Physicochemical effect of activation temperature on the sorption properties of pine shell activated carbon

Agha Arslan Wasim and Muhammad Nasiruddin Khan

ABSTRACT

Activated carbons produced from a variety of raw materials are normally selective towards a narrow range of pollutants present in wastewater. This study focuses on shifting the selectivity of activated carbon from inorganic to organic pollutants using activation temperature as a variable. The material produced from carbonization of pine shells substrate was activated at 250 °C and 850 °C. Both adsorbents were compared with commercial activated carbon for the sorption of lead, cadmium, methylene blue, methyl blue, xylene orange, and crystal violet. It was observed that carbon activated at 250 °C was selective for lead and cadmium whereas the one activated at 850 °C was selective for the organic dyes. The Fourier transform infrared spectroscopy study revealed that AC850 had less surface functional groups as compared to AC250. Point of zero charge and point of zero salt effect showed that AC250 had acidic groups at its surface. Scanning electron microscopy depicted that increase in activation temperature resulted in an increase in pore size of activated carbon. Both AC250 and AC850 followed pseudo-second-order kinetics. Temkin isotherm model was a best fit for empirical data obtained at equilibrium. The model also showed that sorption process for both AC250 and AC850 was physisorption.

Key words | activation temperature, pine shell, selective sorption, sorption, wastewater

INTRODUCTION

Activated carbons produced commercially use a variety of raw materials including coconut coir (Kadirvelu & Namavivayam 2003), saw dust (Malik 2003), coal (Arslan & Pehliván 2007), charcoal (Dias et al. 2007). The raw materials required for the preparation of activated carbon should have high carbon content that is why different agricultural wastes have been explored for their potential to be used as raw material at commercial level. This includes the study of rice husk (Dada et al. 2012; Muniandy et al. 2014), bagasse (Mohan & Singh 2002), eucalyptus bark (Kongsuwan et al. 2009), corncob (Khan & Wahab 2007), Parthenium hysterophorus weed (Ajmal et al. 2006). Pine shell is an agricultural waste produced after removing kernel fruit from the pine nuts. Moreover, for each crop, a fraction of pine nuts which is void of kernels is also considered as agricultural waste. The study of this material for the preparation of useful adsorbent and optimization of experimental conditions to improve its selectivity can be helpful in the reduction of solid waste.

Activated carbon is produced either by physical activation or chemical activation (Park & Kim 2001). Former being carried out at temperature higher than 800 °C utilizing different gases like carbon dioxide, steam, oxygen, or their mixture, to introduce surface functional groups (Angin 2014). Chemical activation requires a prior treatment of raw material with a chemical agent like sulfuric acid, nitric acid, zinc chloride, sodium hydroxide followed by pyrolysis at 400–600 °C.

Activation step plays a significant role in the preparation of activated carbon. It increases the specific surface area of the substrate by increasing the number and size of the pores (Nowicki et al. 2015). Besides porosity, the activation process also introduces functional groups at the surface of activated carbon. This step is highly temperature dependent. Low temperature activation ranging from 200–600 °C yields hydroxyl, carboxyl groups at the surface (Corapcioğlu & Huang 1987), while high temperature activation strips off these functional groups (Ishizaki & Martí 1981). Preparation of activated carbon at different activation temperatures and sorption studies using both inorganic and organic pollutants can provide valuable information about the effect of
activation temperature on the selectivity of the prepared activated carbons. For this purpose, a prior selection of different activation temperatures and a variety of pollutants is required. Activation at 250°C was selected to represent low temperature activation while 850°C was selected to observe the effects of high temperature activation.

There is a wide range of inorganic pollutants including cadmium, copper, lead, zinc, nitrogen, nitrate, nitrite, ammonia, phosphate, etc. However, cadmium and lead ions were selected as representative inorganic pollutants because of their wide range of industrial applications. Improper disposal of devices containing these metals can easily contaminate the natural water reservoirs. Similarly, there is a wide variety of organic pollutants that can be used for sorption on the prepared activated carbons but organic dyes are selected for their greater environmental impact. Besides their pleasant effect, dyes do have adverse esthetic effects. Water streams contaminated with dyestuff appear to be quite offensive. The presence of dyestuff in water bodies can significantly reduce the dispersion of daylight which can reduce the rate of photosynthesis in aquatic plants. Textile dyes are mostly organic; their presence reduces the amount of available oxygen, hence increasing the biological oxygen demand of water body which also has toxic effects on the aquatic life (Saratale et al. 2006). Methylene blue (MB) and crystal violet were selected to represent cationic dyes, xylenol orange as an anionic dye, whereas, methyl blue possess both cationic and anionic groups.

Metal ions mainly undergo chemical reactions through interionic interactions, whereas organic molecules can interact through ion–dipole, dipole–dipole, and interionic interactions. Polarizability in organic molecules also introduces a unique set of properties in them. Interaction of metal ions and organic molecules with the adsorbent can help in the elucidation of nature of interaction along with the type of groups present at the surface of adsorbent.

In this work the effect of activation temperature was studied systematically to evaluate the shift in the sorption affinity of pine shell activated carbon. The raw material was carbonized using concentrated sulfuric acid and activated at two different temperatures, 250 and 850°C labeled as AC250 and AC850 respectively. Both materials were studied for sorption of organic dyes and heavy metals from aqueous medium to study the shift in selectivity of the prepared activated carbons. MB, methyl blue, xylenol orange, and crystal violet were used as the representative of organic dyes, whereas lead and cadmium ions were used as inorganic pollutants. The change in sorption behavior of activated carbons was supplemented with the pH point of zero charge (pzc), point of zero salt effect (pzse), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) spectroscopy studies. Sorption kinetics and isotherms were also studied to evaluate the nature of sorption process for both adsorbents.

**MATERIAL AND METHOD**

**Scheme of preparation**

Hollow nuts of Chilgoza pine (*Pinus gerardiana*) were crushed to remove rotten fruit, washed with tap water, rinsed with distilled water and dried for 8 hours in an oven at 80°C. Dried shells were ground and subsequently sieved at 425 μm mesh size. Activated carbons were prepared according to the scheme mentioned in Figure 1.

Each gram of powdered pine shell was carbonized using 4 g of concentrated sulfuric acid. The substrate and acid were mixed thoroughly for a couple of minutes and heated at 250°C for 2 hours in a muffle furnace. The residue was washed over a Buchner funnel fitted to a vacuum assembly until the filtrate was free of sulfate ions. The activated...
carbon was dried in oven at 100 °C for 4 hours and labeled as AC250. A batch of AC250 was further activated at 850 °C in muffle furnace using porcelain crucible and labeled as AC850. Muffle furnace was purged with nitrogen gas throughout the activation process to maintain an oxygen deficient environment. Commercial activated carbon (CAC) (Merck CAS 7440-44-0) was used as a reference material. Sorption of heavy metals was studied in batch mode using AC250, AC850, and CAC. In each run, 0.05 g adsorbent was treated with 50 mL of 100 ppm Pb solution for 15 min. The initial and remaining concentration of Pb ions in the filtrates was measured using Perkin Elmer 2138 atomic absorption spectrometer. Sorption capacity was calculated instead of % removal in order to compensate a slight run to run variation in the mass of activated carbon. Sorption of Cd was also studied using the same parameters. The initial concentration and contact time were 50 ppm Cd and 30 min respectively.

A 50 mL aliquot of dye solution prepared in distilled water was allowed to interact with 0.05 g of AC250, AC850, and CAC for 15 min. Absorbance of the filtrates was measured on Schimadzu 1601 UV-Vis spectrophotometer. All filtrates were buffered to pH 4.7 before absorbance measurement. The respective initial concentrations of methyl blue, MB, crystal violet, and xylgenol orange were 10, 10, 40, and 25 ppm. The effect of dye sorption on filter paper was minimized by filtration of calibration standards using same procedure used for test samples.

Point of zero charge

In this study a series of solutions was prepared with different pH values ranging from 2 to 10. A 10 mL aliquot of each solution was left to equilibrate with 0.025 g of adsorbent in an airtight container for 24 hours (Khan & Sarwar 2007). Finally, the pH was measured using a calibrated pH meter. The ionic strength of each solution was maintained at 0.015 mol L\(^{-1}\) sodium nitrate. The pH of each solution was adjusted using 0.015 mol L\(^{-1}\) nitric acid and 0.015 mol L\(^{-1}\) sodium hydroxide.

Point of zero salt effect

The pzse for AC250, AC850, and CAC was determined using potentiometric titration method (Vanloon & Duffy 2005). For each titration 1.0 g of adsorbent was suspended in 35 mL aliquot NaCl solution at particular ionic strength, used as supporting electrolyte. The suspension was first titrated with acid solution of same ionic strength. The titration against base was carried out on a fresh suspension with the same ionic strength. HCl and NaOH were selected as acid and base, respectively. The concentration of each titrant was 0.05 mol L\(^{-1}\) and the ionic strength was varied from 0.0001 to 1.0 mol L\(^{-1}\). The titrant was transferred using a micropipette, and a plot of pH against volume of acid or base added was used to determine the value of pzse for each adsorbent.

Sorption kinetics

Sorption kinetics of AC250 was studied using Cd(II) ions, while MB dye was used to study sorption kinetics of AC850. In each case the activated carbon was shaken for a fixed amount of time on a thermostatic horizontal shaker set at 298 K. Same amount of adsorbent and initial concentration of adsorbate were used for each run. The amount of adsorbent used was 0.05 g for 100 mL of adsorbate solution. Initial concentration of Cd(II) ions was 50 mg L\(^{-1}\), whereas the initial concentration of MB was 160 mg L\(^{-1}\). The shaker was set at 100 rpm. Each solution was sampled, filtered, and analyzed after specified time intervals for the remaining concentration of adsorbate. Cd(II) ion was analyzed using atomic absorption spectrometer and MB was analyzed using Schimadzu 1601A spectrophotometer.

Sorption isotherm

Sorption isotherms of AC250 and AC850 were studied in batch mode using Cd(II) ions and MB as adsorbate, respectively. For each run, 0.05 g of adsorbent was exposed to 100 mL of adsorbate solution overnight to reach equilibration. The solution was agitated on thermostated horizontal shaker at 100 rpm at 298 K. Initial concentration of Cd(II) was varied from 50 to 300 mg L\(^{-1}\) whereas for MB the concentration range was 10–320 mg L\(^{-1}\).

RESULTS AND DISCUSSION

Sorption of heavy metals

The sorption capacities of AC250, AC850, and CAC for cadmium and lead are shown in Figure 2. It was observed that AC250 had highest sorption capacity for both lead and cadmium. Sorption capacity of AC850 for the same metal ions was quite low as compared to AC250. However, sorption capacity of AC850 was quite similar to that of H-form CAC.

The reduced sorption capacity of AC850 for lead and cadmium ions can be explained by the loss of active sites,
initially present at the surface of the AC250. Since metal ions are sought to interact by ion–ion and/or ion–dipole interaction it can be said that the activation process would have destroyed the ionic and/or dipole sites of the parent material.

**Sorption of organic dyes**

The effect of activation temperature on the affinity of the prepared carbon for organic compounds was studied using crystal violet, MB, methyl blue, and xylenol orange. Figure 3 summarizes the sorption behavior of methyl blue and xylenol orange. The two dyes had little or no tendency to adsorb on AC250, whereas the sorption was quite significant on AC850. However, maximum interaction was observed for CAC. The sorption trend of these organic dyes was quite opposite to that observed for heavy metals. This behavior may be attributed to the interaction of organic part of the dye with the carbon skeleton of AC850 and CAC. This can be explained using the molecular structure of the dye molecules as shown in Figure 4. Xylenol orange, being an anionic dye, lacks positively charged group in the molecule that can interact with AC250, whereas the positively charged ammonium group in methyl blue is sterically hindered to interact with the AC250.

The sorption data for MB and crystal violet are summarized in Figure 5. Although sorption trend is similar to methyl blue and xylenol orange, AC850 showed significant affinity towards MB and crystal violet, which can be attributed to the polarizable nature of the molecule.

**FTIR study**

The FTIR spectra of substrate, AC250, AC850, and CAC are shown in Figure 6. Broad peak at 3,404–3,452 cm\(^{-1}\) corresponds to stretching of N–H or O–H groups, found usually in most organic materials. FTIR peaks at 2,927–2,933 cm\(^{-1}\) are associated with stretching of sp\(^3\) hybridized C–H bond, mostly from methyl or methylene group. However, the band at 1,629–1,654 cm\(^{-1}\) corresponds to the presence of C=O or C=C stretching. The band at 1,543–1,567 cm\(^{-1}\) is associated with asymmetric stretch of N–O bond.

Sulfonate group peaks, characterized by a strong peak in 1,100–1,300 cm\(^{-1}\) and weak peak in 1,000–1,200 cm\(^{-1}\), were observed in AC250. However, FTIR spectrum of AC850 had quite weak intensity of the peaks indicating loss of sulfonate groups.
groups during activation at 850 °C. The FTIR spectrum of substrate also possesses peaks in this region; however, the pattern of peak intensity was opposite to that observed for AC250. FTIR peaks ranging 1,000–1,300 cm\(^{-1}\) corresponds to the presence of sulfonate (C=S–O) and phosphate (P–O–C asymmetric stretch); may indicate the presence of these groups in the substrate. FTIR spectrum of CAC had a broad peak in 1,000–1,300 cm\(^{-1}\) range having maxima at 1,120 cm\(^{-1}\); this peak was attributed to C–O single bond stretching.

It was observed that the intensity of FTIR absorption peaks which corresponded to polar functional groups (excluding broad peak for the O–H group) was quite attenuated in both AC850 and CAC as compared to that observed for AC250. This led to interpret that observed drop of sorption affinity for ionic inorganic species corresponds to the loss of active polar or ionic sites during their activation at high temperature. However, this high temperature activation may have caused an increase in the polarizability of carbon skeleton of AC850 and CAC (maybe because of increased conjugation) which ultimately enhanced the sorption of organic species.

**Point of zero charge**

Figure 7 shows the pH–pzc plot for AC250, AC850, and CAC. It was observed that AC250 lost most of its property...
to resist change in pH during its course of conversion into AC850. Despite different initial pH values of solutions, the final pH was found to level off at a limiting value of 3 for AC250, whereas AC850 tended to level at pH 5. High temperature treatment of AC250 resulted in a loss of acidic functional groups, which reduced the ability of adsorbent to release protons in the solution, consequently increasing the limiting pH. CAC had a very little tendency to resist change in the pH of the solution. This may be due to presence of even smaller fraction of acidic groups at its surface that can establish an acid base equilibrium.

Point of zero salt effect

Potentiometric titration of adsorbent suspension at different ionic strength was used to characterize the effect of activation temperature on the surface properties of the prepared activated carbons. The plot of pH versus volume of acid or base for AC250, AC850, and CAC is shown in Figure 8. The value of pzc, obtained from the point of intersection of the curves at different ionic strengths, for AC250, AC850, and CAC was 2.60, 5.05, and 5.45 respectively. The protonation or deprotonation of active sites produces net positive or negative charge at the surface of adsorbent particles. This protonation–deprotonation equilibrium depends upon the ionic strength of the medium. The pH at which surface positive becomes equal to the negative charge in the presence of non-reactive electrolyte corresponds to the pzc (Khan & Sarwar 2007). The shape of titration plot and value of pzc for AC850 were quite similar to that for CAC. However, titration plot for AC250 and its pzc value were entirely different. Low value of pzc for AC250 showed that the surface active sites were more acidic as compared to AC850 and CAC. Since AC850 was obtained after heating AC250 at high temperature one can interpret that the process resulted in the loss of acidic functional groups. It was observed that ionic strength affected the acid base equilibrium. The effect of ionic strength was highest in case of AC850 and least in case of CAC.

Scanning electron microscopy

The images obtained from SEM are shown in Figure 9. The images were obtained using 20 kV acceleration potential and ×2500 magnification. It can be seen that the activated carbons were highly porous in nature. However, one prominent feature that is common between AC850 and CAC is the large pore size as compared to AC250. This can be a manifestation of high temperature activation. Loss of volatile matter at high temperature and nitrogen atmosphere would have resulted in an increase of porosity and pore size. From the results of sorption studies, it can be said that increased pore size assisted the sorption of organic dyes. The outcome of large pore size was not synergistic for ionic species which can be due to the lack of interaction between these ionic species and the adsorbent.

Sorption kinetics

The kinetics of Cd(II) ions and MB sorption on AC250 and AC850 was studied at room temperature. Pseudo-first-order model proposed by Lagergren, pseudo-second-order model proposed by Ho and McKay, and Weber–Morris intraparticle diffusion model were applied on the kinetic data. Statistical error functions were used to determine the agreement between empirical and calculated kinetic data. Model
with least values of error functions was considered as appropriate model.

**Pseudo-first-order kinetic model**

Pseudo-first-order model relates the rate of sorption to the difference of sorption capacity at equilibrium and capacity at time instant ‘t’ according to Equation (1).

\[
\frac{dq}{dt} = k_1(q_e - q_t)
\]  

(1)

where \(q_e\) and \(q_t\) are, respectively, the sorption capacity at equilibrium and time instant \(t\) (min). Sorption capacity is the amount of adsorbate adsorbed per unit amount of adsorbent, expressed as \(\text{mg g}^{-1}\). \(k_1\) is the pseudo-first-order sorption rate constant, expressed as \(\text{min}^{-1}\). Integration and rearrangement of Equation (1) transforms it to a linear form as shown in Equation (2).

\[
\ln(q_e - q_t) = \ln q_e - k_1t
\]  

(2)

Linear plots of \(\ln(q_e - q_t)\) versus \(t\) were used to determine \(k_1\) and \(q_e\) as summarized in **Table 1**. Values of statistical error functions for the model are also tabulated in **Table 1**.

**Pseudo-second-order kinetic model**

The mathematical expression for pseudo-second-order model is shown in Equation (3).

\[
\frac{dq}{dt} = k_2(q_e - q_t)^2
\]  

(3)

where \(k_2\) is the pseudo-second-order kinetic constant, expressed as \(\text{g mg}^{-1} \text{min}^{-1}\). The differential equation when integrated gives a linear equation as shown in Equation (4).

\[
t = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t
\]  

(4)

Plot of \(t/q_t\) versus \(t\) was used to determine kinetics constants summarized in **Table 2**.

![Figure 8](https://iwaponline.com/wst/article-pdf/75/5/1158/454679/wst075051158.pdf)
The values of error functions obtained for sorption kinetics of Cd(II) on AC250 revealed that pseudo-second-order model best explains the sorption process. Sum of absolute error (SAE), sum of the square of error (SSE), chi-square ($\chi^2$), and normalized standard deviation ($\Delta q$) were calculated using Equations (5)–(8). Lower the value of the error functions, higher the agreement between the selected model and the empirical data. The error functions values were quite high for pseudo-first-order kinetics model. However, pseudo-second-order model well accommodated the empirical data obtained for sorption of MB on AC850. The pseudo-second-order rate constant ($k_2$) values for AC250 and AC850 were $13.1 \times 10^{-5}$ and $7.21 \times 10^{-5}$ g mg$^{-1}$ min$^{-1}$. Higher value of rate constant for AC250 predicted faster rate of sorption. However, the equilibrium capacity of AC850 was higher than AC250. It can, therefore, be concluded that AC850 shows high extent of sorption at relatively slow rate.

$$\text{SSE} = \sqrt{\frac{\sum_{i=1}^{n} (q_{exp} - q_{cal})^2}{n}}$$

(5)

$$\text{SAE} = \sum_{i=1}^{n} |q_{exp} - q_{cal}|$$

(6)

$$\chi^2 = \sum_{i=1}^{n} \left(\frac{(q_{exp} - q_{cal})}{q_{cal}}\right)^2$$

(7)

$$\Delta q(\%) = \sqrt{\left(\frac{q_{exp} - q_{cal}}{q_{cal}}\right)^2 \times 100}$$

(8)

**Weber–Morris intraparticle diffusion model**

For highly porous material, sorption is assumed to be controlled by the process of intraparticle diffusion. Weber–Morris model expressed using Equation (9) evaluates the role of diffusion in sorption process. A linear plot between $q_t$ and $t^{1/2}$ over the whole time range predicts that sorption is a diffusion

| Table 1 | Kinetics parameters for pseudo-first-order kinetic model and values of statistical error functions at 298K |
|---|---|---|---|---|---|
| Pseudo-first-order | $k_1$ (min$^{-1}$) | $q_e$ (mg g$^{-1}$) | SAE | SSE | $\chi^2$ | $\Delta q$ (%) |
| AC250 | 0.040 | 93 | -107 | 22 | -1.84 | 37 |
| AC850 | 0.025 | 111 | -91 | 19 | -1.55 | 32 |

| Table 2 | Kinetics parameters for pseudo-second-order kinetic model and values of statistical error functions at 298K |
|---|---|---|---|---|---|---|
| Pseudo-second-order | $k_2 \times 10^5$ (g mg$^{-1}$ min$^{-1}$) | $q_e$ (mg g$^{-1}$) | SAE | SSE | $\chi^2$ | $\Delta q$ (%) |
| AC250 | 13.1 | 122 | 0.44 | 1.86 | 0.025 | 3 |
| AC850 | 7.21 | 153 | -18.92 | 8.04 | 0.058 | 12 |
controlled process.

\[ q_t = k_{id}t^{1/2} + C \quad (9) \]

where \( k_{id} \) is intraparticle diffusion rate constant (mg g\(^{-1}\) min\(^{-0.5}\)) and \( C \) is a constant (mg g\(^{-1}\)). Figure 10 shows Weber–Morris intraparticle diffusion plot for the sorption of Cd(II) ions on AC250 and MB on AC850. The presence of curves with different slopes in a single plot showed that sorption process was controlled by more than one type of diffusion process.

**Adsorption isotherm**

Langmuir, Freundlich, and Temkin isotherms models were applied on the sorption data obtained at equilibrium. The best model among them was selected using statistical error functions.

**Langmuir model**

An assumption that the adsorbent has fixed number of sorption sites and only one adsorbate molecule can occupy a particular site forms the basis of Langmuir model. The mathematical expression for this model is shown in Equation (10).

\[ q_e = \frac{K_L C_e}{1 + K_L C_e} q_m \quad (10) \]

The linearized form of this equation is shown in Equation (11).

\[ \frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \]

where \( C_e \) is the equilibrium concentration (mg L\(^{-1}\)) of adsorbate in solution and \( q_e \) is the amount adsorbed per unit mass of adsorbent (mg g\(^{-1}\)). \( q_m \) (mg g\(^{-1}\)) is an estimate of maximum sorption capacity as the amount of adsorbate per unit mass of adsorbent at complete monolayer coverage; \( K_L \) (L mg\(^{-1}\)) is the Langmuir isotherm constant which is related to the energy of sorption. A plot of \((C_e/q_e)\) against \( C_e \) for both adsorbents was used to calculate isotherm parameters for this model as shown in Table 3.

It was also observed that the value of \( q_m \) for AC250 was greater than AC850. This may be attributed to the size of adsorbate. Metal ions are smaller in size as compared to organic dye molecules and AC250 being selective to metal ions can therefore accommodate more adsorbate. The energy of sorption, \( K_L \), was high for AC850, which predicts the sorption process to be more favorable.

**Freundlich model**

The Freundlich model is an empirical model which is described by Equation (12).

\[ q_e = K_f C_e^{1/n} \quad (12) \]

where \( q_e \) (mg g\(^{-1}\)) is the amount adsorbed per unit amount of adsorbent under equilibrium condition. \( C_e \) (mg L\(^{-1}\)) is the equilibrium concentration of adsorbate in aqueous phase. \( K_f \) (mg g\(^{-1}\)(L mg\(^{-1}\))\(^{1/n}\)) is Freundlich isotherm constant that is related to capacity of sorption, whereas \( n \) is a constant related to the intensity of sorption. The theoretical assumptions for this model are that the intermolecular repulsion among the molecules of adsorbed species and adsorbent’s surface heterogeneity can affect the sorption process.
means that active sites have a distribution of sorption energy. The equation for Freundlich isotherm model has the following linearized form as shown in Equation (13).

\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \]  \hspace{1cm} (13)

The isotherm constants for Freundlich model were calculated using slope and intercept of linearized plot for Freundlich model and tabulated in Table 3.

The isotherm parameter \(1/n\) is related to the intensity of sorption and the heterogeneity of the sorption sites. The value of \(1/n\) closer to 1 indicates that the active sites are homogenous (Mane & Vijay Babu 2013). The value of \(1/n\) for AC250 and AC850 is 0.159 and 0.163, respectively. Low values of \(1/n\) predicted high degree of heterogeneity in the nature of active sorption sites.

**Temkin model**

Temkin isotherm model assumes that the heat energy released as a result of sorption process decreases linearly with the increase in the surface coverage. The mathematical expression of this model and its linearized form are shown in Equations (14) and (15), respectively.

\[ q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \]  \hspace{1cm} (15)

In this equation, \(R\) and \(T\) are gas constant (J mol\(^{-1}\) K\(^{-1}\)) and temperature (K) respectively. \(A_T\) is the equilibrium binding constant (L g\(^{-1}\)), and \(b_T\) is Temkin isotherm constant related to the heat of sorption (J mol\(^{-1}\)). A plot of \(q_e\) against \(\ln C_e\) was used to obtain Temkin isotherm parameters as tabulated in Table 3. The values of \(A_T\) for AC250 and AC850 were 6.17 and 343 L g\(^{-1}\), respectively. High value of binding constant, \(A_T\), for AC850 indicates strong interaction between dye molecules and the carbon. The comparison of \(b_T\), parameter related to the heat of sorption, showed parallel trend for both AC250 and AC850. The value of \(b_T\) for AC250 and AC850 was 8.28 and 12.4 kJ mol\(^{-1}\), respectively. High value of \(b_T\) makes the process more favorable for AC850. The experimental values of \(b_T\) were lower than 20 kJ mol\(^{-1}\) which is the threshold value for chemisorption (Rahman & Haseen 2014). Hence it was concluded that sorption process was physisorption for both adsorbents.

The values of error functions and correlation coefficient calculated for each model are summarized in Table 4. High value of correlation coefficient was observed for each model, which made the selection bit difficult. Minimum values of error functions were observed for Temkin model.

**Table 3** Isotherm parameters for sorption on AC250 and AC850 at 298K

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Temkin</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC250</td>
<td>q_m (mg g(^{-1}))</td>
<td>K_L (L mg(^{-1}))</td>
<td>K_f (mg g(^{-1}))(L mg(^{-1}))(^n)</td>
</tr>
<tr>
<td>226</td>
<td>0.0549</td>
<td>88.48</td>
<td>0.159</td>
</tr>
<tr>
<td>AC850</td>
<td>210</td>
<td>0.821</td>
<td>94.43</td>
</tr>
</tbody>
</table>

**Table 4** Error function values for the selected isotherm models for sorption on AC250 and AC850 at 298K

<table>
<thead>
<tr>
<th>Adsorbent: AC250</th>
<th>Adsorbent: AC850</th>
</tr>
</thead>
<tbody>
<tr>
<td>Statistical parameter</td>
<td>Langmuir</td>
</tr>
<tr>
<td>SSE</td>
<td>6.11</td>
</tr>
<tr>
<td>SAE</td>
<td>6.56</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>0.101</td>
</tr>
<tr>
<td>R^2</td>
<td>0.9988</td>
</tr>
</tbody>
</table>
for both adsorbents; therefore, it was selected as the isotherm model for both adsorbents.

CONCLUSION

This study revealed that activation temperature played an important role in the selectivity of adsorbent. AC250 activated at 250 °C has high affinity toward ionic species like heavy metal ions. High temperature activation at 850 °C changed its affinity towards organic substances. The FTIR studies revealed that high temperature activation stripped off the functional groups from the surface of adsorbent. pH-pzc and pze studies revealed that AC250 had acidic functional groups at its surface. FTIR, pH-pzc, and pze studies also revealed that AC850 acts very similar to CAC. SEM images revealed that high temperature activation resulted in an increase in pore size, as observed for AC850. Sorption process for both carbons followed pseudo-second-order kinetics, AC250 being faster than AC850. Temkin model best accommodated the experimental data obtained at equilibrium and predicted the sorption process as physisorption. Moreover, the pine shell appeared as a good alternate for the preparation of CAC. A blend of activated carbon from the two activation temperatures may yield a composite material which can be used for the removal of both organic and inorganic pollutants from wastewater.

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