Removal of 17-α Ethinylestradiol from Water Systems by Adsorption on Polyacrylonitrile Beads: Isotherm and Kinetics Studies

Abstract

An investigation on the removal of 17α-Ethynylestradiol (EE2) from aqueous solutions using Polyacrylonitrile (PAN) beads has been carried out under closed conditions. The kinetic and equilibrium results obtained for EE sorption with different initial concentrations have been analyzed. Experimental data at equilibrium have been correlated with the Langmuir, Freundlich, Tempkin, and Dubinin–Radushkevich (D–R) isotherm models. The applicability of the isotherm equations to the adsorption system has been compared by means of the correlation coefficients. The adsorption data resulted fitted well by the Freundlich isotherm model. Kinetic analysis was performed with three different types of kinetic adsorption models using the pseudo-first-order, pseudo-second-order, and simple Elovich models. Analysis of the kinetic data indicated that the EE2 adsorption was a second-order process. Diffusion mechanisms have been analyzed by means of the diffusion rate equations inside particulate of Dumwald–Wagner and intraparticle models. The actual rate-controlling step involved in the EE sorption process was determined by further analysis of the sorption data by the kinetic expression given by Boyd. All together these results allowed to understand the adsorption mechanism of the process and have shown the usefulness in using PAN beads in removing EE2 from synthetic aqueous solutions, also at concentrations higher than those measured in the environment.

Introduction

Endocrine disrupting chemicals (EDCs) constitute a group of organic pollutants with increasing negative impact on the environment as well as on human and animal health. EDCs interfere with the function of the endocrine system by blocking or mimicking the normal activity of hormones, affecting their synthesis or metabolism, and altering hormone receptor levels [1]. Compounds exhibiting endocrine disrupting activities include a broad range of chemicals, among which steroid estrogens, both natural and synthetic. The synthetic estrogen 17α-ethinylestradiol, EE2, is recognized as one of the EDCs with higher disrupting potency [2, 3]. EE2, derived from the natural hormone estradiol E2, known also as 17β-estradiol, is mainly used in the formulation of oral contraceptives. Thus EE2 and E2 are widely excreted by humans and animals in urine and feces as active free forms or inactive glucuronide and sulfate conjugates. EE2 ends up in the environment as well as on human and animal health. EDCs interference with the function of the endocrine system by blocking or mimicking the normal activity of hormones, affecting their synthesis or metabolism, and altering hormone receptor levels [1]. Compounds exhibiting endocrine disrupting activities include a broad range of chemicals, among which steroid estrogens, both natural and synthetic. The synthetic estrogen 17α-ethinylestradiol, EE2, is recognized as one of the EDCs with higher disrupting potency [2, 3]. EE2, derived from the natural hormone estradiol E2, known also as 17β-estradiol, is mainly used in the formulation of oral contraceptives. Thus EE2 and E2 are widely excreted by humans and animals in urine and feces as active free forms or inactive glucuronide and sulfate conjugates.

Abbreviations

C0: Initial pollutant concentration (mg L⁻¹), C<sub>e</sub>: Equilibrium liquid-phase concentration (mg L⁻¹), q<sub>e</sub>: Equilibrium solid-phase concentration (mg g⁻¹), q<sub>m</sub>: Amount of pollutant adsorbed at time t for mg of adsorbent(mg g⁻¹), q<sub>max</sub>: Maximum adsorption capacity (mg g⁻¹); t: Time (min), K<sub>L</sub>: Freundlich isotherm constant (L mg⁻¹)⁰⁵, K<sub>L</sub>: Langmuir isotherm constant (L mg⁻¹), K<sub>D</sub>: Dubinin–Radushkevich constants (mol² J⁻²), K<sub>d</sub>: K<sub>0</sub>-K<sub>α</sub>-K<sub>β</sub>-Wagner constant (min⁻¹), K<sub>v</sub>: Rate constant of pseudo-first-order kinetic model (min⁻¹), K<sub>D</sub>: Rate constant of pseudo-first-order kinetic model (g mg⁻¹ min⁻¹), α: Constant in Elovich’s equation: (mg g⁻¹ min⁻¹) and (g mg⁻¹), respectively, K<sub>α</sub>: Rate constant of intraparticle diffusion model (g mg⁻¹ min⁻⁰⁵), C: Constant that gives idea about the thickness of the boundary layer (mg g⁻¹), R: Universal gas constant (8.314 J mol⁻¹ K⁻¹), T: Absolute Temperature (K), R<sub>L</sub>: Dimensionless constant separation factor R<sup>2</sup>: Regression correlation coefficient.
have reported the presence of E2 and EE2 in waste and surface waters, in concentrations ranging from ng L$^{-1}$ and μg L$^{-1}$ levels [4–10]. The presence of estrogens in the environment is an emerging problem due to the harmful effects on wildlife and humans, even at ng L$^{-1}$ levels. Concerning the wildlife, EE2 has been shown to cause adverse reproductive effects, such as increased synthesis and secretion of vitellogenin in male subjects or changes in gonad somatic index in female *Pimephales promelas* [11,12]. More interesting are also the recent papers concerning the reproductive systems in zebra fish [13,14] and in *Pimephales promelas* [15]. However the effects of synthetic steroids on fish reproduction are not limited to laboratory exposures. Some researchers [16] conducted a seven–year experimentation on a whole lake in Ontario investigating the effects of EE2 on a population of fathead minnows. The first two years were employed for pre–exposure studies constituting the control, the subsequent three years for exposure studies, and the remaining two years for studying the post–exposure effects. Low levels of exposure (5–6 ng/L) for the three–year period resulted in the feminization of male fish and reduced gonad development. Females also produced vitellogenin beyond their normal breeding season, suggesting an altered reproductive season. The chronic exposure of fathead minnows to EE2 ultimately resulted in almost extinction of the fish population in the lake used for experimentation.

Concerning the human beings, besides the therapeutic use, EE2 reaches the humans through the food chain, water included, owing its potential to bioaccumulate.

Having in mind these risks it becomes imperative to remove from the environment EDCs, and in particular estrogenic steroid hormones. For all these reasons, the European Union has recently added E2 and EE2 to a new “watch list” of emerging aquatic pollutants included in the Water Framework Directive [17].

Since the existing sewage treatment plants have not been designed for the removal of endocrine disruptors, they are not effective barriers to the retention of these emerging pollutants. EE2, therefore, is continuously discharged into the environment. Subsidiary processes, therefore, are used before the release of water effluents into the environment to avoid the risks caused by EDCs in aquatic environments. Three main classes of processes have been utilized: physical, physicochemical and biological. Many times some of these processes have been simultaneously applied [18].

Physical processes are membrane filtration and adsorption. Membrane filtration is a process in which a membrane operates as a separation barrier, and certain substances can pass through it while others are retained. Adsorption is based on the uptake of the pollutant (adsorbate) from the aqueous phase onto a solid phase (adsorbent) and occurs or onto activated sludge or on adsorbent materials.

The physico–chemical processes are the advanced oxidation processes (AOPs) which refer to cases in which the oxidation of organic contaminants occurs primarily through reactions with hydroxyl radicals *OH. AOPs typically involve two stages: The formation of *OH, and the reaction of these oxidants with the organic contaminants in water. Advanced oxidation processes include photolysis, photocatalysis, sonolysis.

Biological processes, classified as bioremediation processes, occur using bacteria from activated and anaerobic sludge, enzymes or plants. In the last years our research has been focused on bioremediation of EDCs by means of immobilized enzymes working in bioreactors operating under isothermal or non–isothermal conditions [19–22].

In this paper we have focused our attention on the adsorption process considering the low cost of the adsorbent materials usually employed and the large employment of this process in the removal of dyes, ions and endocrine disruptors [23–32]. We have pursued the removal of EE2 by absorption on Polyacrylonitrile (PAN) beads. PAN beads have been chosen as adsorbent material owing to our previous experience in their use as enzyme carriers in bioremediation of aqueous solutions polluted by EDCs [21, 33,34] and since they have been already usefully used by other authors in adsorption process [26]. Kinetic studies and adsorption equilibrium data have been obtained. Experimental data have been treated using adsorption isotherm models and adsorption kinetic models. In addition, adsorption mechanisms have been discussed and postulated.

**Experimental**

**Materials**

Acrylonitrile, Sodium Nitrate, Glycerin, 17α-ethinylestradiol, Dimethylformamide, and Acetonitrile were purchased from Sigma–Aldrich (Milan, Italy) and used without further purification.

**Methods**

**Preparation of PAN Beads**

Acrylonitrile powder (54 g), LiNO$_3$ (3 g) and Glycerin (9 g) were dissolved in 234 mL of Dimethylformamide. The homogenized mixture was gently pipetted and precipitated in distilled water. The obtained beads were water–washed and immersed for 24 h in a glycerin aqueous solution 30% (v/v). After this step, the beads were dried in an oven at 70 °C for a time sufficient to reach a constant weight. The average diameter of beads was 3.5 mm ±0.5 mm, as measured with a caliper. This measure was confirmed by SEM observations.

**Characterization of PAN beads**

Scanning Electronic Microscopy observations: SEM analysis were performed on a FEI Quanta 200 FEG SEM in high vacuum using a secondary electron detector and an acceleration voltage of 20 kV. Before analysis, samples were coated with a 15 nm thick Au/Pd layer with a sputter coating system.

FT-IR spectroscopy: A Perkin Elmer Spectrum One FT-IR spectrometer, equipped with a MIR TGS detector, has been used to record FT-IR spectra. Spectral acquisitions were performed with KBr pellets. All spectra have been collected using 4 scans in the range from 2400 to 900 cm$^{-1}$ with a 4 cm$^{-1}$ spectral resolution. Measure-
ments were analyzed in triplicate. The spectra have been ana-
yzed using the application routines provided by the software pack-

17-α-ethinylestradiol determination

EE2 concentration in aqueous solution was measured by high-
performance liquid chromatography, HPLC, using an LC-
20AT apparatus (Shimadzu, Kyoto) equipped with a UV/Visible
Diode Array detector (SPDM20A, Germany) at a flow-rate of
1.3 mL/min. All analyzed samples were pre-filtered through
a 0.2 µm Cellulose Mixed Esters syringe filter (Macherey-
Nagel GmbH & Co. KG, Germany). The mobile phase consisted
of acetonitrile/water. The chromatographic determination
performed by using a gradient: in 3 min acetonitrile from 50
to 90%; for 4 min acetonitrile/water 90% v/v; in 1 min acetonitrile
from 90 to 50%. The retention time was found to be 4 min. By
plotting as a function of concentration the peak area at known
concentrations, it is possible to obtain a calibration curve
from which unknown EE2 concentrations can be determined.
The low detection limit was 1 µM, and the extension of the linear
range was up to 100 µM. The measure repeatability in the same
experiment was less than 1%, while the repeatability between
different experiments at the same concentration was no more
than 3.5 %

Classical adsorption measurements

In batch experiments, 26 g of PAN beads were added into a
250 mL Erlenmeyer flask with plastic stopper, containing
60 mL of EE2 solution. The flasks were shaken at 300 rpm
at room temperature (25±1 °C). During the time, 200 µL of
the solution were extracted and their 17-
α-ethinylestradiol
concentration determined by using HPLC.

To investigate the kinetics of adsorption, the effect of contact
time on the adsorption capacity of PAN beads was studied.
Isotherm studies were performed using different initial
EE2 concentration, ranging from 3.2 to 332 µM. Two direct
parameters are obtained from these studies: the Percentage
Removal at t time, PRt, and the Absorption Capacity (AC). The
PRt is calculated using the expression:

\[ PRt = \frac{C_0 - C_t}{C_0} \times 100 \] (1)

where \( C_t \) is the initial EE2 concentration expressed in the
proper units (mg/L) and \( C_t \) is the residual concentration in
the solution at time t, expressed in the same units. When \( C_t \)
becomes \( C_t \), i.e. the EE2 concentration at equilibrium, equation
1 becomes

\[ PRt = \frac{C_0 - C_e}{C_0} \times 100 \] (2)

The Equilibrium Adsorption Capacity (AC), is calculated
according to equation

\[ (AC)_{eq} = \frac{(C_0 - C_e)V}{W} \] (3)

where \( C_0 \) and \( C_e \) are the initial and equilibrium concentration
of EE2 (mg/L), respectively, \( V \) is the volume of solution (L), and
\( W \) is the mass (g) of PAN beads. Preliminarily to every
experimental approach, the adsorption capacity of PAN beads
as function of pH of the solution must be assessed in order to
find the best pH condition for adsorption.

Adsorption isotherm models

Four adsorption isothermal models are used to draw insights
on the adsorption mechanism and on the surface properties
of the adsorbent: the Langmuir model, the Freundlich model,
the Dubinin–Radushkevich isotherm and the Tempkin
isotherm. The first two models, in particular, are utilized for
distinguishing between homogeneous monolayer (Langmuir)
or heterogeneous (Freundlich) adsorbent surface.

Each model is represented by a linearized equation:

Langmuir isotherm: \[ \frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \] (4)

Freundlich isotherm: \[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \] (5)

Dubinin–Radushkevich isotherm: \[ \ln q_e = \ln q_{D-R} - K_{ad} \epsilon^2 \] (6)

Tempkin isotherm: \[ q_e = \frac{R T}{b_F} \ln K_T + B \ln C_e \] (7)

To choose the right model among the four, the \( R^2 \) value of
each linearized equation will be relevant.

Concerning equation 4, when \( C_e/q_e \) is plotted versus \( C_e \), a
straight line is obtained, from which the values of \( q_{max} \) and \( K_L \)
are calculated. An interesting parameter correlated to the \( K_L \)
constant is the dimensionless \( R_L \) parameter defined by the
formula:

\[ R_L = \frac{1}{1 + C_0 K_L} \times 100 \] (8)

where \( C_0 \) (mg/L) is the initial pollutant concentration and
\( K_L \) the Langmuir isotherm constant. When \( R < 1 \) the absorption
is favorable, for \( R = 0 \) the absorption is irreversible, while for
\( R > 1 \) the absorption is linear, and for \( R > 1 \) the absorption is
unfavorable.

Similarly, with reference to equation 5, where \( q_e \) is the
amount of pollutant adsorbed at equilibrium (mg/g) and \( C_e \)
is the equilibrium concentration of the adsorbate (mg/L), when
\( \ln q_e \) is plotted against \( \ln C_e \), a straight line with slope \( 1/n \)
and intercept \( \ln K_F \) is obtained. \( K_F \) and \( n \) are Freundlich constants
related to the adsorption capacity and adsorption intensity,
respectively. \( K_F \) is roughly an indicator of the adsorption
capacity, and \( n \) gives an indication of adsorption effectiveness.

Considering equation 6, where \( q_e \) is the amount of removed
pollutant per unit of adsorbent mass (mg/g) and \( q_{D-R} \) is the
adsorption capacity (mg/g), the plot of \( \ln q_e \) as a function of
\( \epsilon^2 \) allows calculating the values of \( K_{ad} \) and \( q_{D-R} \). \( \epsilon \) is calculated
by using the equation:
The Elovich equation is:
\[ q_e = \alpha + \beta \ln t \]  

Where \( q_e \) is the initial adsorption rate (mg g\(^{-1}\) min\(^{-1}\)), and \( \beta \) is related to the extent of surface coverage and activation energy for chemisorptions (g/mg).

When the Elovich kinetic is applicable, the plot of \( q_e \) versus \( \ln t \) gives a linear relationship. From the slope and intercept of the equation, the Elovich parameters \( \alpha \) and \( \beta \) are calculated.

### Adsorption mechanisms

The adsorption process can be considered as a series of three sequential steps:

1. Film diffusion, during which the adsorbate goes towards the external surface of the adsorbent;
2. Particle diffusion, during which the adsorbate molecules travel within the pores of the adsorbent;
3. Adsorption of the adsorbate molecules on the internal surface of the adsorbent.

The third step is so very fast that cannot be considered as a rate limiting step and therefore can be disregarded. When the first step is greater than the second, the process rate is governed by particle diffusion, when the contrary occurs the film diffusion governs the process. When the external transport is equivalent to the internal transport, the formation of a liquid film around the adsorbent particles occurs, and the adsorbate diffusion follows its concentration gradient.

To solve this problem, we examined our results by means of three consolidated models: the Dumwald–Wagner model, the Intraparticle Diffusion model, and the Boyd model. Also in this approach to choice among the different models, the \( R^2 \) value of each of the linearized equations describing each model will be the principal criterion.

The pseudo-first-order Langergren’s model \([35]\), once integrated the differential equation representing the model, i.e. the equation
\[ \frac{dq}{dt} = k_1(q_e - q_t) \]  

Becomes
\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  

The adsorption rate constant \( k_1 \) can be experimentally determined by the slope of the linear plot of \( \ln(q_e - q_t) \) vs. \( t \).

The rate of adsorption for the modified pseudo-second-order model \([36]\) is expressed as:
\[ \frac{dq}{dt} = k_2(q_e - q_t)^2 \]  

Which is linearized in the form
\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} \]  

The intercept and the slope of the plot of \( t/q_t \) vs. \( t \) give the \( k_2 \) and \( q_e \) values.

The Elovich model has recently applied to the adsorption process of pollutants from aqueous solutions \([37,38]\).
The Boyd model \cite{41} is used to predict the rate limiting step involved in the absorption process. Kinetic data are expressed according to the Boyd equation:

\[ B_t = -0.4978 - \ln(1 - F) \]

Where \( B_t \) represents the adsorbent fraction adsorbed at time, calculated as \( F = q_t/q_e \), in which \( q_t \) and \( q_e \) are the adsorbate amounts at time and at equilibrium, respectively.

Once calculated \( B_t \) at each value of \( F \), and hence of \( t \), the plot of \( B_t \) versus \( t \) allows to establish the rate limiting diffusion step. Indeed, film diffusion governs the rate limiting of the adsorption process if the straight lines no pass through the axis origin.

**Results and Discussion**

**Preliminary results**

In figure 1a simple characterization of PAN beads is shown by using scansion electronic microscopy (Figure 1a) and FT-IR spectrum (Figure 1b). Figure 1a confirms the spherical shape and the dimensions of the beads. In figure 1b the FT-IR spectrum of PAN-beads in the region 2400-900 cm\(^{-1}\) is reported. The most important structures are: the band at 2245 cm\(^{-1}\) related to the stretching of the triple bond C=N; the large structure with the maximum located at 1735 and at 1634 cm\(^{-1}\) assigned to C=O stretching and to C=C stretching of vinyl group, respectively; the band at 1447 attributed to CH\(_2\) bending; the peaks at 1380 cm\(^{-1}\) and at 1040 cm\(^{-1}\) assigned to NO\(_3\) stretching of nitrate group \cite{42, 43}.

As reported in methods, to know the best yield in EE2 removal by PAN beads, their adsorption capacity has been assessed as a function of pH of the synthetic solutions. Results are reported in figure 2 as relative adsorption capacity (%) as a function of pH. The experimental data refer to the adsorption capacity after a contact time of 80 min, initial EE2 concentration and temperature being respectively equal to 5 \( \mu \)M and to 25 \( \pm \) 0.5 °C.

Figure 2: Relative Adsorption Capacity of PAN Beads towards EE2 as a function of pH of the solution.

From the figure clearly it emerges that the optimum pH for EE2 adsorption on PAN beads occurs at pH 5.0. This result can be indicative of the presence of a net negative charge on the PAN surface. This charge alters the microenvironment around the bead and hence the pH conditions there existing. Taking into account this result henceforward all experiments have been performed at pH 5.0.

An example of a crude result of our experimentation is illustrated in figure 3a showing the decrease of the EE2 concentration as a function of the time of the solution with the PAN beads. The experimental conditions were: \( C_0 = 3.2 \) \( \mu \)M, temperature = 298 K, and pH = 5.0. In figure 3b the results of figure 3a have been elaborated as percentage of EE2 removal during the time, according to equation 1. Figure 3c shows the time dependence of \( q_e \) for the experimental case of figure 1a. Since we used different EE2 concentrations in contact with the same amount of PAN beads, in figure 3d the \( q_t \) value for each solution has been reported as a function of contact time. Results in figure 3d clearly show evidence how at the same time the \( q_t \) values, as expected, increase with the increase of the initial EE2 concentration used. Each experimental point in the figures is the average of three independent experiments. The standard error never exceeded 4.5%.

Figure 3: a) Absolute removal as a function of time; b) Percentage removal as a function of time; c) \( q_e \) as a function of time. Experimental conditions \( C_0 = 3.2 \) \( \mu \)M and \( T_{av} = 25^\circ \)C.

d) \( q_t \) as a function of time for each of used EE2 concentrations.

In figure 4, the adsorption capacity of the PAN beads is reported as a function of the initial EE2 concentration after a contact time of 100 min. The figure shows that the adsorption capacity linearly increases (\( R^2 = 0.999 \)) with the increase of the initial EE2 concentration, so indicating the excess of the number of adsorption sites on the adsorbate molecules.

![Figure 1: a) SEM of the shape and dimension of a PAN bead; b) FT-IR spectrum of the composition of a PAN bead.](image1)

![Figure 2: Relative Adsorption Capacity of PAN Beads towards EE2 as a function of pH of the solution.](image2)
Figure 3: a) Absolute removal as a function of time; b) Percentage removal as a function of time; c) qt as a function of time. Experimental conditions C0= 3.2 μM and Tav = 25°C.

Figure 4: PAN adsorption capacity as a function of initial EE2 concentration.

Results in figures 3, 4 show the usefulness of PAN beads in removing EE2 by adsorption, but not give any information on the adsorption mechanism. This information is provided in the following sections.

Adsorption isotherm models

In figure 5 the experimental data obtained in this research are analyzed according to the four isotherm models reported in the Methods to establish the best model for accounting the isothermal adsorption of EE2. The choice will be made according to the $R^2$ value of the linearized equation characteristic of each model. Adsorption isotherms are mathematical models describing the distribution of the adsorbate among solid and liquid phases. For the adsorption isotherms, the initial EE2 concentration was varied, whereas the pH (pH=5) and temperature of the solution (T=25°C), the agitation speed, and the sorbents weight in each sample were held constant. Data about the four isothermal models are compiled in figure 5.

Figure 5a reports the elaboration of experimental data plotted according to equation 4 representing the Langmuir isotherm model. In figure 5b the plot of equation 5 is done according to the Freundlich model. Figures 5c,d, in turn, represent the Dubinin–Radushkevich and Tempkin models, plotted according to equation 6 and 7, respectively.

Figure 5: Adsorption isotherm models: a) Langmuir; b) Freundlich; c) Dubinin–Radushkevich; d) Tempkin. In each panel the analytical equations best fitting the values of the experimental points are reported together with the $R^2$ value of the correlation coefficient of the respective straight lines.
As reported in Methods, from the values of the slope and intercept of each equation it is possible to calculate the parameters characterizing each isothermal model. These parameters are listed in Table 1. Looking at the $R^2$ values (Table 1) it is possible to deduce that the isotherm Freundlich model better accommodates to our adsorption experiments. This conclusion suggests: i) the absence of an homogeneous adsorbent surface, ii) the absence of homogeneous energy site or limited levels of adsorption, and iii) electrostatic forces play a significant role in the adsorption mechanism of EE2 by PAN beads.

$R^2$ values in table 1 are compiled with the standard deviations (S.D.) calculated by means of the equation:

$$S.D.(\%) = 100 \times \left( \frac{\sum N (1 - (q_{t,cal} / q_{t,exp})^2)^{1/2}}{N} \right)^{1/2} \quad (19)$$

$R_c$ values are congruous with S.D. values: greater is $R_c$, smaller is S.D.

Before concluding this section, it is interesting to consider Figure 6 where the $R_c$ values, calculated according to eq. (8), have been reported as a function of the initial EE2 concentration.

Remembering the meaning of $R_c$ and being this value at all concentration smaller than the unit it follows that the adsorption process is favorable.

**Adsorption kinetics models**

Kinetic studies are necessary in an adsorption process because they allow to calculate the uptake rate of the adsorbate and give information about the control of the residual time of the whole adsorption process. As reported in Methods, three different kinetic models, i.e. pseudo first-order, pseudo second-order and Elovich, were selected in this study for describing the EE2 adsorption process. The results relative at each model are shown in figure 7a.

Figure 7a illustrates the results regarding the pseudo-first-order kinetic model by plotting the experimental data according to equation 12. The value of the first-order rate constant $k_1$ and the value of the correlation coefficient $R^1$, obtained from the slope of the plot $\ln (q_e - q_t)$ versus time for each used concentration, are reported in Table 2. From the table, it is possible to observe that the correlation coefficients, ranging from 0.93 to 0.99, are high enough for the different EE concentrations. However, the calculated values of $q_{t,cal}$ are smaller than the experimental ones, $q_{t,exp}$, and differ enough, so indicating that the model is not appropriate to describe the adsorption process.
Figure 7b reports the experimental results regarding the pseudo-second-order kinetic model by plotting the data according to equation 14. The plot of t/qe versus t gives, at each concentration, a linear relationship. The values of the calculated qe,calc and of k2 can be determined respectively from the slope and intercept of the analytical equation representing the straight line of each model. These values have been tabulated in table 3 together with the values of the correlation coefficients R2 and the S.D.

Based on linear regression values, the kinetics of EE2 adsorption onto PAN appears well described by the second-order model. Also, considering that the calculated values of qe,calc from equation 14 are higher than the experimental ones, qexp, and differ few from the latter, it is possible to draw the conclusion that the model is appropriate enough to describe the adsorption process. This finding suggests that the rate-limiting step in the adsorption process may be chemisorptions involving valent forces through the sharing or exchanging of electrons between sorbent and sorbate [15]. In conclusion, the second-order rate expression fits the data better than the first-order-rate model.

Figure 7c shows, according to equation 15, the plot of qt against lnt for the adsorption of different initial concentrations of EE onto PAN beads. From the slope and intercept of the linearization of the simple Elovich equation, the estimated Elovich parameters have been obtained and tabulated in table 4. The value of β is indicative of the number of sites available for adsorption, while α is the adsorption quantity when lnt is equal to zero, i.e. the adsorption quantity when t is one hour. From this table, it is possible to conclude that the simple Elovich equation fit well with the experimental data but less than the second-order-rate model.

To better choose between the different models, considering the different value of R2 as a function of the concentration, we have reported in the last column of tables 2–4 the average value of R2, i.e. R2 average for each model. According to these values, there are no doubts that the second order model better fits the experimental data.

### Table 1: Langmuir, Freundlich, Dubinin–Radushkevich and Temkin isotherm constants and correlation coefficients.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Constants</th>
<th>qmax (mg g⁻¹)</th>
<th>KL (L mg⁻¹)</th>
<th>R²</th>
<th>S.D. (%)</th>
</tr>
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<tbody>
<tr>
<td>Langmuir</td>
<td>Ce = 1/qmax + Ce/qmax</td>
<td>0.40</td>
<td>0.145</td>
<td>0.65</td>
<td>27</td>
</tr>
<tr>
<td>Freundlich</td>
<td>ln qe = ln Ke + 1/n ln Ce</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dubinin–Radushkevich</td>
<td>ln qe = ln qD-R – Kd e⁻²</td>
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<tr>
<td>Temkin</td>
<td>qe = B ln K + B ln Ce</td>
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</tbody>
</table>

![Figure 6: RL values as a function of the EE2 initial concentration.](image)

![Figure 7: Isothermal adsorption kinetic models: a) Pseudo – first order; b) pseudo – second order c) Elovich model.](image)
Adsorption isotherm mechanisms

As reported in Methods, a typical liquid/solid adsorption process involves three steps: film diffusion, intraparticle diffusion, and mass action. Mass action is a very rapid process and can be neglected in a kinetic study. Thus, the kinetic process of adsorption is always controlled by liquid film diffusion or by intraparticle diffusion. Therefore, adsorption diffusion models have been constructed Figure 8 to describe the process of film diffusion, also known as Dumwald–Wagner kinetic model, and/or intraparticle diffusion.

In figure 8a our results have been elaborated as Log (1–F2) versus the contact time for each of the initial EE2 concentrations, according to equation 16. The resulting linear plots, together with the high values of the R² coefficient, indicate the applicability of the Dumwald–Wagner kinetic model, characterized by equation 17. The diffusion rate constants KD-W, along which the R² values for each of initial concentration used, are reported in table 5.

The intraparticle model is commonly used for identifying the adsorption mechanism. The intraparticle diffusion plot for EE2 adsorption onto PAN beads is given in figure 8b, according to equation 17. Two separate linear portions are observed in the curves. These two linear portions in the intraparticle model suggest that the adsorption process consists of both surface adsorption and intraparticle diffusion. While the initial linear portion of the plot indicates boundary layer effect, the second linear portion is due to intraparticle diffusion [18]. The intraparticle diffusion rates Kd, calculated from the slope of the second linear portion, are given in table 6. The values of C, also reported in the table, provide an idea about the thickness of the boundary layer. The larger the intercept, the greater is the boundary layer effect [19]. Increasing of initial EE2 concentration leads to the increase in boundary layer effect for EE2 adsorption.

Table 2: Rate constants and correlation coefficient for the pseudo – first-order model at each initial EE2 concentration used.

<table>
<thead>
<tr>
<th>C₀ (µM)</th>
<th>K₁/min⁻¹</th>
<th>qₑ,calc/mg g⁻¹</th>
<th>qₑ,exp/mg g⁻¹</th>
<th>R²</th>
<th>R² average</th>
<th>S.D. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>-0.0823</td>
<td>0.002</td>
<td>0.00222</td>
<td>0.99</td>
<td>0.975</td>
<td>1.7</td>
</tr>
<tr>
<td>10.6</td>
<td>-0.0383</td>
<td>0.0066</td>
<td>0.00692</td>
<td>0.94</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>18.4</td>
<td>-0.0334</td>
<td>0.00811</td>
<td>0.01182</td>
<td>0.97</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>45.6</td>
<td>-0.0226</td>
<td>0.013</td>
<td>0.03024</td>
<td>0.97</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>268.0</td>
<td>-0.0202</td>
<td>0.132</td>
<td>0.1754</td>
<td>0.99</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>332.0</td>
<td>-0.0176</td>
<td>0.173</td>
<td>0.2077</td>
<td>0.99</td>
<td>4.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Rate constants and correlation coefficients for the pseudo–second–order model at each of the initial EE2 concentration used.

<table>
<thead>
<tr>
<th>C₀ (µM)</th>
<th>K₂/g mg⁻¹ min⁻¹</th>
<th>qₑ,calc/mg g⁻¹</th>
<th>qₑ,exp/mg g⁻¹</th>
<th>R²</th>
<th>R² average</th>
<th>S.D. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>3428.4</td>
<td>0.00244</td>
<td>0.00222</td>
<td>0.99</td>
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<td></td>
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<tr>
<td>10.6</td>
<td>2367.4</td>
<td>0.00816</td>
<td>0.00692</td>
<td>0.99</td>
<td>2.7</td>
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<tr>
<td>18.4</td>
<td>1129.4</td>
<td>0.01324</td>
<td>0.01182</td>
<td>0.97</td>
<td>4.1</td>
<td></td>
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<tr>
<td>45.6</td>
<td>288.34</td>
<td>0.03155</td>
<td>0.03024</td>
<td>0.99</td>
<td>1.8</td>
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<tr>
<td>268.0</td>
<td>89.72</td>
<td>0.1867</td>
<td>0.1754</td>
<td>0.99</td>
<td>5.3</td>
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<tr>
<td>332.0</td>
<td>129</td>
<td>0.2325</td>
<td>0.2077</td>
<td>0.99</td>
<td>5.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 4: α and β constants and correlation coefficients for different EE2 concentrations in reference to the SimpleElovich Model.

<table>
<thead>
<tr>
<th>C₀ (µM)</th>
<th>α/mg g⁻¹ min⁻¹</th>
<th>β/g mg⁻¹</th>
<th>R²</th>
<th>R² average</th>
<th>S.D. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>0.1836</td>
<td>0.4932</td>
<td>0.9866</td>
<td>0.97</td>
<td>2.4</td>
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<td>-1.0548</td>
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<td>0.9977</td>
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<td>18.4</td>
<td>-0.8998</td>
<td>2.7678</td>
<td>0.9386</td>
<td>6.2</td>
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<tr>
<td>45.6</td>
<td>5.6869</td>
<td>4.9535</td>
<td>0.9223</td>
<td>7.7</td>
<td>7.7</td>
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<td>268.0</td>
<td>-15.399</td>
<td>36.358</td>
<td>0.9842</td>
<td>4.7</td>
<td>4.7</td>
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<td>332.0</td>
<td>-40.237</td>
<td>45.961</td>
<td>0.995</td>
<td>5.5</td>
<td>5.5</td>
</tr>
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</table>

Table 6: Parameters obtained from the intraparticle diffusion model for the different EE2 concentration.

<table>
<thead>
<tr>
<th>C (mg L⁻¹)</th>
<th>K (g⁻¹min⁻¹/²)</th>
<th>C (mg g⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>0.0441</td>
<td>1.7881</td>
<td>1</td>
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<tr>
<td>10.6</td>
<td>0.3889</td>
<td>3.0622</td>
<td>0.94</td>
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<td>18.4</td>
<td>0.2512</td>
<td>8.8929</td>
<td>0.98</td>
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<tr>
<td>45.6</td>
<td>0.3803</td>
<td>24.935</td>
<td>0.86</td>
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<td>268.0</td>
<td>4.4109</td>
<td>111.05</td>
<td>0.94</td>
</tr>
<tr>
<td>332.0</td>
<td>7.6624</td>
<td>94.114</td>
<td>0.97</td>
</tr>
</tbody>
</table>

To characterize what is the actual step involved in the EE2 adsorption process, our data have been analyzed using the Boyd kinetic expression given in equation 18. The calculated \( R² \) values have been plotted against time as shown in figure 8c. The linearity of these plots provides useful information to distinguish between external transport and intraparticle-transport controlled rates. Since each one of the straight lines does not pass through the origin, it is possible to conclude that film diffusion governs the rate limiting of the process.

**Conclusions**

Laboratory studies have been carried out to remove 17α-ethinylestradiol from synthetic aqueous solutions by adsorption onto PAN beads. Significant indications about the adsorption mechanism have been obtained.

Among the four adsorption isotherm models tested, the Freundlich model gave the highest \( R² \) value, i.e., 0.97. The Freundlich and Dubinin–Radushkevich models also, suggest that neither homogeneous site energies nor limited levels of adsorption are adequate to explain the obtained results. It is reasonable to conclude that, in our case, electrostatic forces play a significant role in the adsorption process.

The pseudo–second–order kinetic equation \((R² = 0.99)\) has explained the kinetic of the EE2 adsorption rate.

Different adsorption models have been examined to illustrate the diffusion mechanism of 17α-ethinylestradiol adsorption. The diffusion rate equations inside particulate of Dumwald–Wagner and intraparticle models have been used to calculate the diffusion rate of EE2 onto PAN beads. Since \( E \) values are less than 8 kJ/mol, the adsorption process has a physical nature. To determine what was the actual rate–controlling step involved in the adsorption process, the adsorption data have further analyzed by the kinetic expression given by Boyd.

In all the model studied the \( R² \) values resulted congruous with the S.D. values.

About the adsorption process some conclusions appear conflicting. On the basis of Dubinin–Radushkevich model

Adsorption process appears a physical adsorption process, while on the basis of the Pseudo–second–order model adsorption appears to be governed by chemi–adsorption. This contradiction is only apparent since the adsorption process could be a mixture of more than one process: physical adsorption, chemical adsorption, and mass balance. In our case, the first and main step is the physical adsorption step as proved by D–R model, while the second and rate determined step is the chemical one as proved by the Pseudo–second–order model. The chemical adsorption step raised from the interaction occurred between the charged LiNO₃ component in the PAN beads and the charges on the OH groups of EE2.

Our results clarify the molecular mechanisms at the basis of our adsorption process, and, in addition, confirm the useful employment of the PAN beads in removing pollutant, in particular, EE2, from aqueous systems.

**Acknowledgments**

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**References**


