conducted with a Philips X'Pert Pro X-ray Diffractometer at 40kV and 30mA. It used copper $K\alpha$ ($CuK\alpha$) radiation and a graphite monochromator to produce X-rays with a wavelength of 1.54060 Å. Magnetite nanoparticles were placed in a 10mm specimen length and scanned from 15° to 70°. This scan range covered all major species of iron and iron oxides. The scanning rate was set at 2.0°/min (Step Size, $2\Theta = 0.02$, Scan Step Time = 0.60 sec).

IV. Potentiometric titration

Potentiometric titrations of MNPs suspensions were carried out in 0.01, 0.05, and 0.1 M $NaNO_3$ as the background electrolytes. The concentration of magnetite nanoparticles was fixed at 0.5 gL^{-1} [17]. Standard (0.05 M) acid (HCl) and base (NaOH) solutions were used for titration. After adding acid or bases, about 5 mins of slow and steady stirring was performed before measuring pH of the solution. The pH and corresponding acid or base additions were recorded.

The experimental protocol for titration consisted of the following steps: (i) First, stock solution of $NaNO_3$ (concentration: 1.0 M) was prepared, (ii) The aqueous solutions were prepared by adding required quantities (1 ml, 5 ml and 10 ml) of $NaNO_3$ stock solution in a 100 ml volumetric flask, (iii) The flask was filled with distilled water up to the 100 ml mark. In this way three different concentrations of background electrolytes (0.01 M, 0.05 M and 0.10 M) were prepared. After preparation of the final solution it was taken into a 150 ml glass beaker, (iv) 0.05 g of MNP was added in the required amount of solution to get a final concentration of 0.5 gL^{-1} of magnetite, (v) At the beginning of each experiment the magnetite nanoparticles were dispersed in solution by sonication using a sonication probe (Sonifier®, Branson Sonic Power Company Danbury, Connecticut, Power Supply, B-12.) for 10 mins, (vi) After sonication the sample pH was measured and an equilibration period was allowed so that the pH value remained fixed for about 1 min, (vii) Then required amount of 0.05 M HCl or 0.05 M NaOH solution was added to the solution using a micropipette and the suspension was stirred with a magnetic stirrer for about 10 minutes, (viii) After that the solution pH was measured again in the same way as mentioned in step (vi), (ix) Step (vii) and (viii) were repeated consecutively until a pH range of 3 to 10 was obtained. For one concentration of background electrolyte, titration by 0.05 M HCl and 0.05 M NaOH were carried out in duplicate.

3. Results and Discussions

3.1. BET surface area and pore size distribution

The BET surface areas for MNPs was found to be 37.7 m^2g^{-1} . This value for MNPs differs from that mentioned by the manufacturer (60 m^2g^{-1}). However, the surface area determined from test result is more acceptable than that reported by

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the manufacturer as surface area was determined by nitrogen gas adsorption to particles which was a direct measure for porous properties. As BET analysis was done with nitrogen adsorption on MNP, it was found that maximum N₂ adsorption occurred when partial pressure was close to unity and the value was about 260 ccg⁻¹ of magnetite (Fig. 2).

Reversible Type-II physisorption isotherm was found in BET analysis where it represented unrestricted monolayer-multilayer adsorption [18]. Point B, the beginning of the almost linear middle section of the isotherm, found at Partial Pressure of 0.56 for magnetite, indicated the stage at which monolayer coverage was completed and multilayer adsorption was about to begin. The internal pore size range of MNPs was about 15-28 Å (angstrom). The internal pore diameter was found by desorbing N₂ gas from particle surfaces with the application of BJH model (Fig. 3).

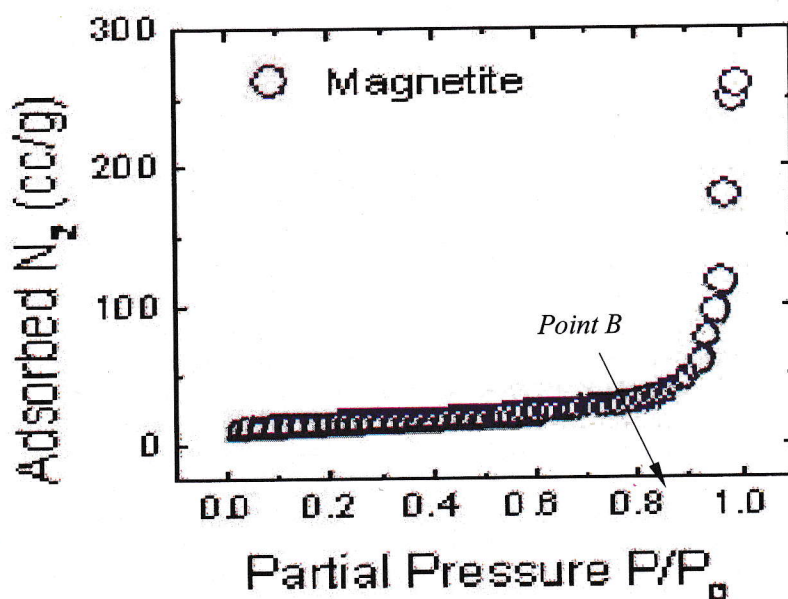


Fig. 2. Adsorption isotherm of N₂ to the MNPs

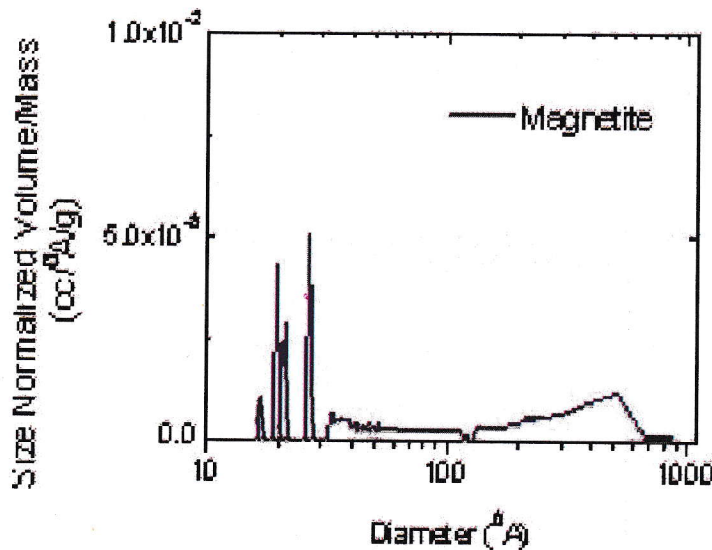


Fig. 3. Pore size distribution of iron nanoparticles generated using BJH model

3.2. Size distribution

The average hydrodynamic radius of MNPs was fairly constant during the entire DLS test (Fig. 4) and was measured as 193.1 ± 5.7 nm. The concentration of the suspensions was 10 mgL^{-1} . But presence of background electrolyte with or without biological buffers, the particle aggregation increased (Fig. 5). This aggregation may be a result of the promotion of double layer compression. The aggregation rate constant (K_{11}) for MNPs shown in Fig. 6 with and without biological buffers was found from Eq. (1) [16], [19]. The rate constant remained almost same for MNPs with and without addition of buffers in NaNO_3 electrolyte. The aggregation rate constants were calculated based on initial aggregation of nanoparticles.

$$\left(\frac{da_h(t)}{dt} \right)_{t \rightarrow 0} \propto k_{11} N_0 \quad (1)$$

where, $a_h(t)$ is the initial rate of increase in the hydrodynamic radius with time t , as measured by DLS; N_0 is the initial (primary) nanoparticles concentration; K_{11} is the initial aggregation rate constant.

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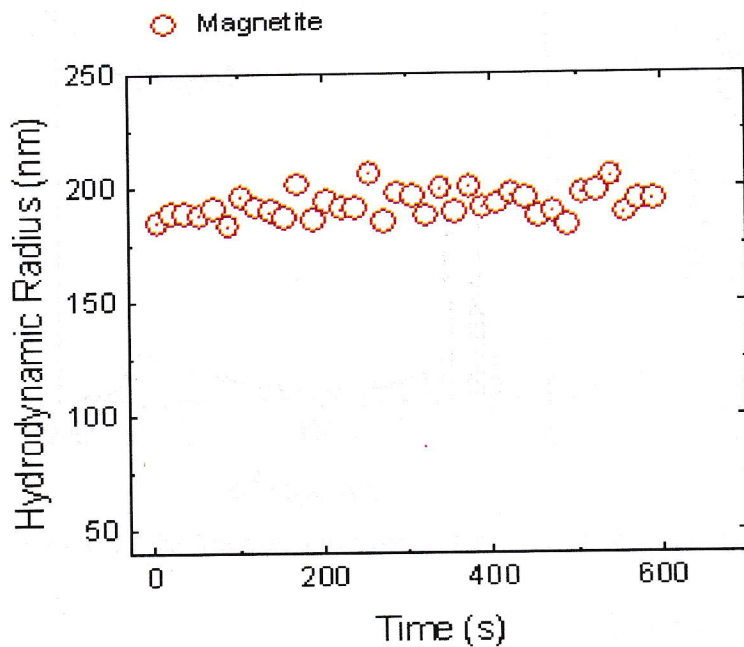


Fig. 4. Hydrodynamic Particle Sizing of MNPs

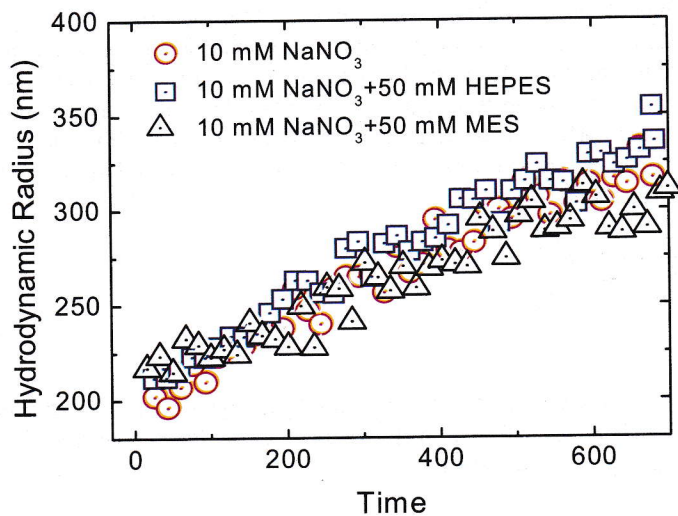


Fig. 5. Aggregation profiles of MNPs with and without the biological buffers

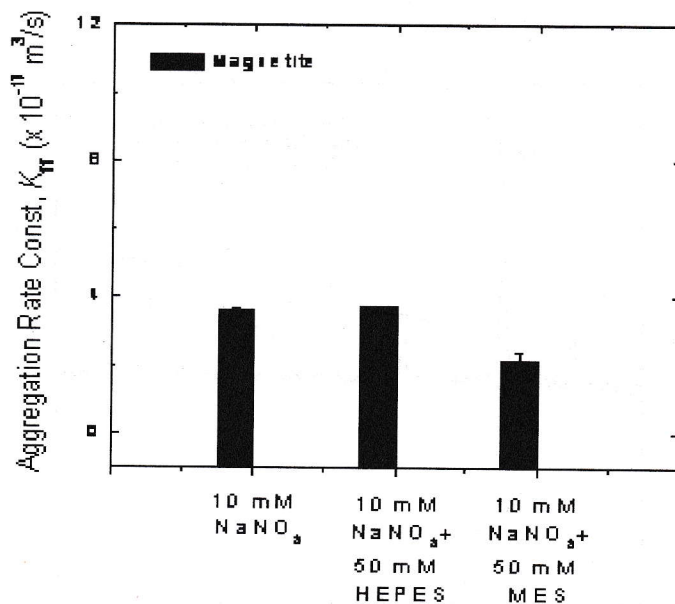


Fig. 6. Aggregation rate constants of MNPs with and without the biological buffers

3.3. Structure and composition of magnetite nanoparticles

XRD measurements were conducted to identify the crystallographic structure of MNPs. Presence of XRD spectrum of magnetite nanoparticles in the Fig. 7 confirmed the magnetite crystal structure [20]. The peak (311) of the figure was observed at $2\theta \approx 36^\circ$ and the mean particle size diameter was estimated to be 22.9 nm. For a spherical particle the specific surface area (SSA) can be calculated by (2).

$$SSA = \frac{\text{Surface Area}}{\text{Mass}} = \frac{\pi d^2}{\rho \frac{\pi}{6} d^3} = \frac{6}{\rho d}$$

where ρ is the density (4800-5100 kg m⁻³ for magnetite) of the solid particle. The theoretical SSA for 22.9 nm particles was therefore 51374-54585 m²kg⁻¹ or 51.374-54.585 m²g⁻¹. However, the data obtained on surface area from the BET analysis (37.7 m²g⁻¹) should be taken to be more precise, as in case of BET analysis the shape of the particle was not considered and surface area was determined on the basis of N₂ adsorption on the surface of magnetite nanoparticles. The BET surface area of magnetite was 37.7 m²g⁻¹. The nominal particle size was calculated to be 31.2 – 33.1 nm from BET surface area measurement.

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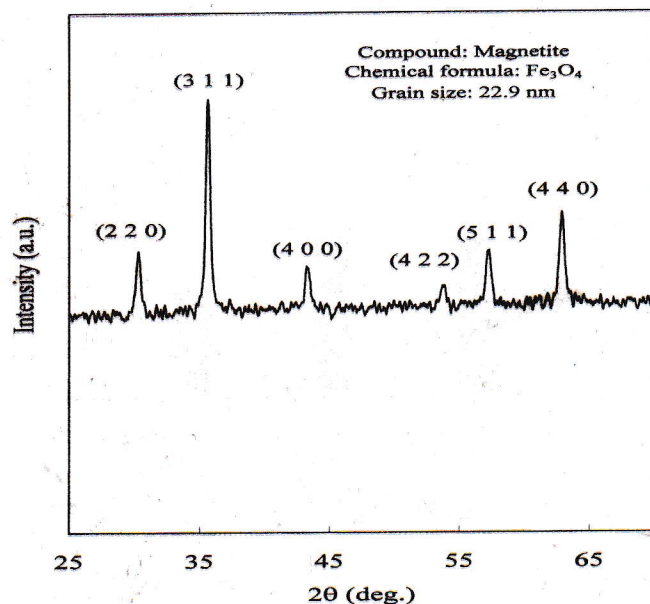


Fig. 7. Plot of X-ray diffraction (XRD) pattern of Magnetite Nanoparticles

3.4. Surface charge density

The pH versus surface charge (σ) for 0.5 gL⁻¹ magnetite suspension was plotted in Fig. 8. The surface charge was calculated as a function of pH from potentiometric titration data according to (3) [21].

$$\sigma(C m^{-2}) = F(C_A - C_B + [OH^-] - [H^+])a^{-1}S^{-1} \quad (3)$$

where F is the Faraday constant (96,485 Cmol⁻¹), C_A and C_B are the total concentrations of acid and base added, respectively (molL⁻¹), $[H^+]$ is the proton concentration (molL⁻¹) given by $10^{-pH}/\gamma_{H^+}$, $[OH^-]$ is the OH⁻ concentration (molL⁻¹) given by $10^{-(pK_w - pH)}/\gamma_{OH^-}$, a is magnetite concentration (gL⁻¹), and S is the specific surface area (m²g⁻¹). The titration curves (Fig. 8) were normalized to unit surface area. The point of zero surface charge (pH_{pzc}) is defined as the pH value at which $\sigma=0$. The magnetite samples for all the three ionic suspensions (0.01, 0.05, and 0.10 M of NaNO₃) in this study had the same pzc (pH of zero particle surface charge) values of pH 7.0. The result of pzc obtained in this research was close to those from the literatures which was 6.6 (experimentally determined) [22], [23]. Fig. 9 is the potentiometric titration curve for total acid base addition in magnetite suspension at three different ionic strengths.

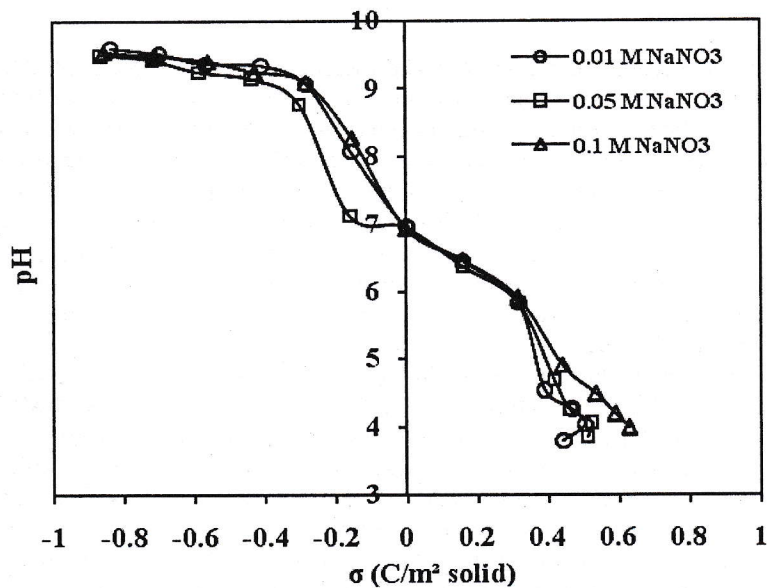


Fig. 8. Potentiometric titration curves for surface charge (pH versus σ , C/m^2 solid)

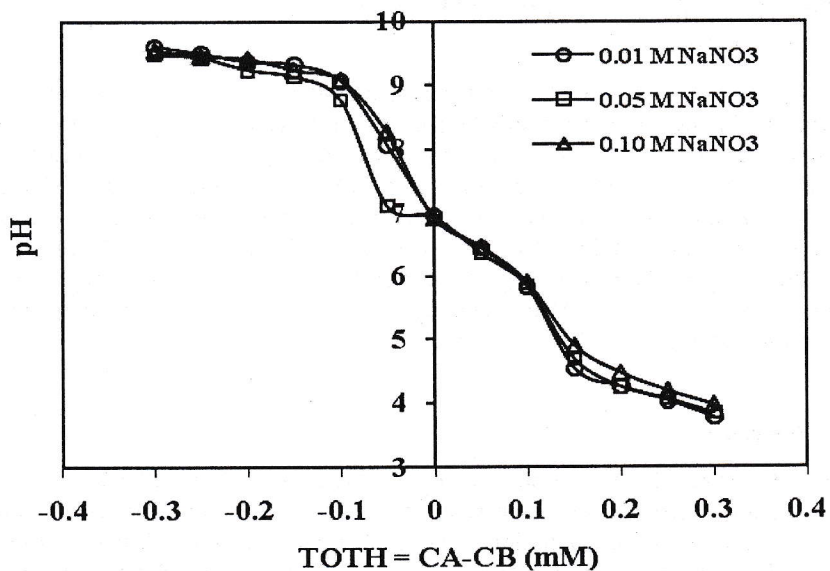


Fig. 9. Potentiometric titration curves for total acid-base (pH versus TOH, mM)

4. Conclusion

There were specific determinations for characterization of MNPs such as specific surface area determination, structure, composition and size distribution of

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MNPs, surface charge characteristics. The specific surface area (SSA) of MNPs found by BET adsorption isotherm method was 37.7 m²g⁻¹. This value for MNPs differs from that reported by the manufacturer (60 m²/g). The adsorption isotherm found by BET method holds the shape of Type-II, where it represents unrestricted monolayer-multilayer adsorption [18]. The pore size distribution was determined by BJH model [11]. The internal pore size distribution for MNPs ranges from 15-28 °Å. The structure and composition of MNPs was assessed by X-ray diffraction analysis. This method gave the approximate mean diameter of magnetite nanoparticles which was 22.9 nm. With this size of particle the calculated specific surface area (SSA) was found around 51.4 to 54.6 m²g⁻¹. The characteristic of hydrodynamic radius (R_h) for MNPs was conducted by Dynamic Light Scattering (DLS) analysis. The hydrodynamic radius of MNPs was found to be 193.1±5.7 nm in aqueous suspension. The hydrodynamic radius of MNPs increased in presence of background electrolyte (NaNO₃) with or without biological buffers and the radius increased almost 1.8 times of its initial hydrodynamic radius. The surface charge characteristic of magnetite nanoparticles was a major finding for equilibrating different experimental adsorption data in adsorption techniques. Potentiometric titration was conducted for this determination. The pH of zero surface charge (pH_{pzc}) for MNPs was found to be 7.0 in this study. Therefore, the surface of MNPs remains positively charged below pH 7.0 and negatively charged at pH above 7.0.

5. Acknowledgement

This research work was funded jointly by Committee for Advanced Studies and Research (CASR) of Bangladesh University of Engineering and Technology (BUET) and MIT-BUET joint research project, and supported by Directorate of Advisory, Extension and Research Services (DAERS), Board of Post-Graduate Studies (BPGS) of (BUET). Special acknowledgements to Dr. Navid Bin Saleh (currently an Assistant Professor at University of South Carolina, USA), Dr. Manjura Hoque (Atomic Energy Commission, Dhaka), and Dr. A. B. M. Badruzzaman (Professor, BUET, Dhaka) for providing valuable guidance and support in performing this research work.

6. References

- [1] G Shan, R Y Surampalli, R D Tyagi and T C Zhang (2009), Nanomaterials for environmental burden reduction, waste treatment, and nonpoint source pollution control: A review. Feature Article, *Front. Environ. Sci. Engin.*, Higher Education Press and Springer-Verlag, China.
- [2] P Sylvester, P Westerhoff, T Möller, M Badruzzaman and O Boyd (2007), A Hybrid Sorbent Utilizing Nanoparticles of Hydrous Iron Oxide for Arsenic Removal from Drinking Water, *Environ. Engi. Sci.*, 24, pp. 1.

- [3] Z Bilkova et al. (2002), Oriented immobilization of galactose oxidase to bead and magnetic bead cellulose and poly(HEMA-co-EDMA) an magnetic poly(HEMA-co-EDMA)microspheres, *J. Chromatogr. B. Analyt. Technol. Biomed. Life Sci.*, 770 (1–2), pp. 25.
- [4] Z Bilkova, M Slovakova, D Horak, J Lenfeld and J Churacek (2002), Enzymes immobilized on magnetic carriers: Efficient and selective system for protein modification, *J. Chromatogr. B. Analyt. Technol. Biomed. Life Sci.*, 770, pp. 177.
- [5] W Sun, F Khosravi, H Albrechtsen, L Y Brovko and M W Griffiths (2002), Comparison of ATP and in vivo bioluminescence for assessing the efficiency of immunomagnetic sorbents for live Escherichia coli O157: H7 cells, *J. Appl. Microbiol.*, 92, pp. 1021.
- [6] S Bucak, D A Jones, P E Laibinis and T A Hatton (2003), Protein separations using colloidal magnetic nanoparticles, *Biotechnol. Prog.*, 19, pp. 477.
- [7] G D Moeser, K A Roach, W H Green, P E Laibinis and T A Hatton (2002), Water-based magnetic fluids as extractants for synthetic organic compounds, *Ind. Eng. Chem. Res.*, 41, pp. 4739.
- [8] G E Fryxell and G Z Cao (2007), Environmental Applications of nanomaterials: Synthesis, Sorbents and Sensors – Hackensack, *World Sci. Pub. Co. Inc.*
- [9] T Masciangioli and W X Zhang (2003), Environmental technologies at the nanoscale, *Environ Sci. & Technol.*, 37, pp. 102A – 108A.
- [10] J C Groen, L A A Peffer and J Perez-Ramirez (2003), Pore size determination in modified micro- and mesoporous materials. Pitfalls and limitations in gas adsorption data analysis, *Microporous and Mesoporous Materials*, 60, pp. 1–17.
- [11] E P Barrett, L G Joyner and P P Halenda (1951), The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms, *J. Am. Chem. Soc.*, 73, pp. 373 – 380.
- [12] S Brunauer, P H Emmett and E Teller (1938), Adsorption of Gases in Multimolecular Layers, *J. Am. Chem. Soc.*, 60, pp. 309 – 319.
- [13] K L Chen and M Elimelech (2007), Influence of humic acid on the aggregation kinetics of fullerene (C-60) nanoparticles in monovalent and divalent electrolyte solutions, *J. Colloid Interf. Sci.*, 309, pp. 126 – 134.
- [14] N B Saleh, L D Pfefferle and M Elimelech (2008), Aggregation Kinetics of Multiwalled Carbon Nanotubes in Aquatic Systems: Measurements and Environmental Implications, *Environ. Sci. Technol.* 42, pp. 7963 – 7969.

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- [15] K L Chen and M Elimelech (2006), Aggregation and deposition kinetics of fullerene (C-60) nanoparticles, *Langmuir*, 22, pp. 10994 – 11001.
- [16]. K L Chen, S. E. Mylon and M Elimelech (2006), Aggregation kinetics of alginate-coated hematite nanoparticles in monovalent and divalent electrolytes, *Environ. Sci. Technol.*, 40, pp. 1516 – 1523.
- [17] S Yean et al (2005), Effect of magnetite particle size on adsorption and desorption of arsenite and arsenate, *J. Mater. Res.*, 20, pp. 12.
- [18] K. S. W. Sing et al. (1985), Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity, *Pure & Appl. Chem.*, 57(4), pp. 603—619.
- [19] S E Mylon, K L Chen and M Elimelech (2004), Influence of Natural Organic Matter and Ionic Composition on the Kinetics and Structure of Hematite Colloid Aggregation: Implications to Iron Depletion in Estuaries, *Langmuir*, 20, pp. 9000–9006.
- [20] W W Yu, J C Falkner, C T Yavuz and V L Colvin (2004), Synthesis of monodisperse iron oxide nanocrystals by thermal decomposition of iron carboxylate salts, *Chem. Comm.*, 20, pp. 2306.
- [21] W Stumm and J J Morgan (1995), *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, Wiley – Interscience, New York.
- [22] P H Tewari and A W McClean (1972), Temperature dependence of point of zero charge of alumina and magnetite, *J. Colloid Interface Sci.*, 40, pp. 267.
- [23] N Marmier, A Delisee and F Fromage (1999), Surface complexation modeling of Yb(III), Ni(II), and Cs(I) sorption on magnetite, *J. Colloid Interface Sci.*, 211, pp. 54.