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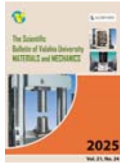

A STUDY ON STABILITY OF MAGNETITE NANOPARTICLES SUSPENSION IN WATER BY ZETA POTENTIAL MEASUREMENTS

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Abstract: *The paper presents an experimental research on the stability of an aqueous suspension containing 35% magnetite nanoparticles (MNPs) using the zeta potential measurement method. The main objective of this study is to determine the variation of zeta potential as function of the suspension's alkalinity. By charging the surfaces of magnetite nanoparticles with negative hydroxyl groups, they produce electrostatic repulsion between magnetite nanoparticles and prevent short- and medium-term magnetic agglomeration and sedimentation. Alkalinising together with ultrasonication treatment are effective methods for stabilising magnetite nanoparticles suspensions used as ferrofluids.*

Keywords: *magnetite, zeta potential, ferrofluid, sedimentation, alkaline pH.*

1. INTRODUCTION

Nanoparticles are generally up to 100 nanometers in average size and display different characteristics than bulk materials because they have a large surface area relative to their volume. Having an understanding of this particularity makes it easier to anticipate how nanoparticles will act. Due to their special properties and adaptability, as well as relatively high chemical stability, magnetite (Fe_3O_4) nanoparticles (MNPs), are used in biomedicine [1-5], high level applications in materials science [6, 7], and environmental protection [8, 9], particularly in their superparamagnetic form.

When the magnetite nanoparticles (MNPs) are used in ferrofluids, the main issue is the aggregation and sedimentation of the nanoparticles, which affects the quality and lifespan of these ferrofluids. Among the effective measures to prevent aggregation and sedimentation are stabilization of MNPs through surfactant coating, ultrasonication, and pH control.

The process of determining the zeta potential relies on observing how electric charged nanoparticles migrate within an electric field, a phenomenon referred to as electrophoresis. An electric field is generated in a chamber filled with a nanoparticle suspension, causing these charged nanoparticles to move towards the oppositely charged electrode, and this is known as the laser Doppler micro-electrophoresis technique. As the nanoparticles are in motion, they are irradiated by a laser beam, and the rays reflected from them undergo a frequency shift; this shift is directly correlated with the speed of the nanoparticles, illustrating the Doppler effect. To calculate the electrophoretic mobility, the measured nanoparticle speed and the applied electric field intensity are used. Subsequently, the zeta potential is determined from this mobility using pre-established models, taking into account the properties of the solvent, such as viscosity.

The zeta potential of nanoparticles depends to the pH level of the suspension in which they are present, impacting the ionisation of their surface. The addition of alkali to suspension lead to the nanoparticles surface acquiring a negative charge because hydroxyl groups bind to them but introducing an acid to a suspension can give the nanoparticles surface a positive charge as protons attach. Additionally, there is a specific pH level where the zeta potential equals zero, and it is referred to as the isoelectric point. At this pH, the nanoparticles exhibit a maximum tendency to aggregate due to the minimum value of repulsive forces between them.

The value of the zeta potential is significantly affected by the ionic strength of the solution, which measures the concentration of salts in the solution. As ionic strength increases, the electric double layer becomes more compact, the surface charge is screened, and the zeta potential decreases. The total surface charge and zeta potential of nanoparticles can be considerably altered by molecules that adhere to their surface. Depending on their charge and interaction with the nanoparticles surface, these molecules could either increase or decrease the zeta potential.

For various applications dealing with nanoparticle suspensions, it is essential to understand and manipulate zeta potential effectively. The zeta potential plays an important role in drug delivery methods, influencing how well nanoparticles remain stable in biological environments and how they electrostatically interact with cell membranes [10, 11]. It is possible to design nanoparticles with a positive zeta potential to interact through electrostatic forces with tumor cell membranes carrying negative charges, resulting in greater accumulation of targeted drugs and enhanced treatment efficiency [10, 11]. On the other hand, changing the zeta potential by modifying the surface of nanoparticles might assist them in avoiding recognition by the immune system, potentially resulting in extended circulation times within the blood and enhanced absorption by the organism [10].

Beyond the biomedical domain, the zeta potential is also a key parameter in ensuring the stability of colloidal systems across the cosmetic and food industries. Maintaining a sufficiently high absolute zeta potential prevents particle aggregation and phase separation, ensuring product uniformity and extended shelf life [12, 13]. Furthermore, in environmental remediation, zeta potential plays a critical role in optimizing adsorption and separation processes, as modulation of surface charge can significantly enhance the efficiency of pollutant removal and water purification using oxide-based nanomaterials [12, 13].

2. MATERIALS AND METHODS

For the study of the influence of pH on the Zeta potential of MNPs suspensions in water, the following experimental plan was followed: magnetite was obtained through chemical coprecipitation; the obtained MNPs were visualised using a TEM microscope, after which five MNPs suspensions in water were prepared, stabilised by ultrasonication and alkaline pH: MNP1 (pH = 8), MNP2 (pH = 9), MNP3 (pH = 10), MNP4 (pH = 11) and MNP5 (pH = 12). These suspensions were subjected to Zeta potential analysis.

2.1. Materials

Ultrapure magnetite nanoparticles (MNPs) were produced through a chemical coprecipitation process, identified as reaction 1, utilizing sodium hydroxide (from Merck) acting like precipitate agent; the process involved iron chlorides solutions comprising iron (III) chloride acquired from Sigma-Aldrich, alongside iron (II) chloride-tetrahydrate from Merck, all conducted at a temperature of 70 ºC in argon protective atmosphere.

$FeCl_2 + 2FeCl_3 + 8NaOH \rightarrow Fe_3O_4\downarrow + 8NaCl + 4H_2O$ (1)

Following the chemical coprecipitation reaction 1, the resulting material underwent separation via a magnetic decantation technique, followed by repeated washes with distilled water and a subsequent filtration step. To prevent the aggregation of MNP, the obtained suspension was stabilised by ultrasonic treatment under an argon atmosphere at 60°C for an additional 2 hours. In this experimental research, MNPs stabilization by coating with surfactant agents was not used. The entire preparation process was completed by slow drying at room temperature in a desiccator.

For the TEM imaging and study of the colloidal stability of a water-based MNPs ferrofluid, an aqueous suspension with 35% MNPs was prepared by mixing and stabilised through ultrasonication. Experimental research on the properties and magnetically guided flow behaviour through a micro-channel of this ferrofluid (35% MNPs) has already been reported [14].

2.2. Methods

To observe the shapes and sizes of the MNPs, images were captured using transmission electron microscopy (TEM) with a Tecnai™ G2 F20 TWIN Cryo-TEM Field Electron (FEI Company, Eindhoven, Netherlands) operating at an accelerating voltage of 200 kV. For TEM imaging, the sample consists of dropping a small volume of 35% MNP ferrofluid onto carbon-coated Tedpella copper grids.

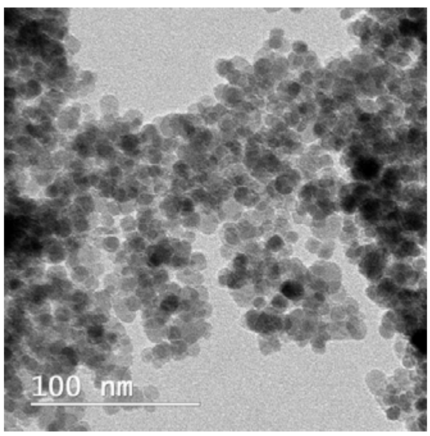
The zeta potentials of MNP samples stabilised in aqueous suspension at varying pH levels within the alkaline range were determined using the Amerigo ZetaView electrophoretic analyser (Cordouan Technologies, Pessac, France). These measurements are based on assessing the mobility of MNPs under an applied electric field. The MNPs samples were investigated in aqueous suspension at a temperature of 25ºC with an applied voltage of 30V. The motion of magnetite nanoparticles was tracked using dedicated software at eleven different points inside the measurement channel, thereby generating the Zeta potential distribution as a function of signal intensity.

The reported values are the average of three independent measurements for each sample. The experimental conditions (conductivity, pH levels, and sample volume) were carefully managed through the application of AmeriQ software to guarantee precision in the data acquired.

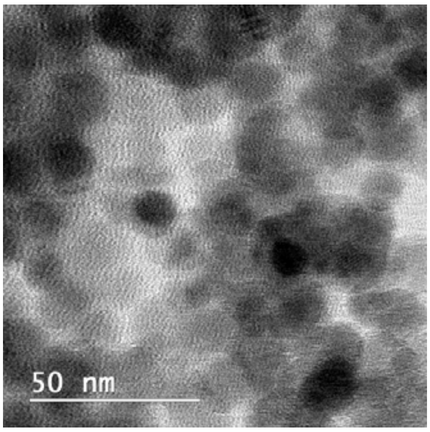
3. RESULTS AND DISCUSSIONS

3.1. TEM imaging

The TEM images of the magnetite sample shown in Figure 1 indicate a tendency of the magnetic nanoparticles to aggregate, forming clusters with sizes of approximately 200 nm.



1a.



1b.

Figure 1. TEM images of MNP sample: (a) image 80000X, (b) image 240000X

The magnetite nanoparticles exhibit a nearly consistent spherical morphology, as shown in Figures 1.a and b, and their size distribution is confined within a narrow range around 10 nm [14].

3.2. Zeta Potential in Measuring the Stability of MNPs in Ferrofluids

To evaluate the colloidal stability of ferrofluids containing 35% MNPs at different pH values in the alkaline range, 5 samples were prepared at different pH values: MNP1 (pH = 8), MNP2 (pH = 9), MNP3 (pH = 10), MNP4 (pH = 11), and MNP5 (pH = 12).

The zeta potential distribution was determined for each liquid sample based on signal intensity. The results show Gaussian-type distribution curves (Figure 2), characterized by maximum zeta potential values that decrease as the pH values increase (Figure 3).

Zeta potential is a measure of the electric charge on the surface of MNPs in aqueous suspension. This charge results from the interaction between the MNPs surface and surrounding negative ions. When a magnetite nanoparticle with a charged surface is suspended in a liquid, it attracts a layer of oppositely charged ions, resulting in what is known as an 'electric double layer'. This layer has the following structure: the inner layer, which is firmly attached, is called the Stern layer, while the outer layer, which is more loosely attached, is termed the diffuse layer.

The magnitude of the zeta potential directly indicates the electrostatic repulsion or attraction between magnetite nanoparticles. Since these MNPs are surrounded by negative hydroxyl groups, repulsive forces have arisen between them, which more or less prevent the aggregation of MNPs.

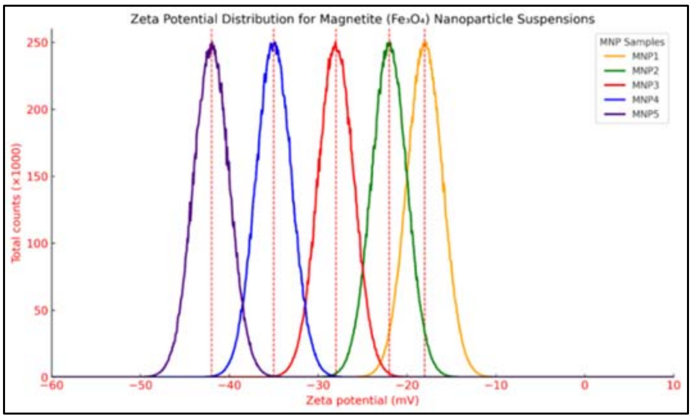


Figure 2. Zeta potential distribution for MNPs suspensions

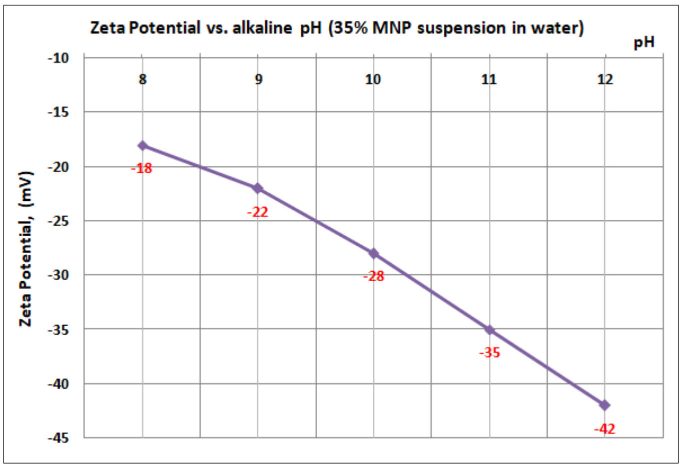


Figure 3. Zeta potential vs. alkaline pH

The high values of the zeta potential (varying from -28 to -42 mV in the MNP3, 4, 5 samples) suggest strong repulsive forces, preventing the aggregation of magnetite nanoparticles and ensuring colloidal stability.

The maximum zeta potential value of the sample MNP3 (pH = 10) is close to the ±30 mV threshold (Figure 2), which is commonly cited in the literature as a marker of electrostatic stability in nanoparticles aqueous suspensions [15]. In contrast, lower zeta potential values of -18 mV (MNP1) and -22 mV (MNP2) indicates medium to minimal repulsive forces, which can lead to relatively rapid aggregation or after a short usage time, and to suspension instability.

4. CONCLUSIONS

The measured values indicate that the ferrofluid samples possess negative zeta potentials, suggesting that the surfaces of the magnetite nanoparticles carry negative charges due to the hydroxyl groups present as a result of alkaline pH levels. These negative surface charges cause electrostatic repulsion between the MNPs, contributing to the colloidal stability and potentially preventing aggregation. The stability of the ferrofluid can be assessed by increasing its alkalinity, even in the absence of surfactants, and can be monitored by measuring the zeta potential of the MNPs.

In summary, the magnetite nanoparticles present in the analysed ferrofluid exhibit short-term stability, as they are prevented from aggregating by the electrostatic forces that keep them separated in an alkaline pH environment.

Abbreviations

The following abbreviations are used in this manuscript:
MNP - Magnetite nanoparticles;
TEM - Transmission electron microscopy.

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