



Removal of phenol from aqueous solutions using raw and modified Syrian natural bentonite

Eng. Karam Haddad*, Dr. Tareq Arraj**, Dr. Mohammad Ghafar***

¹Postgraduate Student, Higher Institute for Environmental Research, Dep. Environmental Chemistry, Tishreen Univ, Lattakia, Syria.

²Professor, Higher Institute for Environmental Research, Dep. Environmental Chemistry, Tishreen Univ, Lattakia, Syria.

³Professor, Higher Institute for Environmental Research, Dep. Environmental Chemistry, Tishreen Univ, Lattakia, Syria.

Abstract In this study, the Syrian natural bentonite ore from Tel Rifaat area in Aleppo governorate was used as a solid phase to remove Phenol (C₆H₅OH) from aqueous solutions. Effect of the contact time (t), Particle size (Vs) and Solution pH value were studied.

It was found that both removal quantity and removal ratio increase with increasing contact time from (1 min) up to balance time (150 min) after this value, we notice Decreasing both removal quantity and removal ratio. Experiments showed that the removal quantity and removal ratio increase with decreasing the Particle size of the solid phase from the range (1-2) mm until reaching the highest amount of removal using the particle size within the range less than (53) micrometers. Removal quantity and removal ratio increase with increasing the (pH) value of the solution until rang (4-6), after this rang, phenol begin turning to the negative phenoxide, resulting in a very low removal quantity and removal ratio.

When we use the surface modification process using HDTMA-Br, the removal quantity and removal ratio of phenol increase approximately six times.

Keywords Syrian bentonite, phenol, removal ratio, removal quantity, HDTMA-Br

Introduction

The term 'bentonite' was first applied by Knight (1898) to highly colloidal, plastic clay. The term was redefined by Ross and Shannon (1926) as buys produced by the in-situ alteration of volcanic ash producing mainly smectite. More recently, the term 'bentonite' has been used to refer to smectite rich material regardless of origin. This is the definition that has been widely adopted in the radioactive waste community.

The bentonite that is typically specified in EBS designs consists primarily of montmorillonite (a smectite group clay mineral), with interlayer calcium or sodium and minor amounts of quartz, feldspar, kaolinite, carbonates, sulphides, sulphates and organic matter [1].

Smectite Mineralogy: Two atomic structural units can be defined from which most clay minerals (including smectites), are formed. The first is an 'octahedral' sheet, consisting of aluminum, iron or magnesium surrounded by oxygen and hydroxyls in an octahedral configuration. The second is a sheet consisting of predominately silicate tetrahedrons. Smectite is a swapping clay mineral that consist of parallel stacks of '2:1' layers, and the cations in



octahedral co-ordination are generally magnesium, iron (II) / (III), and aluminum, although other medium-sized cations such as Li, Cr, and Zn may also be found [1].

Natural Bentonite exists in Syria, subsequently importance and goal of this research is using the Syrian natural bentonite with a low economic cost for phenol removal from aqueous solutions considering that increasing its concentration Lead transfer to humans through the contaminated water and food by phenol.

Using bentonite is currently used and considered the most effective method in removing pollutants. The forces that contribute to this process are the combination of two important factors, the pollutants affinity towards the solvent and the pollutants affinity towards the bentonite. Many materials can be used to remove phenol from aqueous solutions in addition to bentonite such as organo bentonite and activated carbon.

The low removal capacity is the major problem concerning its potential removal capacity. The effectiveness of removal increases if the solid phase is modified [2].

Phenol consists of the association of the hydroxyl group with the aromatic ring, which gives the acidity character, while that group of hydroxyl gives basal character. Phenol is a solid material shaped prismatic crystals and has a characteristic odor. In the molten state, it is a colorless liquid. Phenol has low melting point and its molecular weight (94.11 gr / mole) and the degree of freezing is (40.91°C) [3].

Phenol is used as a chemical toxic to bacteria and fungi as, general and antiseptic mixes hydrated lime to clean floors. It is also used in manufacturing many products including insulation materials, adhesives, coatings, rubber, ink, dyes, perfumes, soap and toys.

Phenol is active against a wide range of microorganisms, and there are some medical and pharmaceutical applications including local anesthesia and eardrops [4-5]. Various methods were attempted to release phenol from aqueous solutions such as biological treatment, catalytic, wet oxidation and adsorption technology.

Phenol is a toxic substance, when exposed through the skin, inhalation or mouth, it is rapidly spread through the blood to digestive tract, liver, lung and kidneys because they are the main receptors.

Phenol risks manifested by causing burns that may not be immediately painful or visible. The threshold concentration of human skin damage of phenol is 1.5% and it may cause permanent eye injury, blindness, muscle weakness, loss of coordination, collapse, coma, convulsions, organ damage and death. The ingestion also causes respiratory irritation, sore throat, headaches, shortness of breath, Irritation, swelling, burns and damage to the mouth, throat, stomach, internal bleeding, vomiting, diarrhea, low blood pressure, shock, collapse, coma and death. Therefore, Phenol is considered a toxic substance [4-5].

Materials and Methods

In this study, the Raw and modified Syrian bentonite were used to remove phenol from aqueous solution. Modified Syrian bentonite were prepared using (HDTMA-Br).

Raw Syrian bentonite was laboratory characterized by determining the ratio of moisture, measuring the specific surface area, and determine the chemical composition.

It was used (1g) of bentonite in removal processes with volume (25 ml) of the liquid phase containing phenol with (25 ppm) concentration.

The removal experiments were carried out by the laboratory temperature and the samples were mixed using the rotating electric mixer.

pH meter Type (Metrohm-744) In was used to measure the pH value, and samples were filtered to obtain filtered phenol solution using a Buchner funnel and a filter paper type (ALBET diameter pore = 0.45 mm).

The remaining phenol concentration was measured (UV-Spectrophotometer) Type (Shimadzu UV-1700) at wavelength (270 nm) [6].

Removal quantity and removal ratio calculations were carried out as follows:

$$\text{Removal \%} = \frac{C_i - C_f}{C_i} * 100 \dots \dots (1)$$

$$q = \frac{C_i - C_f}{C_i} * \frac{V}{m} \dots \dots \dots (2)$$

Where: C_i : initial concentration of nickel ions. (mg/L).



C_f : Final concentration of nickel ions. (mg /L).

V: Liquid phase volume (L).

m: bentonite amount without drying (gr).

q: Removal quantity (mg/g)

The raw bentonite surface modification process was done using hexadecyltrimethylammonium bromide (HDTMA-Br) as follows [7-8]:

Preparation (Na-bentonite) by placing a specific amount of bentonite in (1M) NaCl solution. The mixing process was continued for 24 hours, then the mix was filtered using Buchner filter, then the bentonite was washed several times with distilled water to remove excess Cl^- ions and the amount of salt (NaCl). To be sure ($AgNO_3$) test was done.

Na-bentonite was dried in the oven at (110°C), after that (3g) of Na-bentonite was stirred continuously with (100ml) distilled water, then (100ml) of (0.1M) HDMA-Br was prepared and gradually added to the mix and left for 24 hours with continuous stirring. After 24 hours, the mix was filtered, and modified bentonite was washed several times by distilled water and tested by ($AgNO_3$), finally it dried at (80°C).

Results and Discussion

Characterization of Syrian bentonite

Humidity Measurement

Method ASTM D2216 - 10 was used in the determination of humidity [9]. Bentonite samples were dried and weighed before and after drying. We obtained the following results:

- Bentonite mass with vine before drying ($M_1 = 68.7$ gr)
- The vine mass ($M_2 = 58.65$ gr)
- Bentonite block with vine after drying ($M_3 = 67.52$ gr)

Humidity was calculated using the following equation:

$$W = \left[\frac{M_1 - M_3}{M_3 - M_2} \right] * 100$$

$$W = \left[\frac{68.7 - 67.52}{67.52 - 58.65} \right] * 100 = 13.3 \%$$

Specific Surface area measurement

Specific Surface area was measured using measuring device type (Gemini 2375) to study the specific surface of studied bentonite. It was equal to (119.92 ± 1.2 m²/ g).

As for chemical composition, it was found that the bentonite is composed of oxides shown in Table (1) expressed in the ratio of weight of oxides [10].

Table 1: The chemical composition of the Syrian bentonite

Oxide	Ratio	Oxide	Ratio
SiO ₂	58%	CaO	4.7%
Al ₂ O ₃	10.7%	MgO	7.6%
Fe ₂ O ₃	6.2%	K ₂ O	0.92%
MnO	0.07%	Na ₂ O	0.29%

Determination of contact time:

Equilibrium time was determined when removal quantity and ratio reach a maximum values. We note that the values increase with time increasing due to an increased chance to associate to the bentonite surface until it reaches the highest value at the time (150 min), and that is clear in **Error! Reference source not found.**, which shows Changes in removal quantity by contact time, and **Error! Reference source not found.** shows Changes in removal Ratio by contact time.

Removal quantity and ratio were calculated using equation (1) and equation (2) respectively when (pH = 6.68).



The values increase rapidly at the beginning because the surface sites are empty and after this time a decrease in the value of both removal quantity and ratio because of desorption process. Removal is reversible in this case, therefore potentially transmissible to the environment under different conditions. Time has been adopted (150min) as a time in contact for all subsequent tests.

The preceding discussion and general shape of the curves match with a previous study showed the same behavior developed steel with different contact time depending on the different solid phase [7].

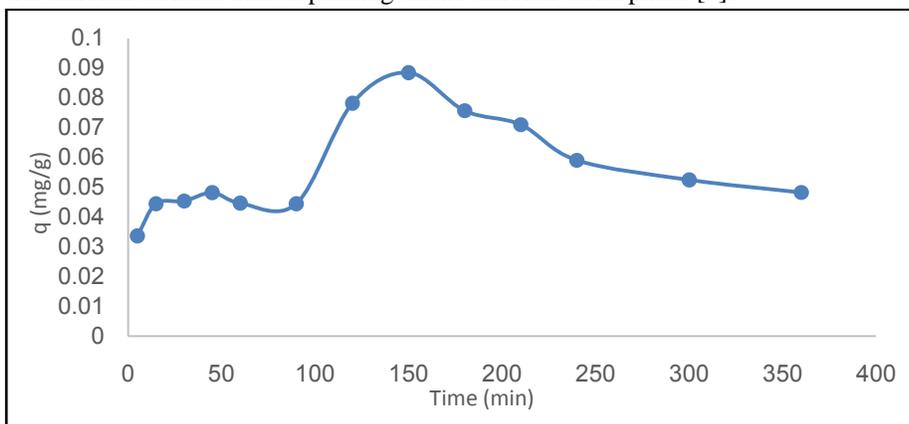


Figure 1: Changes in removal quantity by contact time

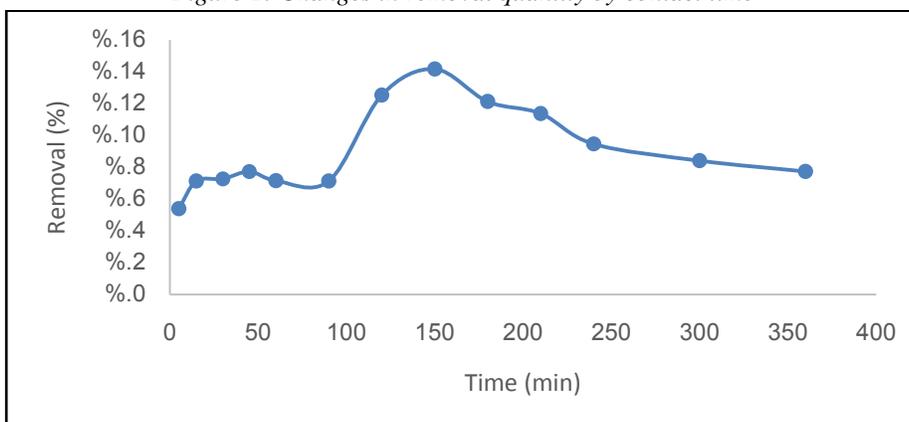


Figure 2: Changes in removal Ratio by contact time

Particle size effect

After grinding raw bentonite and obtaining the particle sizes that shown in Table 2 and conducting an removal and analysis experiment, we got **Error! Reference source not found.**) which represents the relationship between removal quantity and particle size change and **Error! Reference source not found.**) which represents relationship between removal ratio and particle size change.

Both figures show that the removal quantity and ratio are inversely proportional to particle size change. It is noted that values are low when particle size is large and these values gradually increase with decreasing particle size until they reach their highest value at particle size smaller than (53 μm).

The sample (8) is a total particle size used for comparison, and we can explain this change that the specific surface area for bentonite inversely proportional with particle size and thus increase the specific surface area increases the number of binding sites, so removal quantity and ratio increase. The total granular volume decreases the removal quantity and ratio because it contains different particle. These results are consistent with the results of previous



studies concerned with phenol removal using bentonite and other solid phases, all of which combined the inverse proportional between removal quantity and ratio on one hand and the particle size on the other [11-12].

The particle size ($V_s < 53 \mu\text{m}$) for subsequent experiments as it removes the largest amount of phenol from the solution and has the highest removal ratio possible.

Table 2:

Table2: Granular sizes used in phenol removal experiment

Sample	Particle size
1	2 m-1 m
2	1 m-500 μ
3	500 μ -300 μ
4	300 μ -250 μ
5	250 μ -100 μ
6	100 μ -53 μ
7	< 53 μ

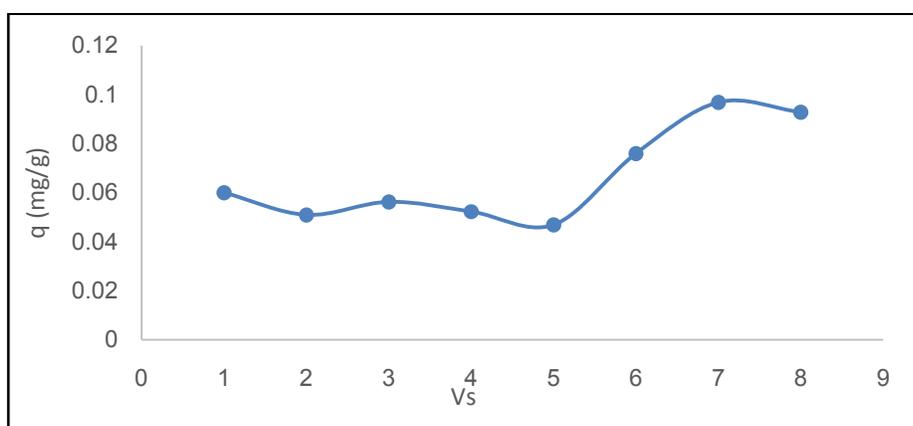


Figure 3: Effect of particle size change on removal quantity

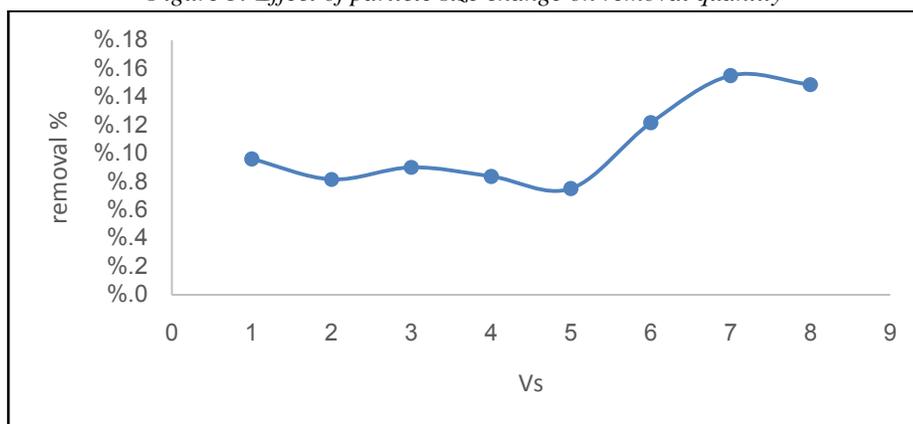


Figure 4: Effect of particle size change on removal ratio

Study of the (pH) solution effect

The effect of phenol (pH) solution on the removal quantity and ratio was studied, (LiOH) solution and (HClO_4) were used to adjust the phenol solution pH. The diagram of the relationship between the pH value and removal quantity (q) and ratio (R %) are shown in **Error! Reference source not found.** and **Error! Reference source not found.** respectively.

In order to discuss the changes the removal quantity and ratio, we can divide the diagram into three areas:

- The first one: the strong acidity and pH values between (2-4), the increase in the removal quantity is observed by increasing the pH value, this is due to the high concentration of hydrogen electrolytes, which occupy the sites on the bentonite surface, and Phenol competes strongly Phenol because it has a positive charge
- The second one: the weak acidity and pH values between (4-6), where the increase in the removal quantity and ratio can be considered the appropriate rang for the occurrence of removal process with the highest yield.
- The third one: It has (pH> 6), noting the low removal quantity and ratio. This is due to two reasons: The first is the acquisition the surface of the bentonite an additional negative charge within this rang increasing the antithesis between bentonitesurface and phenol. The second is that in rang (pH> 7) phenol ionization increases and becomes the negative phenoxide, this increases the strong contrast with the surface, leading to decrease phenol removal until the until the removal quantity and ratio equal approximately to zero at (pH=11).

These results are consistent with the results of previous studies which phenol and bentonite showed similar behavior [13-17].

The pH range between (4-6) can be considered appropriate to remove as much phenol as possible from the water solution.

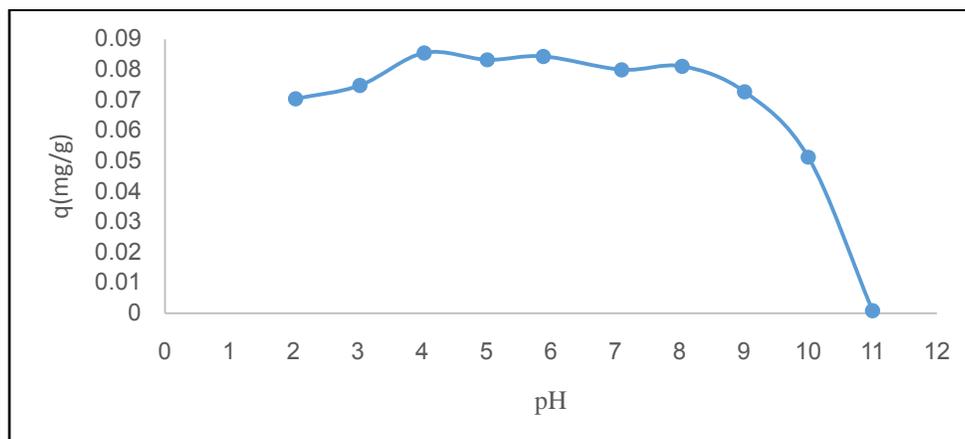


Figure 5: Effect of phenol (pH) solution on the removal quantity

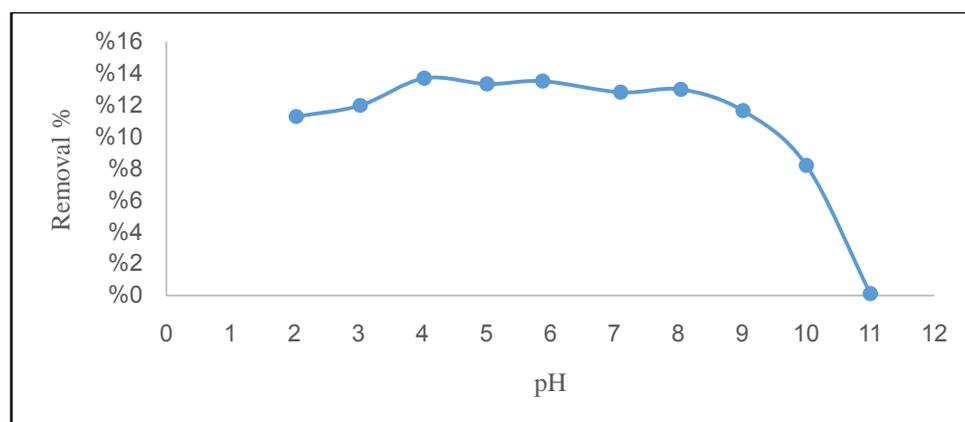


Figure 6: Effect of phenol (pH) solution on the removal ratio



Modification of raw bentonite using (HDTMA-Br)

Modification process has been done using (HDTMA-Br) and the experiment was conducted using modified bentonite according to the terms of experiment using raw bentonite for comparison between removal quantity and ratio in both cases.

The experiment was performed, we determined the amount of remaining phenol and obtained the results as in **Error! Reference source not found.**

Table 3: Comparison results between raw and modified Syrian bentonite

	Removal %	q (mg/g)
Raw bentonite	14%	0.084375
Modified bentonite	76%	0.475

The comparison between the value of both removal quantity and ratio in both cases shows the clear difference between the raw and modified bentonite effectiveness. The results are consistent with previous research results on the comparison of the two species [17-20] which shows the efficacy of modified bentonite in the removal of phenol from aqueous solutions compared with raw bentonite.

Conclusion

Results showed that phenol removal quantity and ratio by Syrian bentonite affected by parameters such as contact time, particle size, pH of the solution. The removal quantity and ratio rise with the increase in the contact time, after that they decrease. With increase the particle size, that phenol removal quantity and ratio increase to reach the greatest value at the smallest particle size, and with increase the pH of the solution, phenol removal quantity and ratio increase then they become steady after that they decrease strongly.

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