Determination of Point of Zero Charge (PZC) of Concrete Particles Adsorbents

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Abstract. In the present study, the pH point of zero charge (pHpzc) was determined for concrete particles adsorbent. The Mass Titration (MT) Method was adopted, and the adsorbent was used to remove the fluoride from water. The pH of point zero charge of concrete adsorbent was found to be 12. The data of pHpzc of the adsorbents give information about the attraction and repulsion between adsorbents and adsorbates. The mass titration technique was found to be an easy way to determine the pHpzc of the studied material.

Keywords: Point of Zero Charge; Adsorbents; Ionic Strengths; The Mass Titration Method.

1. Introduction

In recent time, waste materials were recognized as cheap adsorbents for the elimination of toxic contaminations. Various types of low-cost adsorbents were tested to examine their ability to remove many kinds of impurities from water and wastewater [1, 2]. It is known that; the sorption mechanisms are challenging to recognize because the surface functional groups and chemical structures are not well identified [3, 4]. Besides, pH has a significant impact on the sorption mechanism since its effects on the contaminant adsorption type in solution. Also, the pH influences the ionization of chemically active sites on the sorbent [5-7].

The pH of point zero charge (PZC) is the value of pH at which the components of surface charge are equal to zero for specified conditions of temperature, pressure, and aqueous solution components [8, 9]. It does not mean that there is no charge at the surface for pH of PZC, but there are equal amounts of both negative and positive charges [10, 11]. Several methods have been developed to determine the PZC in soils and other materials [12, 13]. Three different types of points of zero charge have been detected. The first one is the point zero charge, the second is the point of zero net proton charge, and the third is the point of zero net charge [14, 15]. The point zero charge is called the isoelectric point because the particles do not move when exposed to an electric field. The method used to measure the PZC is called the salt addition or salt titration method.

The pH of point zero charge is one of the essential features of the adsorbents that greatly influence the percentage of adsorption and is different from one material to another [16-18]. For example, untreated algal biomass with a pHpzc equals to 5 can successfully absorb the highest amount of fluoride at pH = 5 [19-21]. For a different study, the pHpzc of raw and activated biochar of Colocasia esculenta stem has been estimated to be 6.6 and 8.3, respectively. They both attained the maximum removal of fluoride at pH 4 [22, 23].
For the current study, the mass titration method was used to estimate the pHpzc of concrete particles adsorbent collected from demolished buildings. This method was found to be an easy and straightforward method that gives appropriate results.

2. Materials and methods

2.1 Materials

The concrete adsorbent in this study was made from concrete blocks collected from demolished buildings, and it made within specific determinants [24, 25]. Twenty-one clean plastic bottles and orbital shaker (type TS-2, Turki) have been used in the test. The pH of the mixture was adjusted by using 0.1N HCL and/or 0.1N NaOH solution. The pH was measured with a pH meter (Type EZDO model 6011, China). Potassium Chlorate (KCl) with different concentrations was made to be added to the mixture of adsorbent and water to get three ionic strengths.

2.2 Methods

The pH of point zero charge was determined as follows [12, 26]:

- One gram of concrete particles was placed in twenty-one of plastic bottles. The bottles were arranged in three groups, each group include seven bottles.
- The solutions mixture of base, acid and water in the seven bottles of each group is indicated in Table 1.
- The suspensions have been automatically shaken for one hour, and the pH was determined as $\text{pH}_i (\text{pH}_{\text{water}})$.
- Then, one millilitre of (0.1, 1, 2) mol/L of Potassium Chlorate (KCl) was added to each one of the three groups respectively, to get three ionic strengths.
- The bottles were shaken again for 30 minutes.
- The pH values have been measured again as $\text{pH}_f (\text{pH}_{\text{KCl}})$ and $\Delta\text{pH}$ was computed as follow $\Delta\text{pH} = \text{pH}_i - \text{pH}_f (\text{pH}_{\text{KCl}})$
- $\text{pH}_i$ Versus $\Delta\text{pH}$ has been plotted.
- The point zero charge (PZC) is the vertical projection of the curve.

### Table 1. Solutions for PZC determination.

| Bottle | Volume of 0.1M HCl (mL) | Volume of 0.1M NaOH (mL) | Volume of Water (mL) |
|--------|-------------------------|--------------------------|---------------------|
| 1      | 5                       | 0                        | 15                  |
| 2      | 4                       | 0                        | 16                  |
| 3      | 3                       | 0                        | 17                  |
| 4      | 2                       | 0                        | 18                  |
| 5      | 0                       | 0                        | 20                  |
| 6      | 0                       | 3                        | 17                  |
| 7      | 0                       | 5                        | 15                  |

3. Results and discussion
The experimental curves (plots of $\Delta \text{pH}$ vs $\text{pH}_i$) from the salt addition method are shown in Figures 1, 2, and 3. The Results presented the three ionic strengths (2, 1 and 0.1 M) of KCL and pH$_{\text{PZC}}$ has been recognized. Figure 1 illustrates the plot of $\Delta \text{pH}$ vs $\text{pH}_i$ for 2M of KCL, and the intersect point is 12, which represents the point of zero charge (see Table 2). For the plots of $\Delta \text{pH}$ vs $\text{pH}_i$ for 1M of KCL, the point of zero charge is 12.1 as shown in Figure 2 and Table 3. Moreover, the concentration of 0.1 M of KCL has a 12.04 PZC shown in Figure 3 and Table 4.

| Bottles | $\text{pH}_i$ ($\text{pH}_{\text{water}}$) | $\text{pH}_i$ ($\text{pH}_{\text{KCl}}$) | $\Delta \text{pH}$ |
|---------|---------------------------------|---------------------------------|------------------|
| 1       | 5.7                             | 8.1                             | 2.4              |
| 2       | 6.3                             | 9.36                            | 3.06             |
| 3       | 7.7                             | 9.55                            | 2.45             |
| 4       | 8                               | 10.03                           | 2.03             |
| 5       | 11.75                           | 12                               | 0.25             |
| 6       | 12.0                            | 12                               | 0                |
| 7       | 12.93                           | 12.83                           | 0.13             |

**Table 2.** Data of determine of PZC of 2M KCl.

**FIGURE 1.** PZC Determination Diagram for 2M KCl.

**Table 3.** Data of determine of PZC of 1M KCl.
TABLE 4. Data of determine of PZC of 0.1M KCl.

| Bottles | $\text{PH}_i$ (pH \text{water}) | $\text{pH}_f$ (PH \text{KCl}) | $\Delta \text{pH}$ |
|---------|-------------------------------|-------------------------------|------------------|
| 1       | 6.25                          | 8.5                           | 2.25             |
| 2       | 6.71                          | 9.75                          | 3.04             |
| 3       | 8.3                           | 10.3                          | 2                |
| 4       | 10.7                          | 11.1                          | 0.4              |
| 5       | 11.9                          | 11.94                         | 0.04             |
| 6       | 12.05                         | 12.05                         | 0                |
| 7       | 12.81                         | 12.7                          | -0.11            |

Figure 2. PZC Determination Diagram for 0.1M KCl.
Figure 3. PZC Determination Diagram for 0.1M KCl.

Fluoride adsorption onto concrete particles depended on the pH of the solution as shown in Figure 4, which showed that fluoride uptake increased with the increase of pH of the solution and reached the maximum at pH 6, then decreased when the solution was the same pH value increased. This fact can be explained in terms of the pH point zero charger (pH_{PZC}). The pH_{PZC} of concrete particles is found to be 12, as provided above. The pH_{PZC} means that the net charge on the adsorbent surface is zero. Once the pH of the solution is less than pH_{PZC}, the net surface charge on the solid surface for the adsorbent becomes positive because of the adsorption of excess H^+ which is favoured for fluoride adsorption due to coulombic attraction. On the other hand, the net surface charge is negative because of the desorption of H^+, and the fluoride uptake must compete with coulombic repulsion when the pH of the mixture is bigger than pH_{PZC}. For this reason, a proper removal of fluoride below pH_{PZC} can be noticed due to the presence of positively charged sites on the adsorbent surface.

It can be seen that the amount of fluoride uptake is reduced in low pH even so the pH of the solution is below the pH_{PZC}, which can be ascribed to the company of weak hydrofluoric acid, which lowered the free fluoride ions availability to be adsorbed. Moreover, it can be noticed a drop in fluoride uptake in the alkaline values even if the surface has a positive charge. This behaviour ascribes the fluoride and hydroxyl ions intense competition to bind onto active sites. It is noteworthy that the final mixture pH (after adsorption) is near to 12 for initial pH of (3 to 11), which indicates a presence of a large number of exchangeable OH⁻. These results are consistent with the studies conducted by Raichur, A.M. and M. Jyoti Basu [27] and Tor, A. [28].
4. Conclusion
Knowing the point of zero charge of the adsorbent affords information for the attraction and repulsion between adsorbent and adsorbate. For the current study, the mass titration method was used to estimate the pHpzc of concrete particles adsorbent collected from demolished buildings. The results indicate that the final mixture pH (after adsorption) is near to 12 for initial pH of (3 to 11), which indicates a presence of a large number of exchangeable OH\(^-\). It was also found that the mas titration method is suitable and straightforward to calculate the point of zero charge of concrete particles adsorbent. The calculations were achieved in a short time, and they can be evaluated in a typical laboratory session.

References
[1] Sabreen L. kareem, Sohaib K. Al-Mamoori, Laheab A. AL-MALIKI, Mohammed Q. AL-Dulaimi and AL-ANSARI N 2020 Optimum Location For Landfills Landfill Site Selection Using Gis Technique: Al-Naja City As A Case Study Cogent Engineering
[2] De Gisi S, Lofrano G, Grassi M and Notarnicola M 2016 Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review Sustainable Materials and Technologies 9 10-40
[3] Lei C, Wang C, Chen W, He M and Huang B 2020 Polyaniline@magnetic chitosan nanomaterials for highly efficient simultaneous adsorption and in-situ chemical reduction of hexavalent chromium: Removal efficacy and mechanisms Science of The Total Environment 733 139316
[4] Hamid Rasool M, Al-Maliki L A, Al-Mamoori S K and Al-Ansari N 2021 Estimation of Uplift Pressure Equation at Key Points under Floor of Hydraulic Structures Cogent Engineering 8 1917287
[5] Fiol N and Villaescusa I 2009 Determination of sorbent point zero charge: usefulness in sorption studies Environmental Chemistry Letters 7 79-84
Khoshnam F, Zargar B and Moghadam M R 2019 Adsorption and removal of ametryn using graphene oxide nano-sheets from farm waste water and optimization using response surface methodology *Journal of the Iranian Chemical Society* **16** 1383-90

Al-Maliki L A, Farhan S L, Jasim I A, Al-Mamoori S K and Al-Ansari N 2021 Perceptions about water pollution among university students: A case study from Iraq *Cogent Engineering* **8** 1895473

Kosmulski M 2020 The pH dependent surface charging and points of zero charge. VIII. Update *Advances in Colloid and Interface Science* **275** 102064

Jasim I A, Mahmood T S, Al-Mamoori S K and Al-Maliki L A 2021 The relationship between traffic congestion and land uses: A case study of Al-Kut city, Iraq *Journal of Urban Regeneration & Renewal/ Henry Stewart Publications* **14** 264-71

Bakatula E N, Richard D, Neculita C M and Zagury G J 2018 Determination of point of zero charge of natural organic materials *Environmental Science and Pollution Research* **25** 7823-33

Al-Mamoori S K, Kareem S L, Al-Maliki L A and El-Tawil K 2020 Geotechnical Maps for Angle of Internal Friction of An-Najaf Soil-Iraq Using GIS *Wasit Journal of Engineering Sciences* **14** 262-9

Durán A C, Flores I, Perozo C and Permattle Z 2006 Immobilization of lead by a vermicompost and its effect on white bean (Vigna Sinensis var. Apure) uptake *International Journal of Environmental Science & Technology* **3** 203-12

Al-Mamoori S K and Al-Maliki L A 2016 EVALUATION OF SUITABILITY OF DRAINAGE WATER OF AL-HUSSAINIA SECTOR (KUT IRAQ) TO IRRIGATE COTTON CROP *Kufa Journal of Engineering* **7** 67-78

Hao W, Flynn S L, Alessi D S and Konhauser K O 2018 Change of the point of zero net proton charge (pHPZNPC) of clay minerals with ionic strength *Chemical Geology* **493** 458-67

Mohammad O I and Al-Maliki L A 2014 Evaluation of Suitability of Drainage Water of Al-Hussainia sector (Kut-Iraq) For Irrigation *Wasit Journal of Engineering Sciences* **2** 30-45

Yang T, Xu Y, Huang Q, Sun Y, Liang X, Wang L, Qin X and Zhao L 2021 Adsorption characteristics and the removal mechanism of two novel Fe-Zn composite modified biochar for Cd(II) in water *Bioresource Technology* **333** 125078

Al-Maliki L A J, Al-Mamoori S K, El-Tawel K, Hussain H M, Al-Ansari N and Jawad Al Ali M 2018 Bearing Capacity Map for An-Najaf and Kufa Cities Using GIS *Engineering* **10** 262-9

Al-Mamoori S K, Attiyah A N, Al-Maliki L A, Al-Sulttani A H, El-Tawil K and Hussain H M 2020 *Modern Applications of Geotechnical Engineering and Construction*: Springer pp 329-48

Mukherjee S, Mondal M, Banerjee S and Halder G 2017 Elucidation of the sorptive uptake of fluoride by Ca2+-treated and untreated algal biomass of Nostoc sp. (BTA394): Isotherm, kinetics, thermodynamics and safe disposal *Process Safety and Environmental Protection* **107** 334-45

Al-Mamoori S K, Al-Maliki L A J, El-Tawel K, Hussain H M, Al-Ansari N and Al Ali M J 2019 Chloride, Calcium Carbonate and Total Soluble Salts Contents Distribution for An-Najaf and Al-Kufa Cities’ Soil by Using GIS *Geotechnical and Geological Engineering* **37** 2207-25

Al-Mamoori S K, Al-Maliki L A J, Al-Sulttani A H, El-Tawil K, Hussain H M and Al-Ansari N 2020 Horizontal and Vertical Geotechnical Variations of Soils According to USCS Classification for the City of An-Najaf, Iraq Using GIS *Geotechnical and Geological Engineering* **38** 1919-38

Mukherjee S and Halder G 2016 Assessment of fluoride uptake performance of raw biomass and activated biochar of Colocasia esculenta stem: optimization through response surface methodology *Environmental Progress & Sustainable Energy* **35** 1305-16

Jasim I A, Farhan S L, Al-Maliki L A and Al-Mamoori S K 2021 Climatic Treatments for Housing in the Traditional Holy Cities: A Comparison between Najaf and Yazd Cities *IOP Conference Series: Earth and Environmental Science* **754** 012017

Almaliky E A and Gzar H A 2020 Geomaterials as Cost Effective Sorbent to Remove Fluoride from Water *Key Engineering Materials* **870** 107-21

Al-Shammaa A K M and Al-Mamoori S K 2021 A Design Chart for Optimum Dimensions of Reinforced Concrete Cantilever Beams *IOP Conference Series: Materials Science and Engineering* **1094** 012023
[26] Al-Mamoori S K, Al-Maliki L A, Hussain H M and Al-Ali M J 2018 Distribution of Sulfate Content and Organic Matter in An-Najaf and Al-Kufa Cities’ soil Using Gis KUFA JOURNAL OF ENGINEERING 9 92-111

[27] Raichur A M and Jyoti Basu M 2001 Adsorption of fluoride onto mixed rare earth oxides Separation and Purification Technology 24 121-7

[28] Tor A 2006 Removal of fluoride from an aqueous solution by using montmorillonite Desalination 201 267-76