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Removal of Phosphate Ions from Aqueous Solutions by Using Modified Diatomaceous Earth.

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ABSTRACT

Diatomite (DE), Ferrihidrite- modified diatomite (DFe) and microemulsion modified diatomite (DEM) were used for removal of phosphate ions from their aqueous solutions. The diatomite (DE) and the modified diatomite [DFe and DEM] were characterized by X-ray, IR and SEM also surface area was estimated. The results of characterization indicated that, the phosphate ions sorption capacities of diatomite were improved after modifying by ferrihydrite or microemulsion. The surface area of the modified diatomite increased according to DEM > DFe > DE, so the efficiency of removing phosphate ions with DEM was higher than that of DFe and DE. This behavior may due to the difference in the electrostatic force between phosphate ions and the surface of DE, DFe and DEM. Also, it is found that the removal of phosphate ions by the three samples improved by increase the phosphate concentration in the initial solutions.

Keywords: - phosphate ions, modified diatomite, microemulsion, surface area, electrostatic force

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INTRODUCTION

In the previous works, the authors [1] used some raw materials such as calcite and dolomite to reduce the phosphate contents in their aqueous medium. Also, they used diatomite to reduce the heavy metals contents [2]. They conclude that the efficiency of removing in all cases depend on different parameters such as the pH values, the ratio between the solid and the aqueous and the time of contact. Also, they found that the effective parameter is the surface area of the adsorbent materials. So that different modifications were carried out to increase the surface area of the diatomaceous, some of these are chemical and the other is physical treatment. As continuous of our policy in this field, this work devoted to modify the surface area of diatomite to increase its efficiency for removing the pollutant materials.

Diatomite, DE, is mainly a compound of amorphous hydrated silica. The SiO_2 content of it is usually ranges between 80 to 90%. DE is pale- colored, soft and light weight sedimentary rock. It composed principally of silica microfossils of aquatic unicellular algae. It is highly porous structure, low density and high surface area resulted in a numbers of industrial applications such as filtration media for various beverages and inorganic and organic chemicals. To increase the efficiency of DE to remove the pollutant compounds, a several modification to increase the surface area of the DE were done [3]. Gorren et al [4], modified the surface area of diatomite by purification with HCl followed by calcinations. Khraisheh, et al [5] modified diatomite to be used as filter support in the technical process. Also, Khraisheh, et al [6] modified diatomite by NaOH treatment and Magnesium oxide deposition to improve the adsorption capacity of removal for heavy metals like pb^{+2}, Cu^{+2} and Cd^{+2} from wastewater. Another modification was carried out by treated the diatomite with aluminum sulphate [7] to remove the phosphorous from wastewater. In other techniques, diatomite was modified by using the microemulsion and manganese oxide process for removal of chromium ion(III)from aqueous solution [8].

EXPERIMENTAL

Materials

Natural diatomite (DE) was used without purification as a started material. It washed several times with deionized water and dried at 100ºC overnight. The start material was characterized as described elsewhere [2]. It contains ~ 83.6%, SiO_2 with small percentages of Al_2O_3, Fe_2O_3, CaO and other oxides and its surface area as calculated from the TEM equals to 7.5 m^2/g.

Methods of modification

Two methods of modification to the DE were carried; the first one is treating the diatomite with ferric chloride and the other by using the microemulsion solution

In the first method, (15 g) of diatomite were immersed in 100 ml of 6 M NaOH at 85 ºC for 2 hrs to partially dissolve Si [6,9]. The mixture was immediately added to 100 ml of 1 M $FeCl_2$, and then stirred and oxidized by air at room temperature for 24 hrs. The mixture was then centrifuged to remove the supematant. The obtained solid was transferred to 100 ml of 6M NaOH, and oxidized by air at room temperature for overnight. Then, the mixture was centrifuged to remove excess NaOH. The solid obtained through centrifugation was washed with deionized water and oxidized by air to continue the removal of excess NaOH and the $Fe(OH)_2$ oxidation. The mixture was dried at 50 ºC for 24 hrs and then stored in the desiccator at room temperature. In The second method, modifying diatomite with microemulsion (DEM) was carried. The microemulsion solution was composed of 15 wt% surfactant 20 wt% aqueous phase (deionized water); 35 wt% co-surfactant (isoamyl alcohol, 99% PA) and 30 wt% oil phase (heptane). Amixture of DEM was prepared using 10 g of diatomite and 20 mL of microemulsion solution. The mixture was shaken, then dried at 65ºC and stored in tightly stoppered glass bottles [8].

Characterization

The natural diatomite (DE) and the modified samples were characterized by various techniques. Infrared absorption spectra (IR) was performed by the KBr disc technique using a Fourier transformer infrared between 400 to 4000 cm-1. X-ray diffraction, XRD, was carried out by using Brukur D8 advance diffraction

(Germany) using CuK_∞ radiation. The surface area of the modified and non- modified samples was calculated by using Quanachrome Inst., Quantachrome Nova automated gas sorption version 1.12. The transmition electron microscope profile (TEM) was examined to study the morphology of the three samples.

The removing method of phosphate

To study the effect of modification on the efficiency of removing phosphate anions by DE, a set of experiments were carried out. In this experiment 0.1 gm of the unmodified or the modified DE powders were dispersed in 20 mm^2 of the phosphate solutions. The effect of the pH values of the solution was adjusted by adding 1 N HNO_3 at 30 ºc. Then the solutions were left for 24 hr to attain the equilibrium state. After stilling the solid part was separated by filtration and the concentration of the phosphates were determined in the filtrate by using the spectrophotometer. The effect of the PH values and the phosphate concentration in the initial solution were studied. From the results of chemical analysis, the efficiency of removing for the three samples were calculated using the following formula

$$F\% = C_o - C/C_o$$

Where F is the efficiency and C_o and C are the initial and the final concentration of the phosphates respectively

RESULTS AND DISCUSSION

The characterization of the samples

The original DE without modification as well as the two modified samples DE with Fe and DE by emulsion were characterized by different methods. Fig .1 represents the IR spectra of the three produced samples. The IR patterns show the presence of common broad peaks at ~3500 cm^{-1}, this band represents the OH stretching of interlayer molecules and frame work hydroxyl groups(8). For the three curves of the IR chart Fig 1. It may be observed that:-

1) The presence of the three peaks at ~1000, ~790 and 600 cm^{-1} which observed in the DE samples were shifted by modification to some extent. This finding may due to the rearrangement of the molecules and the unites by the modification.

2) On the curve of the IR chart for DFe and DEM, an absorption bands at ~1740 cm^{-1} were observed, which in the DE appeared at 1636 cm^{-1} that may due to the presence of O-H stretching bonds. The important peak at ~ 821cm^{-1} transfers to the band at ~912cm^{-1} in the case of the treatment of DE by emulsion. This may due to the disturbance of the aromatic hydrocarbon of the surfactants as pointed out by Li et al (8), through the modification by emulsion process.

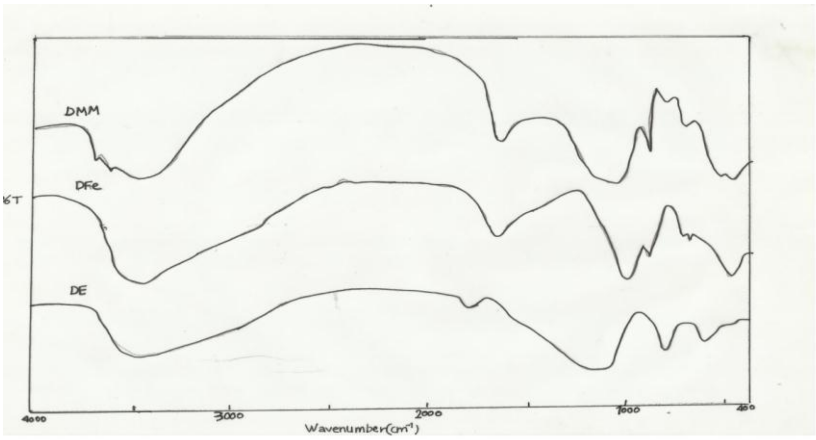

Figure 1: IR. Spectrum of diatomite and modified diatomite

Fig 2, represents the XRD of the three samples under this study. The three pattern charts exhibit a main peaks at $2\Theta= 22.8$, which is the characteristic to the amorphous SiO_2 (JCPDS29 – 0085), indicating that the main constituent of diatomite and its modified sample is SiO_2. In the case of the DE treated with Fe or microemulsion solution, a group of the other peaks were appeared at different 2Θ, between 30 to 48. These peaks may be attributed to the following proposal:

- The ferrihydrite deposited in the diatomite backbone as mentioned in previous work, carried by janney [10] and pan [11].
- In the case of the emulsion modification these peaks indicate that organic compounds deposited into diatomite backbone.

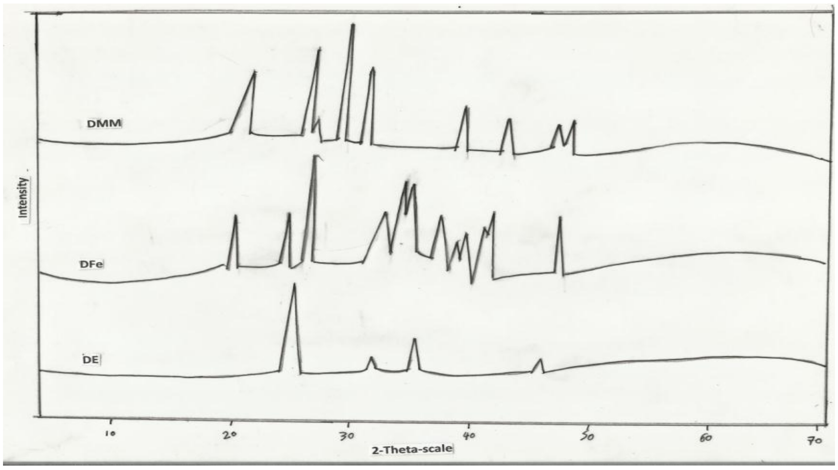

Figure 2. X-ray diffraction of diatomite and modified diatomite

The TEM of both the modified and non-modified DE were performed to study the effect of the modification on the surface and the particle size of the DE (Fig 3 a,b,c). The photo of diatomite without modification Fig 3a, shows that it consists mainly of small number of crystals with sharp edges [12]. For the modified sample with $FeCl_3$, Fig 3b, it is observed that new structure had appeared where the colloidal size (fine size) of ferrihydrate is deposited into the macropores and the larger mesopores of the diatomite molecules [3]. After being fully deposited into the pores of the diatomite, the extra ferrihydrite aggregates on the surface of the diatomite particles causing the formation of the aggregate structure. While Fig 3c which represent the morphology of the modified DE by using emulsion solution shows that the transparent and net surface structure was formed on the DE surface due to the contact between the agglomerate of microemulsion solution and the surface of the substrate DE. In general through the modification, the formation of the ferrohydrate –DE structure or the formation of the transparent surface lead to an additive factors for the surface area of the raw DE.

The calculated surface areas of the three diatomite samples are shown in Table 1. From the values of the obtained results, it may arrange the values of the surface areas in the following sequence. DEM (110.7) > DFe (63.8) > DE (7.3)

Table 1: The surface area measurements and the efficiency of removal phosphates by DE,DFe and DEM

samples	Surface area m^2/gm	Effeciency of removal at pH =4	Effeciency of removal at pH =8.5
DE	7.3	35	19
DFe	63.8	65	50
DMM	110.7	87	86

This arrangement indicates that the modification of DE by Fe increases the surface area by about nine times, while the treatment with emulsion increases the surface area by about fifteen times. Any how the modification leads to increase the surface area which increases the efficiency of diatoms for the removing of the pollutant materials.

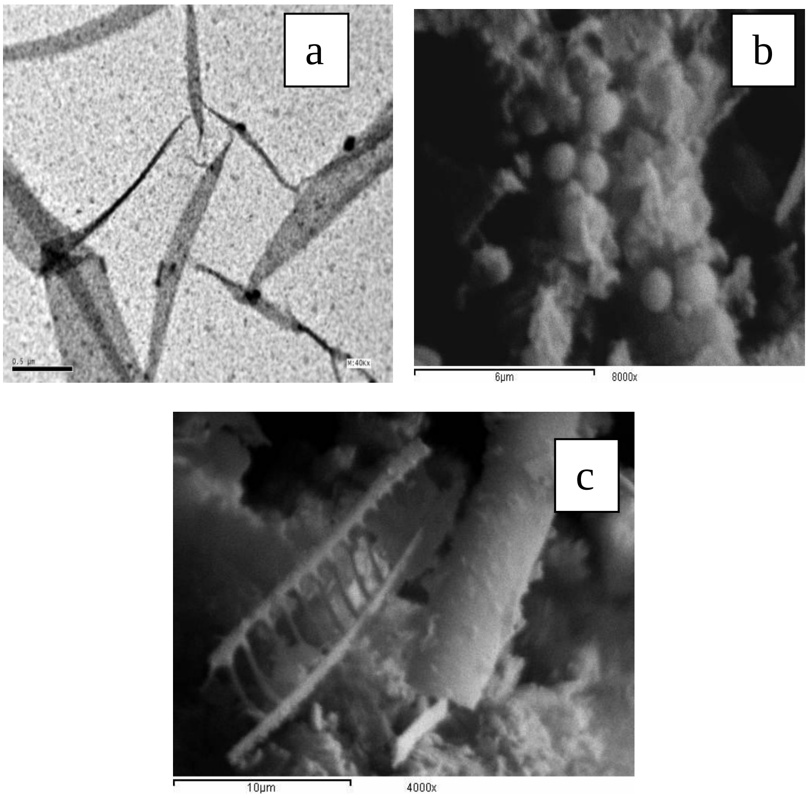

Figure 3: SEM of diatomite and modified diatomite

a) DE b) DFe c) DEM

Removal of phosphate species by modified DE

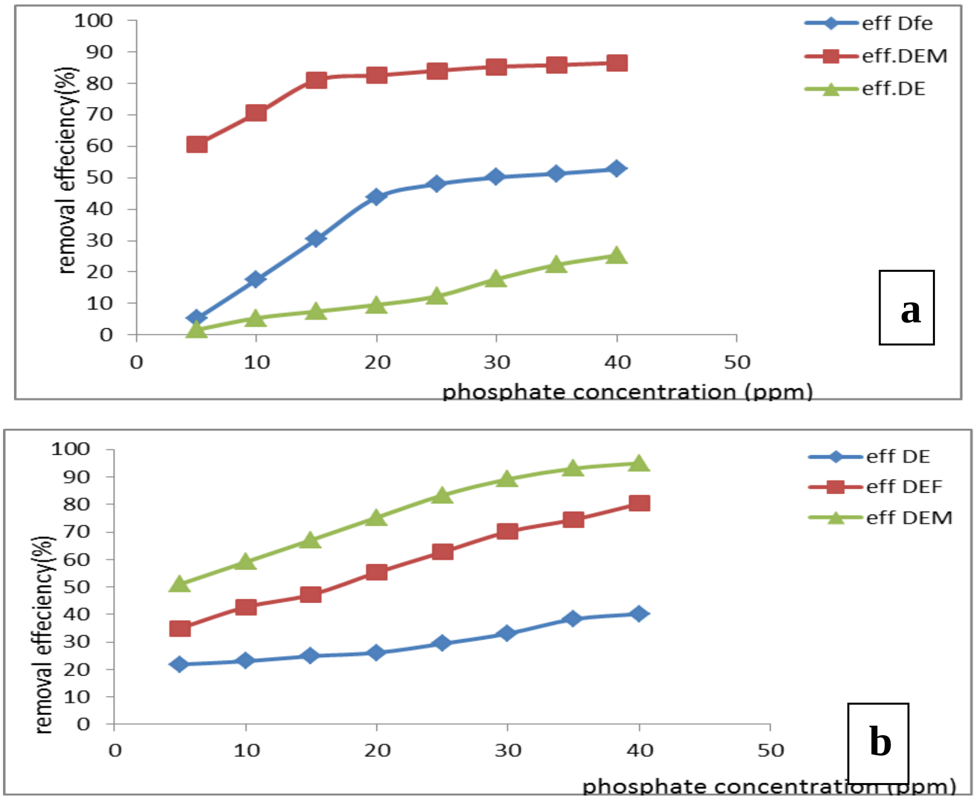

Figure 4: The efficiency of removal phosphate ions by DE, DFe and DED at different concentrations

To study the effect of modification on the efficiency of removing phosphate anions in their aqueous solution, different concentration of phosphate solutions were prepared. The effect of the PH values on the efficiency of removing was also studied. In this part the removing of the phosphate was carried out at acidic medium (pH=4) and at basic medium (pH=8). At pH=4, the efficiency of the DE and the modified DE increases gradually in similar way as the concentration of phosphate increases , but this increase at low concentration of phosphate is more remarkable than that at high concentration of the phosphate. This may due to two reasons: the first is the diffusion of the phosphate content at the low concentration is easier and rapid than that at the higher concentration and to the partially saturation of the adsorbent surface. On other hand, the curves (Fig 4 a) show that at any concentration of phosphate the efficiency of the modified DE is higher than that for unmodified DE and the modification by emulsion is the higher one, this means that the modification with emulsion increases the surface area of DE and create some new cavities inside the balk of DE. At pH=8, the increase in the efficiency was start rapidly until reach to ~ 20% phosphate then it exhibit a slightly increases as the concentration of phosphate changes from 20 to 40, (Fig 4b). The efficiency of removing at pH=4 is always higher than that at pH=8. This may due to role of the PH to produce different species of the phosphate in the aqueous solution. The phosphate species were found in the form of PO_4^{-3}, HPO_4^{-2}, $H_2PO^{4-}$and H_2PO_4 [2]. In the acidic medium, the predominate species are $H_2PO_4^-$ and HPO_4^{-2} while PO_4^{-3} is predominate at the basic medium. These species will be attract to the active sites on the surface of the diatomite which having reach content of Si.

CONCLUSION

From this work, it may conclude that the efficiency of the diatomite to remove phosphate from the aqueous solution increased with modification. The efficiency of removing followed the following sequence, DE < DFe < DEM emulsion

Also, it is observed that the efficiency in the acidic medium is always higher than that for the basic medium. The efficiency of removing at low concentration of phosphate is higher than that at low concentration.

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