Development of Inexpensive Adsorbent from Agro-Waste for Phenol Adsorption

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Potential adsorption of phenols-major pollutants present in various industrial wastewaters onto adsorbent powdered activated mustard cake (PAMC) derived from (mustard cake MC) agriculture waste materials was evaluated. The PAMC had meso porous pore size distribution with surface area (27 m$^2$ g$^{-1}$). The adsorption characteristics of the PAMC primarily attributed to the presence of silica or mixed oxides of Ca, Mg, Al and Fe not by the carbon. The Langmuir, Freundlich, Redlich-Peterson and Temkin models were applied to evaluate the adsorption parameters. The adsorption decreased in the order of p-nitrophenol > p-chlorophenol > phenol. Adsorption kinetics was examined using different kinetics model (Lagrgren first order, pseudo second order and intra particle diffusion model). The best results were achieved with the Langmuir isotherm equilibrium model and followed pseudo second order kinetics ($R^2 = 0.99$). The possible adsorption interactions were discussed. The adsorption mechanism is verified by FT-IR, PZC, effects of pH, urea, ionic strength and comparison between adsorption of phenols derivatives on PAMC. The adsorption mechanism is governed by complex interplay of electrostatic, π–π dispersive as well as by a charge transfer interaction. In cost analysis, it was found that the cost of PAMC ($9.5/- only) have very little compared to commercial activated carbon. The PAMC was found to be very effective for removal of phenols from their aqueous solutions.

Keywords: PAMC, Phenols, Adsorption isotherms, Kinetics, Thermodynamics, Cost-effective

Introduction

Phenol and its derivatives are hazardous materials for living beings, which are released into the aquatic environment by various industries. Phenols cause taste and odor problems to drinking water which invites many problems to human health including diarrhea, liver damage, anemia and dark urine. There are various methods available for the treatment processes for phenols from wastewater. However, in recent years, adsorption systems have been widely employed in the purification of wastewater. The content of phenolic compounds in industrial wastewater (~ 200-2000 mg/L) is usually higher than the standard limits (mostly 0.5 mg/L) established for their release into the aquatic environment. Consequently, extensive research work has been carried out using activated carbons and resins. Many researchers have shown that activated carbon is an effective adsorbent for organic compounds, especially for phenol and its derivatives. However, activated carbon presents several disadvantages. The regeneration of saturated carbon is not economical and is accompanied by loss of the adsorbent. In view of the above considerations, the search for a low cost and easily available adsorbent has led many investigators to seek relatively economic and efficient techniques using natural and vegetative adsorbents. These materials are available in large quantities and may have potential as adsorbents due to their physico-chemical characteristics and low-cost. The objective of the present work was to evaluate the analytical potential of PAMC for effective removal of phenol and its derivatives from their aqueous solutions.

Experimental

All reagents used were AR-grade chemicals. Stock solutions of the test solution were made by dissolving phenol and its derivatives in double distilled water. The pH of the test solutions was adjusted using dilute HCl (0.1 N) and NaOH (0.1 N). The PAMC was derived from an inexpensive, abundantly available and eco-friendly source.

Preparation of PAMC

The mustard cake (MC) samples were taken from a local mill and it was crushed in a pestle and mortars. The material was washed several times with distilled water until the colorless and then sun dried. The de-oiled mustard cake was treated with 20 wt% H$_2$O$_2$
at a ratio of 3:1 at 60°C for 24 h to oxidize the adhering organic matter. The resulting material was washed several times using double distilled water. The powder was dried at 110°C overnight and then burned in Muffle furnaces at 715°C for 25 min in the absence of air. The material was grounded and sieved to desired particle sizes.

**Adsorption procedure**

The adsorption equilibrium was probed by batch technique in 250 ml stoppered conical flasks contacting the PAMC (1.0 g/L) with 100 ml of phenol and its derivatives solutions of known concentrations (25 - 1000 mg/L), shaking at 100 rpm for 2 h at room temperature (30 °C), followed by filtration (0.45 µ) and subsequent analysis of residual phenol and its derivatives (p-chlorophenol and p-nitrophenol) concentration in the filtrate (double beam spectrophotometer Carry-100, Australia) at 269, 280 and 322 nm, (λ_max) respectively. The effect of adsorbate concentration, temperature, pH, ionic strength and effect of urea was investigated. For determining the effect of pH on phenol adsorption, initial pH of phenols solutions were adjusted to the desired value (2 – 10) using 0.1 N HCl or 0.1 N NaOH. The amount of phenols adsorbed by the adsorbent at equilibrium was calculated as follows:-

\[
q_e = \frac{(C_0 - C_e)V}{m} 
\]

where \( C_0 \) and \( C_e \) are initial and equilibrium concentrations (mg l\(^{-1}\)) of phenols in the solution, \( V \) the volume (l), \( m \) the weight (g) of the adsorbent and \( q_e \) is the amount of phenols adsorbed by the adsorbent at equilibrium (mg g\(^{-1}\)).

**Characterization of the materials**

The PAMC was characterized by FT-IR, SEM and BET techniques. The PAMC (2 mg) was mixed with 200 mg of KBr and then pelletized. The FT-IR spectra of the pellets were recorded using a Perkin-Elmer Precisely FT-IR spectrophotometer (model Spectrum BX). The particle morphologies of the PAMC were studied using scanning electron microscope (LEO 430, Cambridge, U.K.). Samples were mounted on aluminum stab with the help of double-sided tape. Mounted stabs were coated with gold palladium prior to analysis using a Polaron sputter coater. Nitrogen and hydrogen adsorption/desorption isotherms were obtained using a Beckmann Coulter SA 3100 surface area analyzer at 77 K. Prior to the measurements, all the samples were degassed at 398 K for 4 h.

The PZC characteristic of PAMC was determined by solid addition method using 0.1M KCl and 0.002M citrimide solutions. KCl and citrimide solution (40 ml) was taken in 100 ml stoppered conical flask. The initial pH values of the solutions were roughly adjusted between 2 and 12 by adding either 0.1N HCl or 0.1N NaOH. The total volume of the solution in each flask was adjusted exactly to 50 ml by adding the KCl and citrimide solution. The initial pH of the solution was then accurately noted. The PAMC (0.5 gm) was added to each flask. The suspensions were shaken and allowed to equilibrate for two days with intermittent shaking. The final pH values of the supernatant liquid were noted. The difference between the initial and final pH values (\( \Delta pH = pH_i - pH_f \)) were plotted against the initial pH value. The point of intersection of the resulting curve at which change in pH is zero gives the PZC. The chemical composition of the PAMC was tested in the different laboratories to confirm the result.

**Results and discussions**

**Physical appearance of the PAMC**

The physical appearance of the adsorbent derived from MC looks like white amorphous powder.

**Elemental Characterization**

An important information can be drawn from the data of elemental analysis that the adsorption characteristics of the PAMC prepared by MC is attributed to the presence of silica (20 – 35%) and CaO (31%) or CaSiO\(_3\) which is a very good adsorbent.

**FT-IR Spectroscopy**

The FT-IR spectra of synthesized PAMC (blanked and studied phenols adsorbed) are shown in Fig 1. The absorption band near at 876 cm\(^{-1}\) is due to Si-OH bond stretching which reveal that the condensation of Si-OH groups was not complete on thermal treatment\(^{14}\). The typical absorption band for Si-O-Si network vibrations were observed at 1040 cm\(^{-1}\) and 876 cm\(^{-1}\) and the absorption band at 1040 cm\(^{-1}\) increase with the amount of SiO\(_2\). Bands at 3464 cm\(^{-1}\) to 3723 cm\(^{-1}\) are due to the chemisorbed water and surface hydroxyl groups \(^{14,15,16}\). The IR band at 476 cm\(^{-1}\) belongs to O-Si-O bonding vibration\(^{17}\). Some of the other bands originating from the sample are characteristics of \( \overline{OH} \) stretching (3454 cm\(^{-1}\)). The FT-IR spectra clearly demonstrate that PAMC
contain mainly silica which is further confirmed by the elemental composition (20-30 % silica) of the PAMC. The strong IR shoulder around 1040 cm\(^{-1}\) (due to high-silica contents) is assigned to the asymmetric stretching vibration of silicon - oxygen bond in SiO\(_2\). For the IR spectra of alumina absorptions were respectively observed at 700-900 cm\(^{-1}\) and at 650-800 cm\(^{-1}\). Consequently, the high frequency strong band around 876 cm\(^{-1}\) and the weak band around 772 cm\(^{-1}\) are associated with the symmetric stretching vibrations of the aluminum-oxygen bond in Al\(_2\)O\(_3\). The mid-frequency band around 476 cm\(^{-1}\) is attributed to bending vibrations of the Al-O-Al or Al-O-Si bonds. IR band at 1425 cm\(^{-1}\) assigned Ca-O symmetric band.

**SEM Characterization**

The SEM images shown in Fig 2 clearly demonstrate the homogenous and uniform distribution of pores. The physical appearances of pores are cylindrical type.

**BET characterization**

The typical definition of pore diameter ranges is as follows: micropores, <20 Å; mesopores, 20-500 Å; macropores, >500 Å. The Brunauer-Emmett-Teller (BET) specific surface area (S\(_\text{BET}\)) is typically 26 m\(^2\)/g and have mesoporous in nature.

**PZC characterization**

The surface potential of the adsorbent may be influenced by the pH value of the coexisting liquid bulk phase. The pH value, at which the surface charge is zero, is called the point of zero charge (PZC). The surface is positively charged at pH < pH\(_\text{PZC}\) and negatively charged at pH > pH\(_\text{PZC}\). Since, pH\(_\text{PZC}\) of the PAMC was determined and found to be about 9.5, at any pH < pH\(_\text{ZPC}\), the surface of PAMC is positively charged and at pH > pH\(_\text{ZPC}\), the surface is negative.

Fig 1 δ FT-IR spectrum of the blank and phenols adsorbed PAMC

Fig 2 δ SEM images of PAMC (100 mesh) at different magnifications
Adsorption equilibrium

The Freundlich, Langmuir, Redlich–Peterson (R–P) and Temkin equilibrium isotherm equations were applied to optimize an adsorption system for the adsorption of studied phenols onto the PAMC. The comparative nonlinear plots for phenols using different isotherm models given in Fig 3, clearly showed that the Langmuir isotherm model was found best fitted among studied models. The non linear regression coefficient \( R^2 = 0.99 \) showed that the Langmuir model was better fitted model in the sorption behavior of phenols from the aqueous solution onto the PAMC than other adsorption isotherm models. It was assumed that the monolayer sorption takes place onto an adsorbent surface with a finite number of identical homogeneous sites defined by Langmuir equation. Different isotherm parameters were tabulated in Table 1.

Kinetics of adsorption

The Lagergren first order, pseudo second order and intra-particle diffusion kinetic models were tested with observed experimental results in order to describe the mechanism of adsorption process. The results of the applied models are represented on the Fig 4. The kinetic parameters of each model are tabulated in Table 2. The second-order kinetic model represents the adsorption data well with \( R^2 = 0.99 \). In the intra-particle diffusion model, the initial portion represents external rapid diffusion stage (the film diffusion). The second linear portion is the particle diffusion controlled by intra-particle diffusion. The intra-particle diffusion model does properly suit to observed data. It was concluded that the adsorption of phenols on PAMC does follow intra-particle diffusion model satisfactorily.

Fig 3 δ Plots illustrating different isotherms for phenol, p-chlorophenol and p-nitrophenol
Effect of surface functionalities and pH of solution

It has been reported that in solution, phenols behave as weak acid (pkₐ of phenol, p-chlorophenol and p-nitrophenol are 9.89, 9.37 and 7.15, respectively). The initial pH of adsorption medium is one of the most important parameters affecting the adsorption process. At pH ≥ 10, the phenols dissociate and phenolate anions are formed, while the surface functional groups are either neutral or negatively charged. The electrostatic repulsion between the identical charges lowers the adsorption capacities in the case of phenol, p-chlorophenol and p-nitrophenol. The effect of pH can also be explained using pHZPC of the adsorbent. In the present study, the pHZPC of PAMC is 9.5. At any pH below pHZPC, the surface of the adsorbent is positively charged and at pH above pHZPC, the surface is negatively charged. The adsorption of phenols on PAMC shows that adsorption decreases with increasing pH (Fig not shown). The pH primarily affects the degree of ionization of phenols and the surface properties of the PAMC. At low pH values, the surface of PAMC would be protonated and resulted in a stronger

Table 1 Different isotherms parameter for phenol, p-chlorophenol and p-nitrophenol adsorption onto the PAMC at 303 K

<table>
<thead>
<tr>
<th>Phenol</th>
<th>p-chlorophenol</th>
<th>p-nitrophenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir Isotherm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kᵢ</td>
<td>5.09×10⁻²</td>
<td>2.83×10⁻²</td>
</tr>
<tr>
<td>qₘ</td>
<td>78.4</td>
<td>95.01</td>
</tr>
<tr>
<td>R² (non linear)</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>Standard error</td>
<td>3.16</td>
<td>3.03</td>
</tr>
<tr>
<td>Freundlich Isotherm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kᵢ</td>
<td>14.34</td>
<td>9.66</td>
</tr>
<tr>
<td>1/n</td>
<td>0.33</td>
<td>0.43</td>
</tr>
<tr>
<td>R²</td>
<td>0.90</td>
<td>0.96</td>
</tr>
<tr>
<td>Standard Error</td>
<td>6.71</td>
<td>6.34</td>
</tr>
<tr>
<td>Temkin Isotherm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bᵢ</td>
<td>17.17</td>
<td>22.10</td>
</tr>
<tr>
<td>Kᵦ</td>
<td>0.47</td>
<td>0.24</td>
</tr>
<tr>
<td>R²</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>Standard Error</td>
<td>4.04</td>
<td>3.40</td>
</tr>
<tr>
<td>R-P Isotherm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>aᵦ</td>
<td>8.41</td>
<td>13.74</td>
</tr>
<tr>
<td>Kᵦ</td>
<td>2.95</td>
<td>9.91</td>
</tr>
<tr>
<td>β</td>
<td>0.82</td>
<td>0.94</td>
</tr>
<tr>
<td>R²</td>
<td>0.98</td>
<td>0.99</td>
</tr>
<tr>
<td>Standard Error</td>
<td>3.46</td>
<td>2.73</td>
</tr>
</tbody>
</table>

Fig 4 Different kinetic models for the adsorption of phenols onto PAMC: (a) Lagergren plot, (b) Pseudo second order plot and (c) Intra-particle diffusion plot
attraction for aromatic ring and electronegative group of phenols. At high pH, OH\(^-\) ions would compete with the phenolate ion for sorption sites\(^{24}\). Sorption of excess of OH\(^-\) ions could convert an initial positively charged surface of PAMC into a negatively charged surface resulting repulsion of negatively charged phenolate ions and thus adsorption decreased. This could also be due to the increased solubility of phenol in alkaline conditions, which results in greater affinity for the phenol molecules to remain in solution rather than to get adsorbed onto the carbon surface. Unionized phenol molecules would also be attracted, possibly, by physical force (H-bonding). When the solution pH is lowered than pH\(_{ZPC}\), the undissociated phenols molecules are more easily attracted by the positively charged surface of adsorbent, favoring the accumulation of phenols molecules on the surface and thus promoting adsorption. On the other hand, when the solution pH exceeded pH\(_{ZPC}\), the phenolate ions are repelled by the negative charged surface of adsorbent, hence, adsorption is decreased\(^{25-27}\).

\[
\text{M-OH} + H^+ \rightarrow \text{M-OH}_2^+ \quad \text{(2)}
\]

\[
\text{M-OH} + \text{OH}^- \rightarrow \text{M-O}^- + \text{H}_2\text{O} \quad \text{(3)}
\]

It was observed that PAMC has a maximum affinity toward phenols at pH \(~ 6.0\) to 8.0. It appears that the dominant sorption process takes place in molecular forms of phenols at lower pH is perhaps given by Eq. 2. Other reactions given by Eq. 3 plays an insignificant role in the overall adsorption of phenol onto the PAMC.

**Effect of ionic strength**

In the present study, the influence of the ionic strength on the amount of the adsorption was investigated. It is anticipated that the hydrophobic force could be the primary driving force for the adsorption of phenol onto PAMC. If a hydrophobic interaction makes a significant contribution to adsorption of phenol onto PAMC, the adsorption density would have increased with the addition of salt due to salting out effect\(^{28,29}\). It was found that the adsorption capacity of phenols exhibits an appreciable increase with addition of KCl. A possible cause is the adsorption of H\(_2\)O onto adsorbent. Due to the presence of hydroxyl groups in adsorbent, water cluster might be formed on the surface by hydrogen bonding, which can interface the adsorption of phenols. In the presence of KCl, water cluster can be demolished. Hence, the adsorption capacity of phenols increases.

**Effect of urea**

To explore the role of hydrogen bonding, adsorption tests were executed in the presence of urea, a hydrogen bond breaker. Adsorption was reduced in the presence of urea suggesting the role of hydrogen bonding in the present case.

**Cost Analysis**

Cost analysis is a very important parameter to establishing the criteria for the adsorbent and the choice for removal of pollutants from waste-water. The utilization of agricultural waste materials to produce adsorbent for water treatment is quite economic and can substitute commercial activated carbon (CAC). When we have compared the cost of developed adsorbents with commercial activated carbon, it was found the cost of synthesized adsorbents have very little, in comparison with CAC (Merck, charcoal activated, pure) which comes at a market value of approx $ 172.96 per kg. The transportation cost is negligible due to the local availability of the raw materials. The cost of storage is also eliminated as the adsorbent is mostly stable under high temperature or pressure. In comparison with commercial activated carbon\(^{30}\), it was found that the studied adsorbents are much economic (Table 3) and their uses for removal of phenols from aqueous solutions were quite beneficial to industries.
Table 3  Cost of PAMC

<table>
<thead>
<tr>
<th>Duration (h) / amount (ml)</th>
<th>Unit cost ($/KWh)</th>
<th>Power rating (KWh)</th>
<th>Price ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost of drying</td>
<td>30 h</td>
<td>0.06</td>
<td>1.5</td>
</tr>
<tr>
<td>Cost of activation</td>
<td>0.5</td>
<td>0.06</td>
<td>1.4</td>
</tr>
<tr>
<td>Cost of chemicals</td>
<td>i</td>
<td>i</td>
<td>i</td>
</tr>
<tr>
<td>Extra charge</td>
<td>i</td>
<td>i</td>
<td>i</td>
</tr>
<tr>
<td>Total cost</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conclusions

PAMC, produced from MC demonstrates high potential for effective removal of phenol and its derivatives from waste water compared to various commercial and vegetative adsorbent. Since the cost of adsorbent is one of the crucial and important factors to know the economic feasibility of the process, the precursor of PAMC is an agricultural waste materials and its cost was negligible. The various equilibrium models such as Freundlich, Langmuir, Redlich-Peterson and Temkin were tested to describe the equilibrium adsorption. However, Langmuir isotherm was found most suitable as representative of the equilibrium adsorption data. The adsorption decreased in the order of p-nitrophenol > p-chlorophenol > phenol. The kinetic modeling of the phenols adsorption onto PAMC indicates that adsorption process is pseudo-second order with the correlation coefficients higher than 0.99. The adsorption properties of studied adsorption system depend on several factors such as pKₐ, polarity and solution condition such as pH, ionic strength and hydrogen bond breaker. The adsorption mechanism is governed by complex interplay of electrostatic, ‘dispersive as well as by the charge transfer interaction. The cost of PAMC have very little compared to commercial activated carbon. The precursor employed for the preparation of the activated carbon (PAMC) is widely available and inexpensive. Hence, scalable for industrial purpose.

Acknowledgements

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References

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