Experimental study and quantum-chemical simulation of piroxicam adsorption on the coal sorbent from walnut shells

E M Evsina¹, T V Alikova² and N V Zolotareva²

¹Department of Automated Design and Modeling Systems, Astrakhan State University of Architecture and Civil Engineering, 18, Tatishchev St., Astrakhan 414056, Russia
²Department of Analytic and Physical Chemistry, Astrakhan State University, 20a, Tatishchev St., Astrakhan 414056, Russia

E-mail: evsinalena@mail.ru

Abstract. The aim of this work was to study the sorption of piroxicam on the surface of activated carbon obtained by heat treatment from walnut shells. The objects of study are piroxicam (a) and model clusters of the sorbent. The quantitative determination and study of the sorbability of piroxicam is based on photometric recording of spectra at λ 400 nm. The most complete sorption of piroxicam occurs at pH 6,8 – 7,3, where the maximum difference in the optical density of the solutions was observed before and after sorption, which indicates the formation of a stable state of piroxicam. The results obtained from three series before and after sorption were subjected to statistical processing. The dependences "sorption – equilibrium concentration" presented at various temperatures made it possible to attribute the obtained curves to the Langmuir solution. Based on the obtained thermodynamic indicators, the following conclusions can be made: the reaction proceeds spontaneously, exothermally. Saturation of the surface of activated carbon with a monomolecular layer of piroxicam does not depend much on temperature changes, which is confirmed by close values of thermodynamic parameters at three temperatures. Quantum chemical calculations of the starting materials and model adsorption complexes in the "piroxicam – activated carbon surface" system were performed using the GAMESS US and MOPAC software. As a result of the work done, it was found that activated carbon obtained by heat treatment of walnut shells is a good and quite promising material for concentrating piroxicam and other drugs with the aim of subsequent determination from water and various biological environments.

1. Introduction

Currently, the concentration of drugs on the surface of coal sorbents occupies a key position in the analytical chemistry of the determination of substances. As coal sorbents they use medical coal; coal obtained from the seeds of fruit trees or coconut shells; composites consisting of coal and hard sand; natural gas, petroleum and coal tar products; modified carbons treated with a mixture of concentrated acids or alkalis, etc. [1-4]. The aim of this work was to study the sorption of piroxicam on the surface of activated carbon obtained by heat treatment from walnut shells. The objects of study are piroxicam figure 1 and model clusters of the sorbent figure 2 (a, b) [5].

Figure 1

Figure 2

DOI: 10.1088/1755-1315/421/3/032002
The quantitative determination and study of the sorbability of piroxicam is based on photometric recording of spectra at \( \lambda \) 400 nm. The most complete sorption of piroxicam occurs at pH 6.8 – 7.3, where the maximum difference in the optical density of the solutions was observed before and after sorption, which indicates the formation of a stable state of piroxicam.

2. Theoretical review

2.1. Study of sorption isotherms

In 10 test tubes, having previously thermostated at \( T_1 \) 277K; \( T_2 \) 298K and \( T_3 \) 318K with a capacity of 10 cm\(^3\) we admixed 0; 0.3; 0.6; 1; 1.2; 1.6; 2; 2.5; 3; 4 cm\(^3\) of a 10\(^{-3}\) M solution of the test drug and the volume was adjusted to 10 cm\(^3\) with distilled water. The optical density of the solutions in a cuvette with a thickness of 1 cm relative to water was determined. In a second series with prepared solutions with a volume of 10 cm\(^3\), 0.2 g of a charcoal sorbent from a walnut shell was added, shaken for 5 minutes and centrifuged for 20-30 minutes at 1500 rpm, and the absorbance was again measured. The results obtained from three series before and after sorption were subjected to statistical processing. Figure 4 shows the statistically processed direct dependencies "optical density – concentration of piroxicam" at various temperatures. Sorption \( S \) (g/g) of piroxicam was calculated by the formula:

\[
S = \frac{(C_{\text{init}} - [C]) \cdot V \cdot M}{1000 \cdot m}
\]

(1)

where \( C_{\text{init}} \), [C] is the initial and equilibrium concentration of piroxicam in solution, mol/dm\(^3\); \( V \) – is the volume of the solution, cm\(^3\); \( M \) – is the molar mass of piroxicam, g/mol; \( m \) – sorbent mass, g.
The dependence of optical density on the concentration of the substance before (gg) and after sorption: 1 – at a temperature of 277K; 2 – at a temperature of 298K; 3 – at a temperature of 318K. According to least square methods: calibration graphic (CG) – $y \cdot 0.403x$.

The dependences "sorption – equilibrium concentration" presented at figure 5 at various temperatures made it possible to attribute the obtained curves to the Langmuir solution.

The limiting sorption ($S_\infty$) was determined by a graphical solution of the Langmuir equation in a straight-line formula:

$$\frac{1}{S} = \frac{1}{S_\infty} + \frac{1}{S_\infty \cdot R} \cdot \frac{1}{[C]}$$  \hspace{1cm} (2)

$$\Delta H = \frac{R \cdot T \cdot T_j \cdot \ln(K_j / K_i)}{T_j - T_i}$$  \hspace{1cm} (3)

$$\Delta G = -R \cdot T \cdot \ln K$$  \hspace{1cm} (4)
\[ \Delta S = \frac{\Delta H - \Delta G}{T} \]  

(5)

where \( K \) is the adsorption constant.

Figure 6 shows a graph of the dependence “\( 1/S - 1/[C] \)" at three temperatures. For three temperatures, sorption constants were found, the change in enthalpy (\( \Delta H \)), isobaric-isothermal potential (\( \Delta G \)), and the change in entropy (\( \Delta S \)) of the sorption process were calculated. Table 1 summarizes the results of calculations for the sorption of piroxicam on the surface of activated carbon obtained from walnut shells. Based on the obtained thermodynamic indicators, the following conclusions can be made: the reaction proceeds spontaneously, exothermally. Saturation of the surface of activated carbon with a monomolecular layer of piroxicam does not depend much on temperature changes, which is confirmed by close values of thermodynamic parameters at three temperatures.

**Table 1.** Thermodynamic indicators of sorption of piroxicam on activated carbon from walnut shells.

| \( T, K \) | \( K \) | \(-\Delta G, \text{kJ/mol}\) | \( \Delta S, \text{J/(mol-K)} \) | \(-\Delta H, \text{kJ/mol}\) | \( S_c \cdot 10^4, \text{g/g} \) |
|----------|--------|----------------|----------------|----------------|----------------|
| 277      | 11,33  | 5,59           | 7,26           | 3,579          | 58,8           |
| 298      | 13,33  | 6,42           | 9,52           | 62,5           |
| 318      | 13,39  | 6,96           | 10,6           | 67,1           |

2.2. **Studying the kinetics of sorption**

25 cm\(^3\) of piroxicam solution with a concentration of 10\(^-3\) M and distilled water up to 250 cm\(^3\) (pH 7) at 298 K were introduced into a flask with a capacity of 250 cm\(^3\). 10 cm\(^3\) of blank sample were taken. 7 g of sorbent was quickly added to the remaining solution and at the same time the stopwatch was turned on and the solution was quickly mixed. After 0,33; 0,5; 0,67; 1; 1,33; 2; 6; 12; 24; 40 minutes, 10 cm\(^3\) of solution was taken, centrifuged, and then the spectrum was taken at \( \lambda \) 400 nm. The experiment was repeated at 278K and 318K. Figure 7 shows isotherms in the coordinates “optical density – time”.

![Figure 7](image)

**Figure 7.** Isotherms of sorption kinetics: 1 – 278  **Figure 8.** Dependency Graph «lnK – 1/T» K; 2 – 298 K; 3 – 318K.

According to experimental data, using the first-order kinetic equation, we calculate the values of sorption rate constants:
\[ K = \frac{1}{\tau} \ln \frac{A_0}{A}, \]  

(6)

\[ E_{act} = \tan \alpha \cdot R = -\Delta H \]  

(7)

\[ \Delta S^\# = R \cdot (\ln pZ_0 - 10.36 - \ln T), \]  

(8)

\[ \Delta G^\# = \Delta H - T\Delta S^\# \]  

(9)

where \( \tau \) – is time, min; \( A_0 \) – initial optical densities (at \( \tau = 0 \)); \( A \) – optical densities, corresponding to \( \tau_i \).

According to the dependency graph «lnK – 1/T», presented in figure 8, we found the value \( \ln pZ_0 \) and \( \tan \alpha \).

Table 2 summarizes the results of the calculation of the kinetics of sorption of piroxicam on the surface of activated carbon obtained from walnut shells.

**Table 2.** Summarizes the results of the calculation of the kinetics of sorption of piroxicam on the surface of activated carbon obtained from walnut shells.

| \( T, K \) | \( \ln pZ_0 \) | \( \Delta G^\#, \text{kJ/mol} \) | \( -\Delta S^\#, \text{J/(mol-K)} \) | \( E_{act}, \text{kJ/mol} \) |
|---------|----------------|-----------------|----------------|----------------|
| 278     | 0,881          | 31,54           | 125,6          |                |
| 298     |                | 34,22           | 126,17         | 3,756          |
| 318     |                | 36,92           | 126,71         |                |

Based on the obtained values, we can say that the results of activation energy and the process enthalpy are comparable. A low value of activation energy indicates the formation of an adsorption complex in the "piroxicam – water – sorbent surface" system.

Highly negative entropy values indicate the formation of an ordered adsorption complex. In this case, a small temperature dependence of sorption of piroxicam on the surface of activated carbon obtained from walnut shells is observed.

3. **Practical importance, implementation and results**

Quantum chemical calculations of the starting materials and model adsorption complexes in the "piroxicam – activated carbon surface" system were performed using the GAMESS US [6] and MOPAC [7] software. The main criterion for choosing the optimal configuration is the magnitude of the gradient norm. The calculation of the main parameters and modeling of the systems was carried out in the gas and water phases by semi-empirical methods MNDO and PM7.

![AC1](image1.png)  

\( AC1 \)

![AC2](image2.png)  

\( AC2 \)

![AC3](image3.png)  

\( AC3 \)
Figure 9. Adsorption complexes.

Of the 20 considered variations, only some of the most invariable and most stable configurations are presented (figure 9). To simplify the writing of adsorption systems, the notation $R_i$ (radical) is introduced. The fixation of piroxicam from a solution on the surface of the sorbent is possible due to such functional groups as $-\text{OH}$, $>\text{C}=\text{O}$, $>\text{N}-\text{H}$ etc. The internuclear distance of interacting molecules varied from 2Å to 5Å. Table 3 summarizes the calculation results. From this line of energy parameters, a selection of complexes was carried out at which consistency with experimental data was observed.

$$\Delta E_{\text{ads}} = ((E_{\text{system. } H_2O} + E_{\text{H}_2O})_0) - (E_{\text{sorbent. } H_2O} + E_{\text{piroxicam. } H_2O})) \times k$$

where $k$ is the correction factor for the solvent, which can be calculated either from the ratio $1/n$, where $n$ is the number of water molecules in the multicomponent system, or also from the ratio $E_0/E$, where $E_0$ is the energy of 1 water molecule, $E$ is the energy of the aqueous solution, i.e., interacting water molecules.

The gradation of thermal effects was carried out in the range from $-15$ kJ/mol to $-0.1$ kJ/mol. As can be seen, when calculating according to PM7, taking into account the explicit solvent, the most similar to the experimental values of the interaction energies of individual complexes were obtained: $\text{AC2} (-3.186$ kJ/mol), $\text{AC4} (-5.415$ kJ/mol). The received results allow us to judge the course of physical adsorption of piroxicam on the surface of the sorbent.

It has been established that, at long distances ($>10$ Å), multiparticle dipole-dipole interactions arise – the functional groups of piroxicam are oriented in the water flow, forming a directed dipole. The movement of piroxicam to the surface leads to the appearance of many-particle interactions formed both through water and directly with the functional groups of the coal surface. At medium distances (2Å ... 6Å), the polarized functional groups of piroxicam are able to form partial hydrogen bonds with the hydrated surface of coal (figure 10).

Figure 10. Scheme of planting piroxicam on the hydrated surface of a coal model.
Table 3. The main parameters of the adsorption complexes.

| №   | By linking         | r, Å       | µ, D       | -ΔEads, kJ/mol | -Exp, kJ/mol |
|-----|-------------------|------------|------------|----------------|-------------|
| AC2 | O...H / H...O     | 1,833 / 1,812 | 8,786      | 0,184          |             |
| AC4 | H...O             | 1,747      | 7,248      | 13,993         |             |
| AC1 | O...H / H...O     | 4,427 / 3,936 | 7,557      | 5,566          |             |
| AC3 | O...H / H...O     | 4,932 / 4,977 | 7,696      | 0,752          |             |
| AC2 | O...(H2O)...H     | 1,871 / 2,794 | 11,278     | 3,186          |             |
| AC4 | H...(H2O)...O     | 1,797 / 1,751 | 8,914      | 5,415          |             |
| AC5 | H...(H2O)...O     | 1,795 / 1,768 | 11,629     | 5,832          |             |

In places of surface rupture, i.e. “Formation of depressions” in the presence of a silicate component, piroxicam also interacts through an aqueous continuum with functional groups HO-Si, O=Si. Averaging the considered variations made it possible to establish that the sorption energy of piroxicam by the MNDO method was -3,312 kJ/mol, the PM7 method with allowance for solvation - 3,796 kJ/mol, which is accorded with the experimental results. Definitely, it is known that van der Waals interactions cannot be the cause of the appearance of any stable molecular associates or complexes in the liquid phase. It is clear that the energy of the van-der-Waals interaction plays a small role in this process, only forming and orienting the dipole of the main molecule in the solution relative to the surface of the coal. Therefore, it can be asserted with certainty that sorption of piroxicam is feasible due to the manifestation of additional interactions, in particular, weak hydrogen bonds [8].

4. Conclusions

As a result of the work done, it was found that activated carbon obtained by heat treatment of walnut shells is a good and quite promising material for concentrating piroxicam and other drugs with the aim of subsequent determination from water and various biological environments [9].

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