Novel Adsorbent for Industrial Wastewater Treatment Applications

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Abstract: In this study, the hydroxyapatite powder is investigated for both of methylene blue and thymol blue in aqueous solution. The physical and chemical properties of the adsorbent were evaluated systematically using different techniques including Microsoft Excel programming, linear regression model and also the coefficient of determination. Batch adsorption experiments were conducted to determine the effect of contact time, solution pH, initial dye concentrations, and also the adsorbent dosage on adsorption. The adsorption kinetic parameters confirmed the better fitting of pseudo-second order kinetic model for both of methylene blue and thymol blue. The isotherm data of methylene blue and thymol blue could be well described by the Freundlich isotherm model which means the adsorption is multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. The maximum adsorption capacity ($K_D$) of methylene blue and thymol blue is found to be 0.2736 (L/mg) and 11.18407 (L/mg) respectively. The high specific surface area and the porous structure with some acidic functional groups on the surface were obviously responsible for high adsorption onto hydroxyapatite (HA). Adsorption kinetics data were modeled with the application of Pseudo first order, Pseudo second order and Intraparticle diffusion models. The results revealed that the Pseudo second order model was the best fitting model. Which means that, the adsorption mechanism followed two stages in which the first one was fast and the other was slower step. Which means the adsorption of dye molecules was limited by intra particle diffusion and film diffusion, as well as, the adsorption rate in both of adsorption system are depends only on the slower step. The Boyd plot exposed that the intra-particle diffusion was the rate controlling step of the adsorption process of both of methylene blue and thymol blue molecules by HA powder. However, the adsorption of methylene blue molecules (basic solution) using of HA as adsorbent particles is found to be extremely preferable than thymol blue molecules.

Index Terms: Hydrothermal, Palladium, Fe$_3$O$_4$, Nanotechnology.

I. INTRODUCTION

Water pollution believed to be one of the most important issues facing our life today due to limitation of fresh water in the earth. According to American meteorological society (AMS), only 3% of the total water in our plant is freshwater and only 0.06% of this water can easily arrived to the people and others existing in form of frozen cap, swamp and underground water. However, water pollution increasing rapidly after industrial revolution due to the releasing of industrial effluent into water system without suitable purification. Dyes produced from dyeing manufacture and textile industries are toxic and non degradable pollutants, as well as, high percentage of these pollutants are released directly into environment without treatment. Therefore, this research was done to develop and measure the adsorption efficiency of new cheapest nanoparticle materials that can be used as adsorbent. Hydroxyapatite has been used to remove two type of dyes (methylene blue and thymol blue) from water at different conditions, because of it has high surface area and simplicity of preparation.

In addition, this research was aimed to determine the adsorption capacity and efficiency for the removal of two types of dyes which are methylene blue and thymol blue.

There are many different methods used for treating wastewater such as Chemical precipitation, ion exchanger, Coagulation & flocculation, membrane filtration and adsorption. These technologies must be designed to provide environmental protection, reuse of water and low cost production. However, adsorption considered to be one of the most effective techniques for removal of different contaminants. The advantages of adsorption are relatively low cost, simple operating and environmental friendly compared with other techniques. Adsorption believed to be one of the most effective methods used for treating water from impurities. The adsorption refers to surface phenomenon, in which the molecules of gas, or liquid, or dissolved solid binding onto solid surface.

Hydroxyapatite has been used from a long time in many applications because it have similar inorganic structure with natural bone. HA exhibit suitable properties such as slow-degradation rate and bioactivity. HA can be find as natural source or can be synthetic. It’s define as a chemical compound can be found naturally in mineral calcium appetite. The structure of hydroxyapatite usually takes shape of hexagonal cylinder with hexagonal system of unit cells. Each unit cell in HA crystals consist of 2 OH$^-$, 10 Ca$^{2+}$ and 6PO$_4^{3-}$. Usually the shape of HA crystals are irregular with approximate dimension of 20 nm width, thickness of 2–5 nm and length of 40–60 nm.
HA consist of very high crystallinity structure with high concentration of hydroxyl group and chemical formula of \( \text{Ca}_3(\text{PO}_4)_2(\text{OH}) \). The crystallography of HA is hexagonal crystals with two crystals system (hexagonal and trigonal) and two lattice system as mentioned above. HA can easily donating and/or replacing OH ions by chloride and/or fluoride and others ions. The calcium phosphorus ratio of hydroxyapatite (Ca/P) almost 2.151 by weight ratio and/or 1.667 by mole ratio.

There are two ionic substitution take place in HA anionic and cationic substitutions. In anionic substitution (OH) and/or (PO4) groups are easily replaced, also carbonated hydroxyapatite (CHA) is important example of anionic substitutions. On the other hand, the cationic substitutions include elements such as K\(^+\), Mn\(^{2+}\) and Na\(^+\). In addition HA exhibit perfect phase stability in aqueous solution with pH above 4.3 (Nayak, 2008).

Dyeing is a chemical process concerned with pigment or color production and their applications in textile industry. Today dyes believed to be more valuable in important industries such as pharmaceutical, cosmetics, food and textiles. The last one (textile industry) consumed dyes more than others. Dyes can describe as organic compounds gives color to substance such as fabrics, food, medicines and others, the dyes resonance usually consist of two aromatics bonded together by side chain, which allows the displacement of adsorption bonds in visible spectrum of the light. Chromogen is aromatic compounds contains naphthalene and benzene usually converted into dyes by suitable chemical reactions. In others word, Chromogen group are colorless compounds have the ability to convert into coloring matter. The structure of Chromogen is responsible for the solubility and adherence properties of dyes.

**II. EXPERIMENTAL WORK**

The analysis and identifications of the experimental data was carried out by using Microsoft Excel programming. This analysis includes physical and chemical analytical techniques, as well as, kinetics analysis depends on the obtained result of each variable. The analytical measurement includes contact time, adsorbent dosage, solution pH and solution concentration. In like manner, kinetic study includes Langmuir isotherm, Freundlich isotherm, PFO, PSO, intraparticle and boyd diffusion models. The aim of this research was achieved by using HA powders and two stock solution of dyes which are methylene blue (2 ppm) and thymol blue (0.05 vol%).

Hydroxyapatite in powder form has been used as adsorbent to remove methylene blue and thymol blue particles from the solution. The batch adsorption system was prepared by using magnetic stirring and 250 mL beakers contains both of substrate and adsorbate as shown in figure 1. Spectrophotometer UV-5100 model (figure 2) has been used to determine the absorbance of the sample before and after adsorption (initial and final concentration of the sample).

**This task was carried out by preparation of a batch adsorption system with six samples that contains the same dye concentration, same pH, and constant amount of adsorbent. The effect of equilibrium time can be determined by measure the concentration change after 5, 10, 30, 60, 90, 120 minutes of adsorption time. The optimum pH can be found by preparing different pH values ranging as (2, 4, 6, 9, 10 & 12) of methylene blue (2 ppm) and thymol blue (0.05 Vol%) solutions, by using HCl (0.1N) and/or sodium hydroxide (0.1N) drops. After that, batch adsorption system is prepared with fixed amount of adsorbent (HA) and same contact time for all samples. The relation can be calculated by fixing all the variables except the initial concentration of the adsorbate, which change as the following equation:**

\[
C_i \times V_i = C_f \times V_f
\]

For example, to prepare 2 ppm of methylene blue solution:

\[
10 \times V_1 = 2 \times 250
\]

Where, 250 is the beaker volume in mL and 0.5 is the initial concentration in ppm and \( V_i \) is the required volume (50 mL) of the concentrated methylene blue solution (10 ppm), therefore to prepare 2 ppm of thymol blue pipette 50 mL of concentrated methylene blue (10 ppm) into 250 mL beaker and complete the volume by distilled water.

To study the effect of adsorbent dose the other variables should be fixed such as the adsorption time, solution pH and initial concentration of both of methylene blue and thymol blue.
III. RESULTS AND DISCUSSION

Figure 3. The relation between the removal percentage of methylene blue solutes against adsorption time

Figure 4. The relation between the removal percentage of thymol blue solutes against adsorption time

It was observed that the removal percent of both of methylene blue and thymol blue increased rapidly at the first, then mild increasing with time unit reach to the optimum time where the most of dye removed and the equilibrium between the solute and adsorbent molecules is take place. The time period (90 - 120 min) considers to be the most effective time in which 80% and 61% of methylene blue and thymol blue removal can achieved. From the charts, it can inference that the higher HA-adsorption is achieved in acidic condition compared to neutral and alkaline conditions of methylene blue and thymol blue solutions. The adsorption of both of methylene blue and thymol blue are increases in acidic medium with pH range 2 to 4, where the optimum pH of both of dyes (highest point in the chart) is found to be 4.

In this case the electrostatic interaction between dyes molecules and adsorbent surface is only the step involved in adsorption process

Figure 5. Initial dye concentration vs. adsorption efficiency for both of methylene blue.

Figure 6. Initial dye concentration vs. adsorption efficiency for thymol blue

The adsorption of methylene blue and thymol blue molecules onto the surface of HA is decreased when the initial concentration of the dye increase as shown in the previous charts. For methylene blue the most effective adsorption occurs with initial dye concentration between 0.5 to 1.3 ppm, where 96-90% of the solute in water is removed, and for thymol blue the most effective adsorption occurs with initial concentration equal to 0.05 vol%, where 84% of the solute in water is removed.

The adsorption rate start to decrease rapidly at high dye concentration and this considered to be logical because of the active sites on HA surface are rapidly occupied by dye molecules and stop or reduce adsorbent activity.

Figure 7. Plot of HA dosage against the removal efficiency of methylene blue.
The removal percent of both of methylene blue and thymol blue are proportional to the adsorbent doses, where the removal percent of solute increased as the weight of adsorbent increase, where the maximum removal of methylene blue (99.8%) is achieved with 0.35 gram of the adsorbent. In the other hand the maximum removal of thymol blue (82%) is achieved with 0.05 gram of the adsorbent. This consider to be logical because more adsorbent weight means high surface area for adsorption reaction and more available active sites on the surface of adsorbent. The previous table provide a comparison between the adsorption of two types of dyes in batch adsorption system involves HA as adsorbent. From the previous it can be conclude that, the HA adsorption system has the same optimum for both of methylene blue and thymol blue, where the removal percent of both dyes are 80.3% and 61.2% respectively. The optimum pH is found to be the same for both of methylene blue and thymol blue (pH =4), in which the removal percent of both dyes are 99.2% and 61% respectively. The removal efficiency of methylene blue increases as the decreases in the initial concentration, for methylene blue the initial concentration is found to be 0.5 ppm with efficiency equal to 96% and 50 ppm for thymol blue with efficiency equal to 82%. The increasing in adsorbent mass will increase the surface area of the adsorbent which means more active sites are available. The optimum adsorbent dose are 0.35 g and 0.05 g for both of methylene blue and thymol blue respectively.
Table 2. Comparison between the kinetic parameters of two type of adsorbate (methylene blue & thymol blue) into HA particles.

<table>
<thead>
<tr>
<th>Kinetics parameter</th>
<th>Methylene blue</th>
<th>Thymol blue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir isotherm model:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9919</td>
<td>0.9929</td>
</tr>
<tr>
<td>$q_m$ (mg/g)</td>
<td>0.07684</td>
<td>0.210247</td>
</tr>
<tr>
<td>$K_l$ (L/mg)</td>
<td>66.704</td>
<td>12.53967</td>
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<tr>
<td>Freundlich isotherm model:</td>
<td></td>
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<tr>
<td>$R^2$</td>
<td>0.9965</td>
<td>0.9977</td>
</tr>
<tr>
<td>$n$</td>
<td>2.2222</td>
<td>1.38966</td>
</tr>
<tr>
<td>$K_f$ (L/mg)</td>
<td>0.2736</td>
<td>11.18407</td>
</tr>
<tr>
<td>PSO:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9946</td>
<td>0.8871</td>
</tr>
<tr>
<td>$q_e$ (ppm)</td>
<td>0.1606</td>
<td>1220.95</td>
</tr>
<tr>
<td>$K_2$</td>
<td>0.0366965 min-1</td>
<td>0.0262542 min-1</td>
</tr>
<tr>
<td>PSO:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9988</td>
<td>0.9769</td>
</tr>
<tr>
<td>$q_e$ (mg/g.min)</td>
<td>0.1912</td>
<td>1666.7</td>
</tr>
<tr>
<td>$K_2$</td>
<td>0.03214 x10-3 (mg/g.min)</td>
<td>0.66974</td>
</tr>
</tbody>
</table>

From the previous table and according to coefficient of determination($R^2$), it can be concluded that the adsorption of both the dyes followed Freundlich isotherm and hence the HA particles had heterogeneous surfaces with multi-layer adsorption. The kinetic data were tested with PFO and PSO models. It was concluded that the adsorption of both the dyes followed the pseudo second-order kinetics.

As shown the previous figures, the both of models line does not passes through the origin, which means the adsorption of methylene blue and thymol blue onto the active sites of HA is limited by both of intraparticle diffusion and film diffusion. The first linear portion represent the boundary layer diffusion and the other linear portion indicates to intra particle diffusion.

The chart line is slightly deviated from the origin, which means that, the intra particle diffusion is only the controlling step in the mechanism of adsorption of methylene blue and thymol blue particles into the surface of the adsorbent (HA).
IV. CONCLUSION

The aim of this research is to determine the adsorption capacity and the efficiency of HA-adsorption system by using analytical measurement techniques and kinetics analysis. Analytical technique is used to measure the effect of some parameters on the adsorption efficiency, as well as, determine the optimum condition the HA-adsorption system such as optimum adsorption time, optimum pH, optimum adsorbent dose and the optimum concentration. Kinetics study is accomplished in order to study and understand the adsorption mechanism in case of the interaction between the adsorbate molecules and the surface of hydroxyapatite. The aim of this research was achieved by using HA powders and two types of dye which are methylene blue and thymol blue. This work was done by study the effect of adsorption time, pH of dye solution, dye concentration and adsorbent dose on the efficiency of HA adsorption system.

These tasks are accomplishment by preparing batch adsorption system with constant rotation velocity (150 rpm), as well as using laboratory equipment such as spectrophotometer to measure the absorbance of the sample and pH meter that used to measure and adjust the pH of the adsorbate solution. The research result was shown that, the optimum equilibrium time of the adsorption of both of dyes are the same and is found to be 120 min, the optimum pH of the both of methylene blue and thymol blue where the optimum adsorption is achieved is equal to 4. The removal efficiency of methylene blue and thymol blue is proportional to the adsorbent doses in which the percentage removal of dyes increased as the weight of adsorbent increase, this consider to be logical because more weight of adsorbent means high surface area for adsorption reaction and more available active sites on the surface of adsorbent. The adsorption of both the dyes followed Freundlich isotherm and hence the HA particles had heterogeneous surfaces. The kinetic data were tested with PFO and PSO models. It was concluded that the adsorption of both the dyes followed the pseudo second-order kinetics. From this research we can conclude that, the HA powder is very efficient porous adsorbent for dyes removal under the optimum conditions specially for basic dyes such as methylene blue.

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REFERENCES


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