Kinetics and Mechanism of removal of Phenol from Aqueous Solutions with Flyash

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Abstract

Adsorption technique is widely used for removal of toxic organic contaminants from aqueous streams. Although commercial activated carbon is an effective adsorbent, it’s widespread used is restricted due to its high cost and substantial lost during regeneration. The aim of this study is to investigate the possibility of flyash as an alternative adsorbent for phenol removal from aqueous solution. The removal of phenol from aqueous solution by flyash were investigated under various conditions of contact time, particle size, pH, concentration and temperature. The level of uptake of phenol by flyash decreased with increasing particle size and pH but increases with temperature. Rate constants for different conditions were evaluated in terms of first-order kinetics. The study is followed the pseudo-first-order rate kinetics and is found that the sorption data fit well the Lagergren equation. The main mechanisms involved in the removal of phenol from solution by flyash were the interaction between lone pair of electron present on oxygen atom of OH group of the phenol and the silica and alumina present as major constituent at the surface of the flyash. It was found that these low cost flyash adsorbent demonstrated good removal capability of phenol and hence can be used economically on large scale.

Keywords: Adsorption, flyash, phenol, kinetic parameter, Lagergren equation.

Introduction

The quest to meet and satisfy the human needs has led to the rapid industrialization which triggered increased disposal of wastewater into the environment, an action which often exceeded the admissible sanitary standards of living and results in the adverse impact on not only the aquatic environment, but consequently also on human health. The major pollutants in this wastewater include heavy metals, poly aromatic hydrocarbons, synthetic materials, etc. These pollutants accumulate in living tissues and organs, posing accumulative poisoning and serious health problems such as cancer, brain damage and even sudden death. The chemical industries globally are facing the challenges of stringent environmental regulations amidst severe market competitiveness. There is a growing demand for chemical processes that are clean, energy efficient, intrinsically safe and responsive to market demands. In order to meet these objectives, chemical industries are driving towards more environmentally friendly processes that meet requirements such as generation of nearly zero waste chemicals, less energy consumption, use of less hazardous chemicals, recyclable materials, etc. Wastewater treatment has received greater attention over the years due to the global awareness of the environmental deterioration. However, the application of various treatment techniques needs to agree with the wastewater properties. Scientists have therefore taken on the challenge to examine different means, techniques, processes and methods of removing these pollutants from aqueous media and wastewater. Due to its low cost - effectiveness, high efficiency and simple operational steps, adsorption technology is regarded as the most promising one to remove heavy metal ions and organic pollutants from effluent among the techniques mentioned above. Several types of materials such as activated carbon and rice husk, clay minerals, carbonized maize tassels, acacia leucocephala bark powder, coal have been researched to adsorb metal ions and organic pollutants from aqueous solutions. Phenol in water is considered as one of the priority pollutants by US Environmental Protection Agency. It enters into the water bodies via industrial activities such as those from steel industries, domestic wastewaters, paint industries, agricultural activities, etc. Report has shown that utilization of phenol contaminated waters causes protein degeneration, vomiting, smoky colored urine, paralysis of the central nervous system and also damages the kidney, Liver and pancreas in human body. Therefore, the World Health Organization (WHO) has established the maximum permissible concentration of phenol in drinking water as 1.0 mgL⁻¹. Thus, the elimination of phenolic compounds is a necessity in order to preserve environmental quality.

The present paper deals with the study of the feasibility of removal of phenol by flyash under kinetic conditions in an endeavor to use the data for the design of an economical and flexible batch reactor system of phenol removal.

Material and Methods

Preparation and application of Adsorbent: Flyash was obtained from Thermal Power Station, Chachai A noopur, Shahdol (M.P.) India. The flyash was sieved through standard
Charaterization of Coal Flyash: The chemical constituents of flyash are determined by Indian Standard methods¹ along with other characteristics such as loss on ignition (LOI) at 800°C. The specific gravity, surface area and porosity and are shown in table 1. The chemical compositions of different fractions of flyash are also determined by Indian Standard methods² and are shown in table 2. The results indicate that silica and alumina oxide are the major constituents of flyash. The chemical analysis data indicates that the sample consists of silicate (CaSO₄·6H₂O), quartz (SiO₂), magnetite (Fe₃O₄), anhydrite (CaSO₄), hematite (Fe₂O₃), and lime (CaO) as the major phase.

<table>
<thead>
<tr>
<th>Specific Gravity</th>
<th>Surface Area</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.75</td>
<td>7000 – 9000 cm²</td>
<td>0.34 - 0.62</td>
</tr>
</tbody>
</table>

Adsorbate: Stock solutions were prepared by dissolving 1 g of phenol in 1 L of double distilled water. The stock solutions were then suitably diluted and used for sorption experiments. The concentration of phenol is determined using UV-VIS spectrophotometer (Shimadzu Model UV-1601) at wavelength of 270 nm. It should be noticed that below 250 nm the absorption band is not specific to Phenolic compound because a lot of organic compounds have an absorption in their spectral windows.

Kinetic studies: Sorption experiments will be performed by agitating 1.0 g of flyash with 25 ml of an aqueous solution of phenol in different conditions like various particle sizes (150, 106, 45 µm), pH values (2.0, 4.0, 6.5, 8.0, and 10.0) concentrations (500, 300 and 200 mg l⁻¹), and temperatures (30°C, 40°C, and 50°C) in separate glass stoppard bottle in a shaking thermostat having speed of (65± 5 rpm) will be maintained for each run throughout the experiment to ensure uniform mixing. The stirring rate was maintained at (65±5) rpm in order to reproduce in the laboratory similar to the one present in the natural water system. At the end of predetermined time intervals the sorbent will be removed by centrifugation and the progress of sorption will then be determined using spectrophotometer. The supernatant liquid was analyzed for phenol using UV-1800 Shimadzu UV- Spectrophotometer by monitoring the absorbance changes at a maximum wavelength of 270 nm. Phenol solution was buffered at desired pH value (2.0, 4.0, 6.5, 8.0, and 10.0) with 0.05M phosphate buffer to stabilize the pH.

Results and Discussion

Chemical analysis of fraction of Flyash: The flyash was analyzed by Indian standard Method of chemical analysis of fire clay and silica refractory materials³. The physical and chemical characteristics of flyash shown in table 1, 2 indicate that major constituents are silica and alumina.

<table>
<thead>
<tr>
<th>Chemical Composition (Percentage by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
</tr>
<tr>
<td>59.54</td>
</tr>
<tr>
<td>67.00</td>
</tr>
<tr>
<td>77.75</td>
</tr>
</tbody>
</table>

Kinetic Studies: The kinetics of sorption of phenol on flyash was studied on the basis of the Lagergren equation as shown in equation 1.

\[ \log (q_e - q_t) = \log q_e - k t/2.303 \]  

Where q (mg g⁻¹) is the amount of phenol adsorbed at time t, qₑ (mg g⁻¹) is the amount adsorbed at equilibrium and k is equilibrium rate constant of adsorption. The straight line plots of \( \log (q_e - q_t) \) vs. t for phenol under different conditions indicate the validity of equation 1 and the process follows first order rate kinetics. The k value of phenol under different condition will be calculated from the linear plots of slopes.

Effect of particles sizes: The chemical analysis data for flyash listed in table 2 shown that the material is aluminosiliceous having the oxides of aluminum and silicon together with other minor constituents. The amounts of the major constituents like alumina and silica are increased as the particle size decreased. The silica and alumina contents of fly ash play a major role in the sorption of phenol. This is because of the strong chemical bonding between the lone pair of electrons present on the –OH group in the phenol and the central ion of the silicate (Si⁴⁺) as well as the presence of a weakly acidic alumina surface. From the structural viewpoint, silica is composed of SiO₂ units in which each oxygen atom is shared between two adjacent tetrahedral. According to Pauling, the Si-O bond is about 50% ionic due to the large difference in the electro negativities of oxygen and silicon. Thus, materials such as fly ash that contain this bond should be capable of adsorbing large amounts of polar molecules such as phenol. The surface area also increased as the particle size decreased and so active site increases². Hence, in addition to the increase in alumina and silica content with decreasing particle size, the increases in the specific surface area also contributed to the observed enhanced adsorption of phenol.
onto the flyash fraction containing the smallest particles as shown in figure-1. These may be summarized in table-3 which is calculated from figure-2.

\[ k_{45 \mu m} > k_{100 \mu m} > k_{150 \mu m} \]

The similar results are also obtained by Singh et al.\(^{10\text{-}11}\).

### Table-3

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Condition</th>
<th>Rate constant (min(^{-1}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>Particle Size (µm)</td>
<td>150 3.68 x 10(^{-2}) 0.991</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>106 3.92 x 10(^{-2}) 0.991</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>45 5.53 x 10(^{-2}) 0.993</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>2.0 4.38 x 10(^{-2}) 0.987</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.0 3.92 x 10(^{-2}) 0.989</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.5 3.68 x 10(^{-2}) 0.991</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.0 3.22 x 10(^{-2}) 0.992</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.0 2.99 x 10(^{-2}) 0.998</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Concentration (mg/L)</td>
<td>250 3.68 x 10(^{-2}) 0.997</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>350 4.15 x 10(^{-2}) 0.999</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>500 4.38 x 10(^{-2}) 0.991</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature (K)</td>
<td>303 3.68 x 10(^{-2}) 0.991</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>313 3.92 x 10(^{-2}) 0.999</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>323 4.15 x 10(^{-2}) 0.999</td>
<td></td>
</tr>
</tbody>
</table>

**Effect of pH:** The hydrogen in concentration (pH) primarily affects the degree of ionization of the phenolic adsorbate and the surface properties of the sorbent. Thus, the pH value of the phenol solution plays an important role in the whole adsorption process. The rate of adsorption is strongly pH-dependent, i.e. they both increase with decreasing pH. Any oxide surface creates a charge (positive or negative) on its surface. The magnitude of this charge is proportional to the pH of the solution surrounding the oxide particle\(^{11}\). As mentioned above, the principal constituents of fly ash are meal oxides containing mainly Al and Si. Such metal oxides form metal hydroxide complexes at the solution interface leading to the development of a positive or negative charge on the surface. When the pH of the solution decreases, the surface becomes positively charged and the adsorption capacity towards phenols increases as shown in figure-3. Positively charged surface sites on the adsorbent surface favours the adsorption of phenols due to electrostatic attraction. This can be explained on the basis of the formation of a positively charged surface in an acidic medium and a negatively charged oxide surface in a basic medium from the hydroxylated oxide surface of the fly ash. The whole process may be represented by the following set of equations:

\[
\begin{align*}
\text{H}^+ + \text{OH}^- & \rightarrow \text{H}_2\text{O} \quad \rightarrow \text{MOH} \rightarrow \text{MO}^- + \text{H}_2\text{O} \\
\text{H}_2\text{O} + \text{M}^+ & \rightarrow \text{MO}^- + \text{H}_2\text{O}
\end{align*}
\]

**Figure-1**

**Adsorption Kinetics of Phenol on flyash; condition: 500 mg/l; pH 6.5; Temperature 30°C**

**Figure-2**

**Laguerren plot for the adsorption of phenol on flyash; Concentration 500 mg/l; pH 6.5; Temperature 30°C**

**Figure-3**

**Adsorption Kinetics of Phenol on flyash; condition : 500 mg/l; size 150 µm; Temperature 30°C**

At lower pH values, the lone pair of electrons on the oxygen atom of the undissociated–OH group present in the benzene ring coordinated with the highly positively charged surface. This was also confirmed by the observation that the increase in rate observed at decreasing pH values may be caused by an alteration in the adsorbent surface, particularly a variation in its...
Electrokinetic character with changing pH. A low pH quite probably resulted in lowering the negative charge on the adsorbent surface, thus enhancing adsorption of the negatively charged adsorbate. At higher pH values, the dissociated phenoxide ion ($C_6H_5O^-\cdot$) was repelled by the highly negatively charged oxides on the surface. Thus, the equilibrium rate constant values calculated from linear plot from figure-4 according as equation at different pH values varied as follows and listed in table-3.

\[
pH \ 2.0 > pH \ 4.0 > pH \ 6.5 > pH \ 8.0 > pH \ 10
\]

Similar results were also obtained by Singh et al.\textsuperscript{10-11}.

Effect of concentrations: The removal rate of phenol increased as the phenol concentration increased as shown in figure-5. Similarly, the adsorption rate and the amount adsorbed both increased with increasing concentration\textsuperscript{12}. However, the sorption rate constant, $k$, as calculated from linear plot in figure-6 according as equation varied in a reverse manner because the fractional adsorption is low at high concentration. Thus, the values of $k$ varied in the order as

\[
K \ (500 \ mg/L) < K \ (350 \ mg/L) < k \ (250 \ mg/L)
\]
as listed in table-3 calculated from linear plot from figure-6. Similar results were also obtained by Singh et al.\textsuperscript{10-11}.

Effect of temperature: The sorption rate constant of the fly ash increased as the temperature increased over the range 30-50°C as shown in figure-7 probably as a result of the increase in the number of active surface centres available for adsorption. However, the net increase would depend upon the nature of the solute. This suggests that the removal of phenol on flyash involves a chemical process. The increase in uptake of the phenol with temperature may also have been due to a change in the pore size. The variation of the adsorption rate constant parameters at different temperatures as obtained from linear plot from figure-8 given in table-3 according as equation follows the order: $50^\circ C > 40^\circ C > 30^\circ C$.

Similar results were also obtained by different authors\textsuperscript{13-15}. 
Figure-8

Lagergren plot for the adsorption of phenol on flyash;
Concentration 500 mgl-1; Size 150µm ; pH 6.5

Conclusion

The present study shows the potentiality of flyash for phenolic wastewater treatment. This treatment is simple and economic. The kinetic data thus generated may be used for designing a treatment plant for phenolic effluents wherein continuous removal or recovery can be achieved on a large scale.

Acknowledgement

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References