STUDY OF THE MODIFICATION OF THE DIATOMITE SURFACE BY CHEMICAL ACTIVATION FOR A PRACTICAL APPLICATION

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Abstract

The diagrams of X for the natural and modified diatomite show remarkable modification on the surface of this material, we were tested the modified diatomite for filtration of water, using adsorption process.

The adsorption isotherm on diatomite was studied using UV Spectrophotometry, the surface of diatomite was modified with Sulphuric acid by using chemical activation method, and the trapping behavior of the modified diatomite for phenol was investigated.

The influence of some parameters such as the pH of the medium and the initial concentration of the pollutant on the process of adsorption was also evaluated.

Diatomite and modified diatomite are effective adsorbents for removal of phenol from solution at pH 5.

It was shown in the present investigation that the treatment of diatomite by sulphuric acid improves its performance as adsorbent for phenol and, when the adsorption capacity was increased after chemical treatment.

The experiment results show that adsorption isotherm fits in Freundlich equation.

Key words: Surface modification, material, diatomite, environment, pollution
1. Introduction

Phenol is produced through both natural and anthropogenic processes. It is naturally occurring in some foods, in human and animal wastes, in decomposing organic material, and is produced endogenously from the metabolism of protein. Phenol has been isolated from coal tar, but it is now synthetically manufactured. Currently, the largest use of phenol is as an intermediate in the production of phenolic resins. People are also exposed in consumer products such as medicines and lotions, as well as in some foods and in tobacco smoke; therefore the phenol has been found in drinking and waste water. [1]

Phenols and related compounds are potentially toxic to humans and aquatic life; the central nervous system may initially be stimulated followed by severe profound depression progressing to the coma. The heart rate may increase then become slow and irregular. The blood pressure may increase slightly and then fall markedly with dyspnoea and fall in body temperature. Death may occur from respiratory, circulatory or cardiac failure. [2]

Phenolic compounds create an oxygen demand (COD) in receiving waters, and impart a taste and odour to drinking water with even minute concentrations of their chlorinated derivatives. Water treatment plants normally disinfect water by chlorination, consequently forming the undesirable chlorophenols when phenols are present. [2]

Within literature, many treatment processes have been proposed for the removal of phenolic compounds. Chemical precipitation, membrane filtration, ion exchange, alum coagulation and adsorption are some of the most commonly used methods for the treatment, and disposal, of organic compounds wastes water. Adsorption is considered to be a particularly competitive and effective process for the removal of these compounds.

There are many adsorbents in use. Activated carbon is the most widely used for the removal of a variety of organics from waters, but the disadvantage associated with it is the high regeneration cost and the generation of carbons fines, due to the brittle nature of carbons used for the removal of organic species.[3]. For that we chose a diatomite as low-cost natural adsorbents.

Diatomite is a material of sedimentary origin consisting mainly of an accumulation of skeletons formed as a protective covering by diatoms. The skeletons are essentially amorphous hydrated or opaline silica but occasionally are partly composed of alumina. Diatomite usually contains other sediments such as clay and fine sand but its deposits sometimes consists of diatom shells only. [4]

However, the raw diatomite frequently contains an important rate of impurities that can restrain its efficiency in many applications. Several works reported its use in the heavy metal ions adsorption and basic textile dyes in wastewater. [5]

In this study, acid treatment diatomite was attempted to enhance the adsorptive capabilities of diatomite for phenol. The effect of some operational parameters such as initial phenol concentration and pH on the adsorptive capacity of the diatomite was tested. The equilibrium and kinetic data of the adsorption process were then studied to understand the adsorption mechanism of phenol molecules onto the modified diatomite.

2. Materials and Methods

2.1. Adsorbent

In Algeria, the principal deposits of diatomite belong to the category of the deposits of continental context, formed in lake mediums with lagunaire of age Miocene (-10 AM). It is the acid volcanicity of this period which brought the silica stock favourable to the
development of the diatoms: these deposits are located in the tertiary basins of miocene of the west of Algeria, where one finds events volcanic in the form of domes and rhyolitic extrusions. There are 7 interesting deposits distributed in the west of Algeria like as: Mostaganem, Tlemcen and Mascara, from where deposit of Sig is located at the south-west of Mascara.

The Algerian diatomite is particularly polluted by a high rate of calcium carbonates that can exceed 10% and it gave a basic pH because of the formation of basic complexes during the dissolution of CaCO₃ [5]. The pre-calcinations process (about 600°C) has been used for diatomite in industrial applications, but this technique did not produce sufficiently porous material for use in filtration applications because it was increased the powder qualities. [6] For that, we were selected a chemical method for modification of raw diatomite, using sulphuric acid.

Generally, diatomite is material comprising of an amorphous form of silica (SiO₂·H₂O) and containing a small amount of microcrystalline material, chemically stable and inert. The silica surface contains silanol groups that spread over the matrix of the silica. When the diatomite was modified, the active group on the diatomite surface (OH groups) was removed and the surface acquires more and more hydrophobic properties by forming siloxane groups. Through the presence of these siloxane groups, it may be possible to impregnate compounds onto the diatomite surface. [7]

Diatomite was obtained through the natural resources of deposit of Sig (west of Algeria). The samples were washed with distilled water to remove fines and other adhered impurities, dried at 100°C, desiccated and stored in tightly stoppered glass bottles. Surface modification was accomplished by treating the diatomite with sulphuric acid. Samples of diatomite (30 g) were immersed in 5M of H₂SO₄ at 90°C for 6 hours; the mixture was then placed under a moderate agitation. [8] The activated material was filtrated and separated from the supernatant and was then washed with water, dried at 100°C, desiccated and stored in tightly stoppered glass bottles.

2.2. Adsorbate
The phenol (C₆H₆O) is a solid, crystallizes in the form of needles under the usual ambient conditions; its properties are illustrated in this table:

**Table 1. Properties of phenol** [1]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>94.11 g/mol</td>
</tr>
<tr>
<td>Water solubility at 19°C</td>
<td>50-100 mg/ml</td>
</tr>
<tr>
<td>pKₐ at 25°C</td>
<td>9.92</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>182°C</td>
</tr>
<tr>
<td>Vapor Pressure at 25°C</td>
<td>0.350 mmHg</td>
</tr>
<tr>
<td>Melting Point</td>
<td>40.90°C</td>
</tr>
</tbody>
</table>

Solution of 1000 mg/l was prepared by dissolving phenol in 1 litre of distilled water and diluted solutions were prepared from this solution.
2.3. Analysis and characterization techniques

The samples were characterised by different techniques. First, X-ray florescence (XRF) analysis method (Philips instrument) was used to determinate the chemical composition of the raw diatomite.

A Philips powder diffractometer was used to obtain powder XRD patterns for the purpose of observing the changes in crystallinity between the samples, using CuKα radiation; in the range of $2\theta = 5-120^\circ$.

The surface textures of the samples were observed using scanning electron microscopy (SEM) Philips XL 30 and EDAX image analysis.

The UV spectra absorption of phenol was recorded using a Jenway 6300 UV/Vis spectrophotometers instrument, the maximum wavelength of the phenol solutions, $\lambda_{\text{max}} = 271$ nm. The pH values of solutions were measured on digital Hanna pH meter.

2.4. Adsorption procedure

The equilibrium isotherms are very important in designing adsorption systems. To estimate the adsorption characteristics of an adsorbent, the isotherm adsorption of that adsorbent with a specific adsorbate is carried out. Concentration variation method is used to calculate the adsorption characteristic of adsorbent and the process. It is mainly carried out by selecting an appropriate concentration range of the adsorbate with a fixed mass of adsorbents.

We will study the influence of the initial concentration of the phenol ($C_0$). We put a solution of known concentration of phenol with and mass of 2 g of the samples has to study. After, to consider the mass of adsorbent sufficient to reach the equilibrium with maximum rate of remediation, we put solutions of phenol in several flasks of 100 ml and varying the weight of adsorbents. The variation of the residual concentration of the organic pollutant in water is then given (by measurement of the absorbance) after 2 hours from the operation. The suspensions were then centrifuged for 10 min at 3000 rpm and deposited for 30 min. The supernatants collected were analyzed for phenol.

In addition to study the effect of pH, mixtures of 100 mg/ml of phenol solution and weight of adsorbents, were prepared at various pH.

Adsorption isotherm experiments were conducted by adding weight of adsorbent to 100 ml of phenol solution in a glass bottle with screw cap. The initial concentrations of phenol were: 50, 100, 150, 200, 250, 300 mg/l.

The mixture was then placed at room temperature at 20°C. The particle size range from, 45 to 200 μm was used. The pH of the solutions was adjusted to its appropriate value by adding either 1 M HCl or 1 M NaOH (pH range from 2 to 11). After 2 h, equilibrium was reached and equilibrium concentration was estimated.

3. Results and discussions

The chemical composition of sample of diatomite obtained by X-ray florescence (XRF) is:

- 62.16% SiO$_2$
- 3.63% Al$_2$O$_3$
- 1.73% Fe$_2$O$_3$
- 14.77% CaO
- 0.71% K$_2$O
- 0.198% TiO$_2$
- 0.60% MgO
- 0.04% MnO
- 19.76% of LOI (Loss on ignition)

It appears, as expected from the obtained values, that diatomite is mainly composed of SiO$_2$ in addition of water molecules and impurities consisting of CaCO$_3$, Al$_2$O$_3$, and Fe$_2$O$_3$, alkaline and alkaline earth oxides as MgO, with smaller amounts of TiO$_2$ and K$_2$O.

It is noteworthy that CaCO$_3$ is distinguishable by its high rate that exceeds 14%, and which surely contaminates the surface of the raw material.
For characterizing some of their composition and resulting properties and to recognize eventual new phases, the raw and modified samples were analysed by XRD.

The X ray pattern of Fig. 1 revealed that the raw diatomite exhibits, in addition of amorphous SiO₂, crystalline phases; SiO₂ (quartz form and Tridimite), CaCO₃ in the calcite and Ankerite [5, 9, 10].

The interpretation of the results of the XDR of figure 1 for a diatomite sample is carried out by Maud software. The identification of the phase is classified in the table 2.

**Table2. Results of the XDR for Diatomite sample**

<table>
<thead>
<tr>
<th>Phases</th>
<th>Formula</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>SiO₂</td>
<td>57</td>
</tr>
<tr>
<td>Ankerite</td>
<td>Ca(Fe,Mg)(CO₃)₂</td>
<td>8</td>
</tr>
<tr>
<td>Tridimite</td>
<td>SiO₂</td>
<td>3</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>23</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>9</td>
</tr>
</tbody>
</table>

**Fig.1. XRD diffractogram of raw diatomaceous earth (D.B)**
The comparison between untreated diatomite sample indicating; the presence of a high rate of CaCO₃ calcite on the untreated diatomite disappeared from the modified material diffractogram. On the other hand, one can discern the emergence on the actived diatomite pattern of a peak of important which is ascribable to CaSO₄ anhydrite, fact that makes it reasonable to assume the efficiency of the applied treatments by sulphuric acid (Fig.2).

3.1. Adsorption Isotherms

In the isotherm experiments the amount of phenol adsorbed at equilibrium, qₑ (mg adsorbate /g adsorbent), was calculated using the following mass balance equation by:

\[ qₑ = \frac{X}{m} = \frac{(C₀ - Cₚℎ)}{(m \cdot V)} \]  

(1)

The amount of the phenol adsorbed by the adsorbents was calculated by difference and remediation yield was calculated by:

\[ \text{Removal} \% = \left[ \frac{(C₀ - Cₚℎ)}{C₀} \right] \times 100 \]  

(2)

Where \( C₀ \) and \( Cₚℎ \) (mg/l) are the initial and equilibrium liquid-phase concentrations of the adsorbate, respectively, \( V \) is the solution volume (L), \( X \) is rate of adsorption and \( m \) is the adsorbent mass (g).
Firstly, the kinetics was established for the raw and modified diatomite. The results obtained are represented in figure 3.
In both cases, the kinetics of adsorption is fast. The greatest quantity of phenol was retained during the first 30 minutes. The time of balance of adsorption necessary for a maximum fixing of this organic pollutant on the various studied samples was reached at the end of 2 hours. We notice that the residual concentration does not change even anymore after 24 hours of the operation for all the cases.

![Fig.3. Variation of adsorption capacity with adsorption time at various initial phenol concentrations for the raw (DB) and activated (DT) diatomite, $T=20^\circ C$, $m=2$ g, pH=6.5, and mixing speed of 400 rpm.](image)

It is noticed that the capacity of maximum adsorption increases with the increase in the initial concentration of the pollutant, of which the quantity to be adsorbed is very important for a solution with high initial concentration which can support much the adsorption of large the quantity of the organic compounds.

For optimize the mass of adsorbent sufficient to reach the equilibrium with maximum rate of remediation and to identify the effectiveness of the chemical activation of the adsorbent, one has the results of optimization in the form of the yields of the each adsorbent.

![Fig.4. Variation of adsorption Removal% with weight of adsorbents at $T=20^\circ C$, pH=6.5, $C_0=100$ mg/l and mixing speed of 400 rpm.](image)
As seen from figure 4, the yield of treatment is increased with the mass of adsorbent for two adsorbents. We notice that yield of adsorption by the treated diatomite is higher those by the natural diatomite. The yield of adsorption increases with the mass of the adsorbent until reaching to a best performance of 51% for the modified adsorbent and 28% for the raw diatomite one. According to these results, we can conclude that chemical modification of the adsorbent is very important.

The effect of initial solution pH on the adsorption of phenol was shown in figure 4, showed the adsorption efficiency of treated adsorbent was much better than that of raw adsorbent at pH value of solution loss than 5. The best adsorption efficiency was achieved at the pH 5, while pH was higher than 5 the adsorption efficiency decreased.

From above researches, we also found that under any adsorbent, it is necessary to identify the value pKa, whose Snoeyink and coll (1969) showed that the adsorbed quantities of phenol decrease if adsorption is done with pH higher than the pKa (9.89) or with very low pH. For pH > pKa, the phenol takes the form negatively charged phenolate. The repulsion between the surfacing of the adsorbent and the anion involves a reduction in adsorption. In this case, the interactions of the electrostatic type take a particular importance (Muller and coll, 1985, quoted by Dabrowski and coll, 2005). In very acid medium, the protons are adsorbed on the sites carbonyls thus competing with the phenol (Liu and Pinto, 1997, quoted by Dabrowski and coll, 2005). [11]

![Graph showing the effect of initial solution pH on the removal (%)](image)

**Fig.5.** The effect of initial solution pH on the removal (%). at T=20°C, m=9 g, C<sub>0</sub>=100 mg/l and mixing speed of 400 rpm.

Adsorption isotherms of phenol on raw and treated diatomite are shown in figure 6. According these results, we notice that the isotherm is of type II for both adsorbent, whose adsorbent having an important macroporous volume.
The above results confirmed the potential of acid treated diatomite as an adsorbent towards phenol, when the adsorption capacity was increased after chemical treatment.

3.2. Adsorption isotherms according to model

The Freundlich isotherm based on adsorption on a heterogeneous surface is as follows:

\[ q_e = K_F C_e^{1/n} \]  

(3)

\( K_F \) and \( n \) are equilibrium constants indicative of adsorption capacity and adsorption intensity, respectively. The linearized form of Freundlich adsorption isotherm is:

\[ \ln q_e = \ln K_F + \left( \frac{1}{n} \right) \ln C_e \]  

(4)

Table 3. Adsorption coefficient \( K_F \) and adsorption constant \( n \) of Freundlich isotherm

Fig.6. Adsorption isotherm for phenol using the untreated and acid treated diatomite at \( T=20^{\circ}C, pH=4, C_0=100 \text{ mg/l}, m=9 \text{ g} \) and mixing speed of 400 rpm.

Fig.7. Adsorption isotherm (Linearization according to Freundlich model) for phenol using the untreated and acid treated diatomite at \( T=20^{\circ}C, pH=4, C_0=100 \text{ mg/l}, m=9 \text{ g} \) and mixing speed of 400 rpm.
Freundlich plots for the phenol adsorption at room temperature (20±1°C) were given in Fig. 7. It illustrated that adsorption of phenol onto adsorbents obeyed the Freundlich isothermal model as well. The corresponding Freundlich isotherm constants $K_F$ and $n$ together with the correlation coefficients $r$ were also listed in Table 3. Values of $K_F$ derived from the Freundlich theory are an indicator of the adsorption capacity of a given adsorbent. The exponent $n$ was greater than unity at room temperatures indicated a favourable adsorption processes. We also found that for modified and untreated diatomites, the values of $K_F$ and $n$ orderly increased, which further confirmed the ordinal improved adsorption capacity.

4. Conclusion

Diatomite has a high porosity; it is the main reason for choosing it as a potential adsorbent for phenolic compounds. Diatomite contains more than 50% of amorphous silica and 62%SiO$_2$. The comparison between untreated diatomite sample indicating; the presence of a high rate of CaCO$_3$ calcite on the untreated diatomite disappeared from the modified diatomite and one can discern the emergence on the activated diatomite pattern of a peak of important which is ascribable to CaSO$_4$ anhydrite.

The adsorbents were successfully prepared with raw material. The satisfying adsorption efficiency was achieved with adsorption time 2 hours at 20 °C for tow adsorbents. Diatomite and modified diatomite are effective adsorbents for removal of phenol from solution at pH 5.

It was shown in the present investigation that the treatment of diatomite by sulphuric acid improves its performance as adsorbent for phenol, when the adsorption capacity was increased after chemical treatment.

The research of adsorption isotherm demonstrated that, for tow adsorbents, adsorption reactions belonged to Freundlich model.

References


