

# Influence of modifiers on point of zero charge ( $\text{pH}_{\text{PZC}}$ ) of PMMA modified and PMMA-PEG modified $\text{MnFe}_2\text{O}_4$ nanoparticles

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**Abstract-** pH is a very important parameter because pH influences chemical speciation of the metals in solutions and also on the ionization of chemically active sites on the adsorbent surface. In this paper, influence of modifiers on point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of PMMA and PMMA-PEG modified  $\text{MnFe}_2\text{O}_4$  nanoparticles were investigated. The  $\text{pH}_{\text{pzc}}$  was determined by using 0.010 g of the nanoadsorbent and 50 ml of 0.01N solution of NaCl. For initial pH ( $\text{pH}_i$ ), in the range was between 2 to 8. The obtained values for  $\text{pH}_{\text{pzc}}$  were 6 for PMMA modified  $\text{MnFe}_2\text{O}_4$  NPs and 7 for PMMA-PEG modified  $\text{MnFe}_2\text{O}_4$  NPs. It was concluded that PMMA and PMMA-PEG modified  $\text{MnFe}_2\text{O}_4$  NPs could be efficiently employed in the adsorption of cations above pH 6 and 7 and could be potentially effective in the adsorption of anions below pH 6 and 7 respectively.

**Keywords:** Manganese ferrite, PMMA, PEG, modification, point of zero charge

## I. INTRODUCTION

Toxic metals are being discharged into the environment predominantly as industrial wastes and constitute a major problem to human health, living resources and ecological systems. The treatment methods for heavy metals' removal are essential due to their toxicity and tendency to accumulate in living organisms [1]. Among numerous methods for water treatment, sorption technologies such as adsorption and ion exchange have gained the most attention because of low cost and easy operation [2]. There are many factors that influence the removal efficiency of heavy metals such as: temperature, heavy metals or adsorbent concentrations, pH, etc. Among the mentioned factors, pH is the most important factor in the process of adsorption is because it influences chemical speciation of the metals in solutions and also on the ionization of chemically active sites on the adsorbent surface [3].

The pH dependent surfaces and surface charge changing of the aqueous metal oxide dispersions is an significantly important area of research, therefore, determination of their point of zero charge ( $\text{pH}_{\text{pzc}}$ ) becomes salient [4]. Point of zero charge is used to define the state of the surface of a dispersed solid phase at a solid-electrolyte solution interface. The  $\text{pH}_{\text{pzc}}$  of the surface of an adsorbent is important because it indicates the acidity/basicity of the adsorbent and the net surface charge of nanoadsorbent or nanoparticle (NPs) in solution, respectively. When adsorbents are suspended in an aqueous electrolytic solution; due to the dissociation of the surface hydroxyl groups and the complexation of the electrolyte ions, a surface electrical charge is generated. Point of zero charge is the pH where the charge on the surface of an adsorbent is zero. Alternatively it can also be defined as the pH value where negative ( $[\text{MO}^-]$ ) and positive ( $[\text{MOH}^+]$ ) surface concentrations are equal, i.e., surface charge,  $\sigma_0 = 0$ . The charge on the surface is negative at  $\text{pH} > \text{pH}_{\text{pzc}}$  and positive at  $\text{pH} < \text{pH}_{\text{pzc}}$ . The isoelectric point is the pH at which the zeta potential of a molecule or surface is equal to zero,  $= 0$  [5-7].

The hydrogen ( $\text{H}^+$ ) and the hydroxide ( $\text{OH}^-$ ) ions in solution are considered to be the potential determining ions [8]. Thus, depending on the pH of the solution and concentration of the electrolyte, these surfaces tend to behave as cation exchangers having net negative charge, or anion exchangers bearing positive charge or neutral species having no charge at all [9,10].

In addition, several workers reported, point of zero charge as a tool for the determination of chemical properties of soil samples and mineral oxides or hydroxides by applying geochemistry principles [11-16]. Despite the importance of charge properties to sorption of ionic and neutral solutes for the above-mentioned materials,  $\text{pH}_{\text{pzc}}$  have not been investigated for a number of other adsorbents in detail. The present paper is an attempt to describe the properties of two potential adsorbents based on the concept of surface charge balance. A

rigorous apprehension of the point of zero charge enables researchers to select adsorbents for their specific applications.

In the present study we took into consideration two polymer modified nanoparticles as potential nanoadsorbents, the synthesis and characterization of which had already been carried out by the authors previously. This work is in continuation of the previous work. The already synthesized PMMA modified  $\text{MnFe}_2\text{O}_4$  NPs and PMMA-PEG modified  $\text{MnFe}_2\text{O}_4$  NPs were studied and their  $\text{pH}_{\text{pzc}}$  was determined in order to exploit them as potential nanoadsorbents in future research. Nanoparticles as potential adsorbents were selected owing to their fascinating properties such as: small size, high surface to volume ratio consequently resulting in large number of active sites. Furthermore, nanoparticles due to their highly reactive surface cause two major setbacks: the first being formation of an oxide layer on its surface and the second being the agglomeration with other particles. In order to overcome these shortcomings it is necessary to coat them with a modifier. For this purpose a number of modifiers are being used such as: polymers, surfactants, ligands, organic molecules, etc. However, in the present study two polymers polymethyl(methacrylate) (PMMA) and polyethylene glycol (PEG) were used.

## II. EXPERIMENTAL

Analytical-grade reagents were used without further purification. Deionized water was used throughout the work. NaCl, NaOH, HCl.

To a series of eight 250 ml Erlenmeyer flasks, 50 ml of 0.001N NaCl was initially taken. Then the initial pH was adjusted between the range 2 and 9 with intervals of one, using 0.01N HCl and 0.01NaOH. Once a constant value of  $\text{pH}_{\text{initial}}$  was obtained, 0.010 g of the PMMA modified  $\text{MnFe}_2\text{O}_4$  NPs was added to the flask and capped immediately. The solutions were stirred for 24 hours to reach equilibrium. After 24 hours the pH of the solution was measured and was marked as  $\text{pH}_{\text{final}}$ . The  $\text{pH}_{\text{pzc}}$  of PMMA modified  $\text{MnFe}_2\text{O}_4$  NPs is the point when  $\text{pH}_{\text{initial}} = \text{pH}_{\text{final}}$ . This method was followed in accordance with the work reported by Vergis and co-workers using a slight modification [17]. Similar procedure was adopted and followed for PMMA-PEG modified  $\text{MnFe}_2\text{O}_4$  NPs.

## III. RESULTS

To determine the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of PMMA and PMMA-PEG modified  $\text{MnFe}_2\text{O}_4$  NPs drift method was followed [18]. In the plot between  $\Delta \text{pH}$  and  $\text{pH}_{\text{initial}}$ , the  $\text{pH}_{\text{pzc}}$  is the point of intersection where the curve of  $\text{pH}_{\text{final}}$  vs  $\text{pH}_{\text{initial}}$  intersects the line i.e.  $\text{pH}_{\text{initial}} = \text{pH}_{\text{final}}$ . The  $\text{pH}_{\text{pzc}}$  for the chosen adsorbents are given in Table 1 and 2. At the  $\text{pH}_{\text{pzc}}$  there is no surface charge to be neutralized by ions in the diffuse swarm, and any adsorbed ions that exist must be bound in surface complexes. The  $\text{pH}_{\text{pzc}}$  of both the adsorbents studied is equal to or below 7, showing the existence of perfect charge balance in the acidic region among the equilibrated ions in an aqueous solution. The results implied that more charges developed on the surface, and the adsorption of protons increased at low pH, whereas desorption of protons occurred at high pH [19,20].

As depicted in Fig. 1, the  $\text{pH}_{\text{pzc}} = 6$  for PMMA modified  $\text{MnFe}_2\text{O}_4$  NPs. This implies that below pH 6, the charge on the surface of the adsorbent is positive therefore, anions can be adsorbed readily. On the contrary, above the  $\text{pH}_{\text{pzc}}$  value, the charge on the surface of the adsorbent would be negative, therefore aiding the adsorption of cationic species.

As illustrated in Fig 2, the  $\text{pH}_{\text{pzc}}$  for PMMA-PEG modified  $\text{MnFe}_2\text{O}_4$  NPs was found to 7.0 suggesting that at pH 7 the net charge on the surface of the adsorbent is zero and at pH values below  $\text{pH}_{\text{pzc}}$ , adsorbent surface charge is positive. So, at pH below 7.0, the electrostatic interaction is increased between the anions and the positively charged surface of the adsorbent. However, at alkaline pH, adsorption of anions by PMMA-PEG  $\text{MnFe}_2\text{O}_4$  NPs is decreased, because an electrostatic repulsion comes into play between the negatively charged surface adsorbent and anions [21-22].

The  $\text{pH}_{\text{pzc}}$  for PMMA and PMMA-PEG modified  $\text{MnFe}_2\text{O}_4$  NPs were found to be 6 and 7 respectively. It is very well perceived from the literature that the  $\text{pH}_{\text{pzc}}$  of bare  $\text{MnFe}_2\text{O}_4$  was 6.8 and therefore, after surface modification of  $\text{MnFe}_2\text{O}_4$  with PMMA and PEG, the  $\text{pH}_{\text{pzc}}$  was observed. This further indicated that after encapsulation with PMMA, the buffering capacity of the adsorbent decreased whereas in case of PMMA and PEG modified  $\text{MnFe}_2\text{O}_4$  NPs, it increased [20].

This exhorts a good possibility of using the polymer (PMMA) and combination of polymers (PMMA-PEG) modified nanoparticles as nanoadsorbents for the removal of various cations and anions, heavy metal as well as cationic and anionic dyes. Thus the study on the importance of  $pH_{pzc}$  finds a wide application in the field of remediation of environmental contaminants.

Table 1:  $pH_{initial}$  and  $pH_{final}$  values for PMMA modified NPs

	$pH_{initial}$	$pH_{final}$
1.	2	2.3
2.	3	3.7
3.	4	5.3
4.	5	5.9
5.	6	6
6.	7	7.8
7.	8	7.9
8.	9	8.1

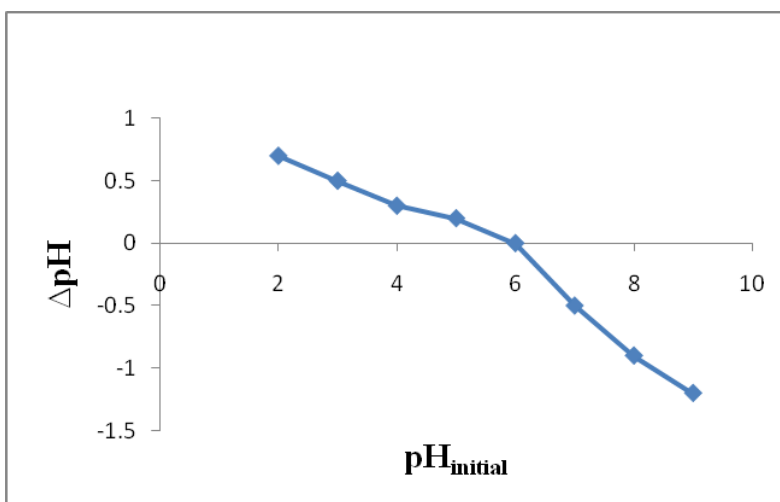


Fig. 1: Point of zero charge ( $pH_{pzc}$ ) of PMMA modified  $MnFe_2O_4$  NPs

Table 2:  $pH_{initial}$  and  $pH_{final}$  values for PMMA-PEG modified NPs

	$pH_{initial}$	$pH_{final}$
1.	2	2.4
2.	3	3.9
3.	4	5.2
4.	5	5.6
5.	6	6.5
6.	7	7.0
7.	8	7.7
8.	9	7.9

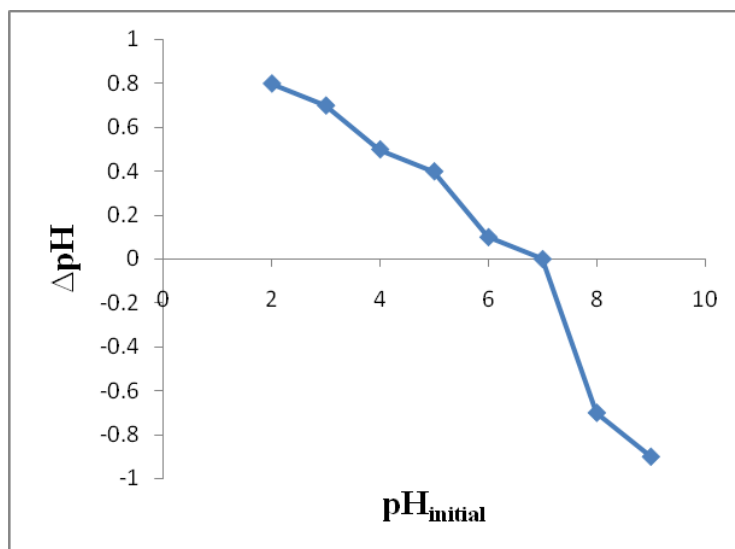


Fig. 2: Point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of PMMA-PEG modified  $\text{MnFe}_2\text{O}_4$  NPs

#### IV. CONCLUSION

Two nanoadsorbents, PMMA modified  $\text{MnFe}_2\text{O}_4$  NPs and PMMA and PEG modified  $\text{MnFe}_2\text{O}_4$  NPs were used to evaluate the difference in their point of zero charge, so that they can be efficiently exploited in future in adsorption studies and geochemistry for the removal of various impurities and contaminants from water bodies and soil. The  $\text{pH}_{\text{pzc}}$  of the studied adsorbents was found to be below 7, showing the existence of perfect charge balance in the acidic region among the equilibrated ions in aqueous solution. The information gathered from these experiments can be utilized for characterizing the adsorption properties of the adsorbents including the ion exchange capacity.

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