Removal of Estrogen Hormones (17β-Estradiol and Estrone) from Aqueous Solutions Using Rice Husk Silica

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The aim of this study was to investigate the removal of estrogen hormones (17β-estradiol and estrone) from aqueous solutions using rice husk extracted silica. Rice husk was collected from rice factories in Mazandaran province (Iran) and the adsorbent was prepared in a furnace at 800 °C for 4 h, after acid leaching with hydrochloric and sulfuric acid mixture. Optimal operating parameters for estrogen removal were determined, including initial pH values (4–9), adsorbent dosages (0.5, 1, 1.5, and 2 g L^{-1}), contact times (30, 60, 90, and 120 min), and initial concentrations of 17β-estradiol and estrone (10, 40, 70 and 100 ng L^{-1}); one-factor-at-a-time method was used. The method of electrochemiluminescence was used to measure the concentration of hormones. Kinetic adsorption models and adsorption isotherms were also studied. The maximum removal efficiency (%) of 17β-estradiol (E2) and estrone (E1) hormones of 95.5 and 93.1 %, respectively, was obtained at optimal conditions of pH 4, 1.5 g L^{-1} of adsorbent dosage, 60 min of contact time and 10 ng L^{-1} initial concentrations of E2 and E1. Pseudo first-order kinetic model and Langmuir adsorption isotherm had the best fit with experimental data for both estrogen hormones, following nonlinear regression procedure. Rice husk silica could be considered as effective and accessible adsorbent for removal of estrogenic hormones.

Keywords
17β-estradiol, adsorption, estrone, rice husk

Introduction

Low concentrations of steroid hormones have been found in aqueous environments such as surface and ground waters, and wastewaters in various studies all over the world. The first reports about the presence of human hormones in water were published in 1965[1] and showed that steroids are not removed completely in common wastewater treatment processes. Today, hormones are considered as the ever-present pollutants in urban and hospital wastewaters treatment plants[1]. In recent years, many studies have been conducted to determine the prevalence and effects of hormones, as the main category of endocrine disrupting compounds[2]. Endocrine-disrupting compounds (EDCs) are the chemical compounds with potential for negative effects on the human and animal endocrine systems[2]; their entry into the environment has adverse effects on the freshwater organisms, ecosystem stability and human health. Therefore, they pose a great con-

cern to the general health in communities today[3]. Among EDCs, steroid hormones have created more special concern due to the more severe effects[4,5]. Steroid hormones are divided into five groups of progestins (progesterone), glucocorticoids (cortisol), mineralocorticoids (aldosterone), androgen (testosterone), and estrogen[6]. Estrogen hormones have attracted more attention due to more severe effects, complexity, diversity of chemical structures, and transference to free and compound forms[7]. The most important adverse consequences of estrogenic hormones are: 1) effects on human health, includes reduction of sperm count, increased incidence of breast, testicular, and prostate cancer, and endometriosis and, 2) effects on the environment includes delayed opening the eggs of bird, fish, and turtle eggs, change of the sex of male fish to female fish, disturbance in the reproductive system of fish, reptiles, birds and mammals, and changes in the marine mammalian immune system[8]. The most released estrogens in the environment are estrone (E1) and 17β-estradiol (E2) hormones that are normally excreted by all humans and animals[9]. More than 100 million women in the world use contra-

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ceptive pills which contain the female estrogen hormone responsible for the destruction of the gene. Like many other drugs, this drug is not completely absorbed into the body and the remainder enters to the sewage system[10].

Estradiol is present at low concentrations and it may exhibit severe hormonal activity in the environment even in low doses (ng L^{-1}). Its mean concentration in surface waters is 0.2–3.6 ng L^{-1} and in ground waters 0.3–4 ng L^{-1} [11], and it usually enters the environment[12] with wastewaters of urban treatment plants[13], hospital wastewaters[14], and wastewaters from animal husbandry activities[15]. In the conducted research in Brazil on five urban wastewater treatment plants in 2010–2012, the concentrations of E2, E1, and EE2 (17α-ethynylestradiol) of 566, 143, and 421 ng L^{-1} were measured, respectively[13]. Another research in the US in 2010 on estrogens distribution in wastewater treatment lagoon measured E1 and E2 concentrations of 169 and 126 ng L^{-1}, respectively[16]. Concentration of less than 0.1 ng L^{-1} is sufficient to produce significant estrogenic effects[12].

In recent years, efforts have been made to remove these hormones[2] and several methods have been investigated and developed for this purpose, such as advanced oxidation methods, improved coagulation, and chemical adsorption. However, most of these removal methods are not available for use in developing countries due to their high costs and sophistication[17]. Adsorption by activated carbon is one of the very effective physical methods in removing the pollutants from water and wastewaters[18]. However, the use of the commercial activated carbon is costly for pollutant removal. Today, researchers are attempting to obtain a low-cost adsorbent instead of activated carbon. Rice husk is one of the by-products of rice production, which contains 20 % of rice weight averagely. In some countries, rice husk is not considered a valuable material, but is used variously in some other countries for preparing cheap adsorbent materials, because producing adsorbent from rice husk amounts to 1 % of the costs of producing commercial activated carbon[19]. The great amounts of husk are burned in situ, which pollutes the environment. Rice husk promotes the adsorption process due to great amounts of fiber, protein, silica, and specific functional groups[20]. Rice husk is also insoluble in water due to its grain structure, and it possesses high mechanical durability and chemical stability[21]. Therefore, using rice husk as an adsorbent will not only be low-cost and accessible, but it will also reduce environmental pollution[22]. In this study, the effect of rice husk silica on the removal of 17β-estradiol and estrone from aqueous solutions was studied. Also, the kinetic and thermodynamic parameters of adsorption were determined.

Materials and methods

Materials

All materials were purchased from Merck KGaA Company, which included sulfuric acid (H$_2$SO$_4$ – 10 %), hydrochloric acid (HCl – 30 %), hydrochloric acid (HCl – 0.1 N), sodium hydroxide (NaOH – 0.1 N), and acetonitrile (CH$_3$CN – 99.9 %). Estrone (E1) and 17β-estradiol (E2) hormones were provided from Zist Azma Knowledge-based Company (Iran). The raw rice husk was obtained from rice factories in Mazandaran province, north part of Iran.

Preparing the adsorbent

Firstly, raw rice husk was washed and drained several times by double-distilled and deionized water to remove contamination. It was then oven-dried at 110 °C for 24 h. The dried shells were milled completely using an A11 Basic IKA mill (IKA, Staufen, Germany) equipped with a stainless steel beater to <1 mm particle size and then saturated applying the acid washing process with 10 % sulfuric acid and 3 % hydrochloric acid in the ratio of 50 g rice husk to 1 L of the mixture of these two acids for 2 h. It was then washed with distilled water, and finally put in a furnace at 800 °C for 4 h to produce rice husk silica[19,23]. SEM, FTIR, and XRD were conducted for the purpose of structural property studies of the silica prepared from rice husk[24].

Conducting the experiment

This experimental research was conducted at laboratory scale. In this research, the effect of operating parameters, including initial pH (4–9), adsorbent dosage (0.5, 1, 1.5, and 2 g L^{-1}), contact time (30, 60, 90, and 120 min), equal initial concentrations of 17β-estradiol and estrone in a single solution (10, 40, 70, and 100 ng L^{-1}) on adsorbent efficiency for simultaneous removal of estrogens was investigated, using one-factor-at-a time experimental design[25]. Distilled water and acetonitrile in a ratio of 2:1 were used to prepare the aqueous solution containing 17β-estradiol (E2) and estrone (E1) hormones, where the hormoneses were completely soluble. NaOH and HCl (0.1 N) were used to adjust the acidity. The needed amounts of adsorbent (0.05, 0.1, 0.15, and 0.2 g) were added to 250-mL beakers containing 100 mL test solution. The solutions were then shaken on a shaker at 125-rpm speed for the mentioned contact times. The solutions were then passed through Whatman No 41 filter paper, and the non-adsorbed hormones in the solution were measured by electrochemiluminescence (ECL) method and Elecsys device[26] (Cobas e 411 model, Roche/Hitachi company). All experiments were conducted

in an incubator shaker (jell 10 L model) to keep the temperature constant at 25±1 °C. Desorption experiments were performed on the saturated adsorbent after the adsorption at optimum conditions. Double-distilled water and acetonitrile (solution without hormone) were used for desorption, and filter paper was used to separate adsorbent from the solution[27]. Three adsorption/desorption cycles were performed.

Analytical methods

In the first experiment the influence of pH on the removal of E2 and E1 hormones was evaluated in the range of 4–9 at a constant hormone concentration of 10 ng L^{-1}, adsorbent dosage of 0.5 g L^{-1}, and contact time of 30 min. Optimal pH value was used in subsequent experiments. The optimal values of other parameters (adsorbent dosage, contact time, initial concentration, respectively) were then determined.

The removal efficiency (%) was calculated based on equation (1):

$$RE\left(\%\right) = \sqrt{\frac{C_0 - C}{C_0}} \cdot 100 \qquad (1)$$

where RE is removal efficiency, C_0 and C are input and output concentrations of hormones[28,29].

The obtained results of the effect of contact time on hormone adsorption were examined using non-linear and linear regression analysis based on pseudo-first-order and pseudo-second-order kinetic models to determine the adsorption kinetics. Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich equations were used to determine the adsorption isotherm. To evaluate the models used, the coefficient of determination (R^2) and root-mean-square error (RMSE) were used. The lower value of RMSE (eq. 2) and R^2 value closer to 1 show the better fit.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}\left(q_e - q_c\right)^2}{n}} \qquad (2)$$

where q_e is the obtained value from model fitting, q_c is the obtained value from the experiment, and n is the number of data points[30]. All experimental data are expressed in terms of arithmetic averages obtained from three repetitions.

Results and discussion

Adsorbent properties

In this study, as shown in Table 1, the amount of SiO_2 in rice husk increases after acid washing and heating; in contrast, the amount of carbon, hydrogen, and nitrogen tend to decrease.

Table 1 – *Results of chemical analysis of raw rice husk and rice husk silica*

Element %	Raw rice husk	Rice husk silica
C	38.91	0.16
N	0.61	0.17
H	5.83	0.27
SiO_2	48.55	94.21

The Scanning Electron Microscope (SEM) images of raw rice husk and rice husk silica showed that cell structure was destroyed and material porosity increased when raw rice husk was exposed to acid leaching and combustion processes at high temperatures. This issue can increase the adsorption rate (Fig. 1).

IR technique is one of the most sensitive and common techniques for detecting functional groups in materials[31]. FTIR spectra of raw rice husk and rice husk silica are shown in Fig. 2. As far as rice husk is concerned, numerous peaks are obvious: in particular, a broad band between 3750 and 2800 (centered at 3426) can be assigned to the O–H stretching vibration of adsorbed water[32]. There are also intense asymmetric vibrations for Si–O–Si bonds in 1108 cm^{-1}, and symmetric stretching and
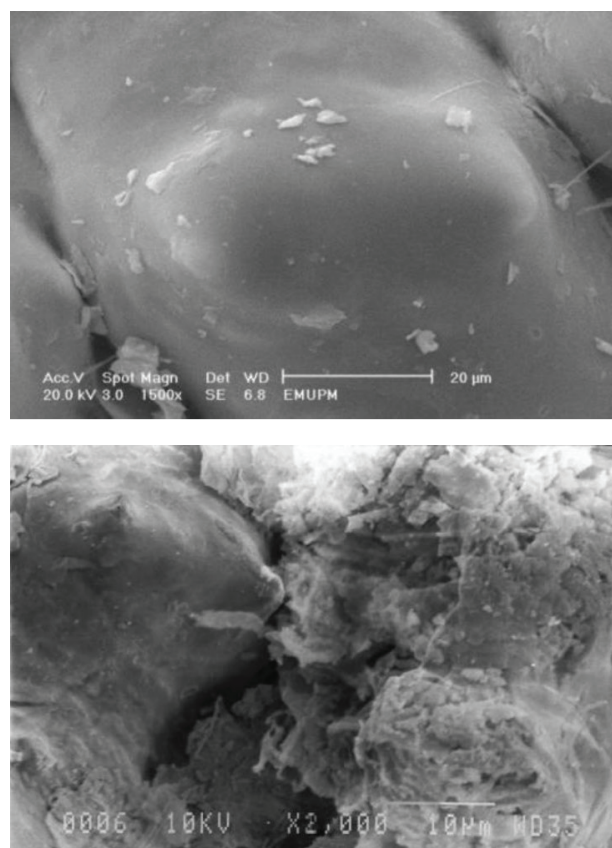

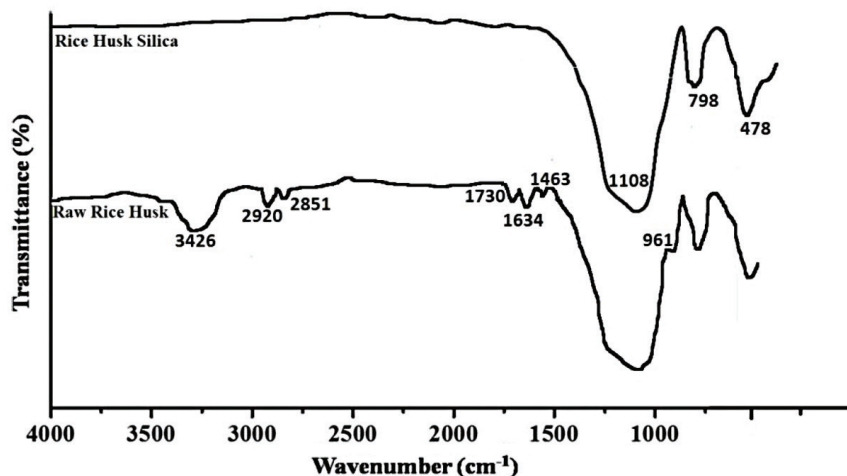Fig. 1 – *SEM of rice husk, left: raw rice husk, right: rice husk silica*

F i g . 2 – *FTIR spectrum of raw rice husk and rice husk silica*

bending vibrations for Si–O bonds in 798 and 478 cm^{−1}, respectively. The other peaks can be assigned to cellulose, hemicellulose, and lignin (the main components of rice husk). Among those peaks, it is possible to discriminate the contribution of each component, even though most of them are ascribed to cellulose and hemicellulose (namely, ν(OH) at 3426, ν(CH$_2$) at 2920, δ(OH) at 1634, δ(CH$_2$) at 1463, δ(CH), and δ(OH) at 961 cm^{−1}. In addition, for hemicellulose a less intense peak at 1730 cm^{−1} can be attributed to the C=O stretching vibration of carboxyl groups). On the other hand, the presence of lignin is detectable only by the presence of methyl groups and aromatic skeletal vibrations (at 2851 and 1634 cm^{−1}, respectively). After silica extraction, all the bands of cellulose, hemicellulose, and lignin disappear, and only the Si–O–Si and Si–O bonds vibrations are still detectable[32] that are responsible for the adsorption of estrogen hormones[33].

The X-ray diffraction method is very important because it is a direct method in determining the type of phases and crystalline structure of materials. Ac-

tually, development of phase identification, mineralogy, and crystallography in recent years has been tied to the discovery of XRD[30]. The X-ray diffraction of rice husk is presented in Fig. 3, showing that raw rice husk and rice husk silica are mostly in the amorphous phase (there is one peak around $2\theta =$ 22.5 that is related to SiO$_2$), but the crystallinity value increased substantially in the rice husk silica[34]. The burning temperature and time are two important factors to define whether the silica remains amorphous or becomes crystalline[35]. Previous research showed that silica produced from rice husk at temperatures of 700–800 °C and times of 3–4 hours, due to the loss of some of the functional groups, such as OH, CH$_2$, and CH and staying in the amorphous phase, had the best absorption properties[24,36–38].

Effect of pH

The pH of the aqueous phase is an important and controlling parameter that has a profound effect
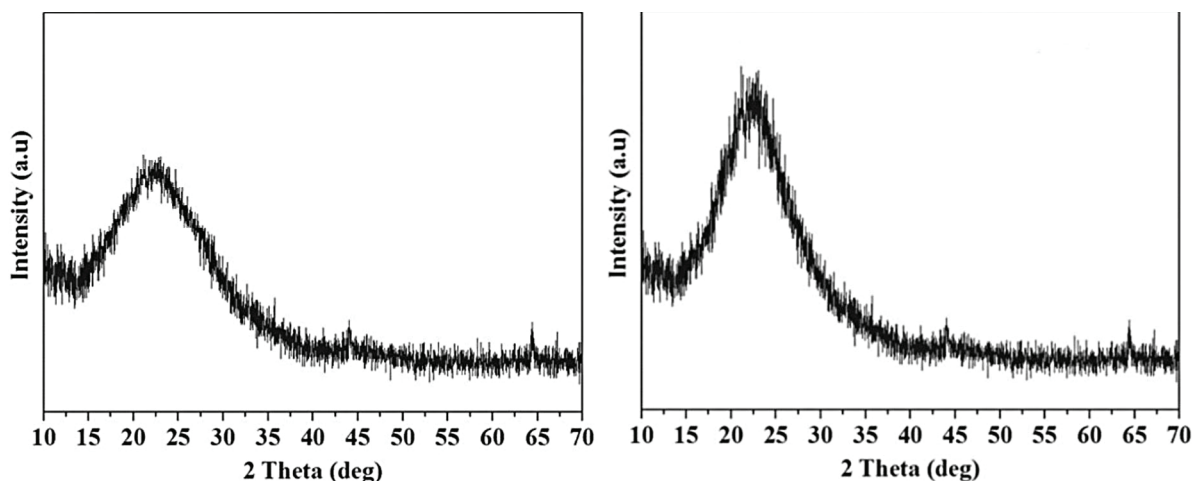

F i g . 3 – *X-Ray diffraction of rice husk, left: raw rice husk, right: rice husk silica*

on adsorption from aqueous solutions. The influence of pH on the removal of E2 and E1 hormones was evaluated in the range of 4–9 at a constant hormone concentration of 10 ng L⁻¹, adsorbent dosage of 0.5 g L⁻¹, and contact time of 30 min. According to Fig. 4, the maximum removal efficiency of these two hormones by rice husk silica was obtained at pH 4. The removal efficiency of E2 and E1 hormones decreased with increasing pH from 4 to 9. This can be interpreted as follows: with increasing pH of the environment, the concentration of OH⁻ ions increases in the environment. Since the external surface of the adsorbent (rice husk silica) has a positive charge and silica tends to absorb high amounts of oxygen, OH⁻ is adsorbed on the adsorbent in alkaline pHs which reduces adsorption capacity[33]. OH⁻ groups present on the adsorbent surface make it negative and bring a repulsive force between the adsorbent and anionic molecules. Lewis *et al.* and Andaluri *et al.* found that the values of acid dissociation constant (pK_a) of 17-beta estradiol and estrone hormones were 10.71 and 10.77, respectively, indicating that these two hormones are weak acids and are dissociated, and therefore negatively charged only at high pH values[39,40]. On the other hand, Khan *et al.* obtained pH_{zpc} of rice husk silica at 6.5, which justifies the effect of pH in this study. This point states that at pH less than 6.5, the surface charge of absorbent will be positive and there will be no repulsion between surface and neutral hormone molecules, which will increase the removal efficiency[41]. Therefore, in this study pH of 4 was chosen as the best level and used for further experiments. The results of this study are consistent with the results of Wang X *et al.*[33] and studies of Zhang and Zhou[31].

Effect of adsorbent dosage

The effect of adsorbent dosage on estrogen removal was evaluated at a constant pH of 4, contact time of 30 min, and hormone concentration of 10 ng L⁻¹. The adsorbent dosage at four different quantities of 0.5, 1, 1.5, and 2 g L⁻¹ was studied. The maximum removal efficiency of E2 and E1 hormones was obtained at 1.5 and 2 g L⁻¹ adsorbent dosage (Fig. 5). The removal efficiency of E2 and E1 hormones was increased by increasing dosage of rice husk silica. Such increase can be due to increasing surface area and number of active sites on the adsorbent[42]. The mild progression in adsorption of E2 and E1 hormones for higher concentrations can be due to the partial accumulation of adsorbent, which reduces the effective surface of adsorption. With regard to the insignificant difference in removal efficiency for 1.5 and 2 g L⁻¹ adsorbent dosage and from the economical point of view, 1.5 g L⁻¹ adsorbent dosage was considered as optimum.
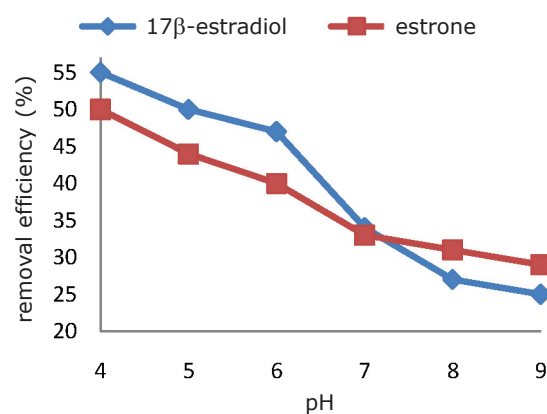

F i g. 4 – *Effect of pH on the efficiency removal (%) of E2 and E1 (adsorbent dosage of 0.5 g L⁻¹, contact time of 30 min and 10 ng L⁻¹ concentration of E2 and E1)*
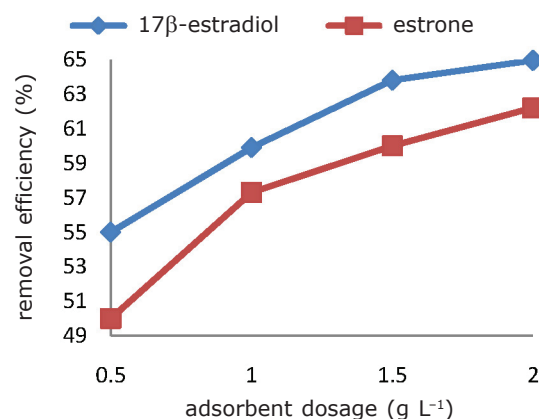

F i g. 5 – *Effect of adsorbent dosage on the removal efficiency of E2 and E1 (30 min of contact time, pH 4, and 10 ng L⁻¹ concentration of E2 and E1)*

In agreement with current work, the study of Kong *et al.*[43] reported that the removal rate of E2 increased monotonously as the adsorbent dosage increased before reaching a maximum removal (dosage less than 2 g L⁻¹), and then the removal rate changed slightly, indicating that the adsorption had reached saturation point. Similar results were also observed by Mor *et al.*[44] using agro-waste rice husk ash.

Effect of contact time

Contact time is one of the most important parameters for successful usage of adsorbents for practical applications. The studies were conducted at contact times of 30, 60, 90, and 120 min to determine its effect on removal of E2 and E1 at a constant pH of 4, adsorbent dosage of 1.5 g L⁻¹, and hormone concentration of 10 ng L⁻¹. Fig. 6 shows that adsorption efficiency for estrogen removal is a function of time, and removal efficiency increases with increased contact time. Maximum adsorption took place in the initial minutes, and then with in-
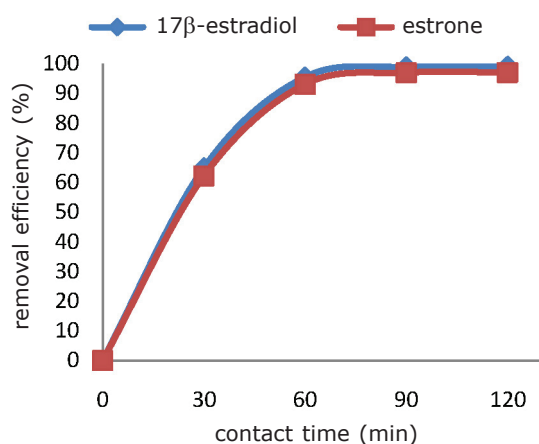
F i g . 6 – *Effect of contact time on the removal efficiency of E2 and E1 (adsorbent dosage of 1.5 g L⁻¹, pH of 4, and 10 ng L⁻¹ concentration of E2 and E1)*
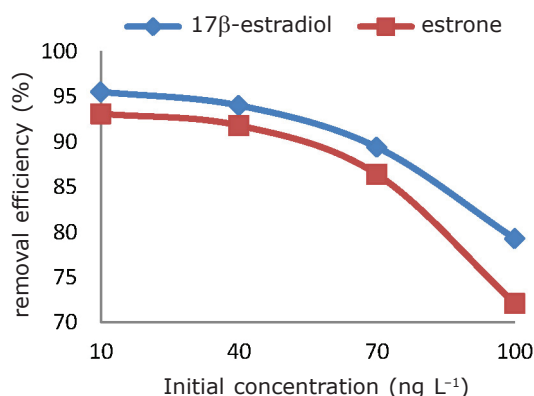

F i g . 7 – *Effect of initial concentration of E2 and E1 hormones on removal efficiency (adsorbent dosage of 1.5 g L⁻¹, 60 min of contact time and pH of 4)*

creased contact time, the removal efficiency increased but its rate decreased. The reason is that, in the initial times of contact, there are vacant sites on adsorbent surfaces to absorb hormones, and over time, these sites are occupied gradually, which leads to rejection of hormones from the adsorbent surface and reduction of the adsorption process[45,46]. Therefore, the contact time of 60 min was selected for the subsequent experiments. In agreement with the current study, the study of Ferandin Honorio et al.[46] showed that, as the contact time increased, the amount of estrogen adsorption on rice husk increased, and the equilibrium times in batch systems were 60 min for the estrone, and 120 min for 17β-estradiol.

Effect of initial concentration of estrogen hormones

Initial concentrations provide the required thrust force to cope with all the resistances of the mass transfer between the solid and liquid phases.

The concentrations of 10, 40, 70, and 100 ng L⁻¹ of E2 and E1 hormones were investigated to determine the initial concentration effect of hormones on removal efficiency. The results showed that the increase in the amount of E2 and E1 hormones reduced their removal efficiency (Fig. 7). This can be due to the competition of hormones to find adsorption sites on the adsorbent[19,47]. There were relatively more adsorption sites at low concentrations for both hormones. Therefore, the adsorption efficiency was high. Lack of bonding sites and their saturation at high concentrations of hormones limited the adsorption efficiency. However, adsorption capacity increased with the increase in initial concentration of E2 and E1 hormones. Similarly, Kumar et al.[47] and Mehdinia et al.[19] reported that with increased initial concentration, the removal efficiency in the adsorbent had decreased.

Adsorption kinetic studies

The kinetic models are used to investigate the adsorption process and its potential rate-controlling steps including mass transfer and chemical reaction processes[48]. Moreover, adsorption kinetics information is needed to select the optimum conditions for the implementation of discontinuous adsorption processes in the real scale.

The results of kinetic modeling (Table 2) showed that the application of nonlinear regression based on pseudo-first-order model, produced the best fit with the laboratory data for both estrogen hormones as proved by the highest determination coefficient (R^2) and the minimum RMSE. The pseudo-first-order equation is based on the assumption that the adsorbing species connect only to one absorption site on the adsorbent surface[49]. The results of this study are consistent with the results of Ferandin Honorio et al.[46] and Kumar and Bandyopadhyay[50].

Adsorption isotherm studies

The proper analysis and design of the adsorption separation processes requires knowing the adsorption isotherms. In the equilibrium, there is a specific relationship between the concentration of the dissolved material in solution (C_e) and the adsorbed state (q_e) (in terms of the amount of the adsorbed material per unit weight of the adsorbent). Some of the adsorption isotherms that are initially developed for the adsorption from gas phase are available and easily accepted for the correlation of adsorption of many materials[52].

The results from experiments on the effect of initial concentration on the adsorption of hormones on rice husk silica were analyzed using Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherms. The results showed (Table 3) that Lang-

Table 2 – *Results of adsorption kinetic models of E2 and E1 hormones on rice husk silica (adsorbent dosage of 1.5 g L^{-1}, pH of 4, and 10 ng L^{-1} concentration of E2 and E1)*

Model / Regression type	Eq.	17β-Estradiol $q_{e\,exp}$=6.64				Estrone $q_{e\,exp}$=6.51			
		q_e (ng g^{-1})	k	RMSE	R^2	q_e (ng g^{-1})	k	RMSE	R^2
Pseudo-first-order/ linear regression	$\ln(q_e - q_t) = \ln(q_e) - k_1 t$ 33	6.8	0.0494 min^{-1}	0.3133	0.9629	6.75	0.0485 min^{-1}	0.310	0.9579
Pseudo-second-order/linear regression	$t/q_t = 1/k_2 q_e^2 + (1/q_e)t$ 51	6.97	0.0199 g ng^{-1} min^{-1}	0.5866	0.9801	6.85	0.01895 g ng^{-1} min^{-1}	0.5942	0.9773
Pseudo-first-order/ Nonlinear regression	$q_t = q_e[1 - \exp(-k_1 t)]$ 46	6.72	0.0345 min^{-1}	0.236	0.9909	6.60	0.033 min^{-1}	0.248	0.9894
Pseudo-second-order/Nonlinear regression	$q_t = (q_e^2 kt)/(1 + q_e kt)$ 43	8.02	0.0049 g ng^{-1} min^{-1}	0.3674	0.9775	7.96	0.0045 g ng^{-1} min^{-1}	0.3748	0.9755

muir model gave the best fit of the experimental data for both hormones as evidenced by the highest determination coefficient (R^2) and lowest RMSE. This shows that the adsorption of both hormones on the surface of rice husk silica occurs homogeneously in the form of a single layer covering the surface with the same adsorption energy and without interaction between the adsorbed molecules[53,54]. One of the essential characteristics of the Langmuir isotherm could be expressed by a dimensionless constant called equilibrium parameter, R_L (eq. 3).

$$R_L = 1/(1 + kC_0) \qquad (3)$$

where C_0 is the initial solute concentration. The values of R_L indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$)[51]. It has been shown that the adsorption of E2 ($R_L = 0.27$) and E1 ($R_L = 0.32$) hormones on rice husk silica is favorable. In this respect, the results of this study are consistent with the results of Kumar *et al.*[47] and Jiang *et al.*[55]

The information on the type of adsorption cannot be obtained with the Langmuir isotherm. The Dubinin-Radushkevich isotherm is used to find the type of adsorption. This isotherm also gives information on the binding energies. The calculation of the average free energy, ε, of a molecule of adsorbent, expresses the energy released when a molecule of adsorbate passes from the solution into the adsorbent[56]. The energy was calculated from equation 4:

$$\varepsilon = 1/\sqrt{2\beta} \qquad (4)$$

where β is a constant, and ε is the mean free energy of adsorption per mole of the adsorbate. If the magnitude of ε is between 8 and 16 kJ mol^{-1}, the adsorption process occurs by ion exchange, while for the values of $\varepsilon < 8$ kJ mol^{-1}, the adsorption process is of a physical nature[56]. The experimental energies of adsorption of E2 and E1 hormones on rice husk silica are consistent with the values characteristic for ion exchange (with $\varepsilon = 15.07$ kJ mol^{-1} for E2, and $\varepsilon = 11.47$ kJ mol^{-1} for E1). The values of the Freundlich constants, n, determine if the adsorption of the hormones on the studied adsorbent is favorable or not. If n lies between 1 and 10, the adsorption is favorable[49]. The experimental values of n are between 1 and 10 (Table 3) for the adsorption of E2 and E1 hormones on rice husk silica, which points to favorable adsorption. The Temkin adsorption model explains the nature of adsorbent-adsorbate interactions while giving energy-related information of the adsorption process. If Temkin constant, b, is positive, the adsorbent-adsorbate interactions are attractive, and in the contrary case, they are repulsive[57]. For this study, b is positive, thus, the silica-hormone interactions are attractive.

Desorption studies

An important parameter in adsorption studies is the possibility of desorption of the adsorbed species. Desorption studies determine the stability of the adsorbate on the adsorbent surface and reduction in adsorbent capacity. Desorption process was performed in three cycles (adsorption/desorption, see Fig. 8) on the saturated adsorbent after the adsorption performed at the optimum conditions determined previously. The desorption medium was double-distilled water and acetonitrile (solution without hormones), and filter paper was used to

Table 3 – *Results of adsorption isotherm models of E2 and E1 hormones on rice husk silica (adsorbent dosage of 1.5 g L⁻¹, pH of 4, and contact time of 60 min)*

Name of Eq.		Langmuir	Freundlich	Temkin	D-R
	Eq.	$C_e/q_e = 1/bq_m + C_e/q_m$ [44]	$\ln q_e = \ln K_f + (1/n)\ln C_e$ [49]	$q_e = b\ln a + b\ln C_e$ [57]	$\ln q_e = \ln q_m - \beta\varepsilon^2$ [56]
E2	q_{max} (ng g⁻¹)	62.5	–	–	41
	b	0.265 L ng⁻¹	–	12.35 kJ mol⁻¹	–
	a (L g⁻¹)	–	–	3.5761	–
	K_f (ng g⁻¹)(L g⁻¹)$^{1/n}$	–	11.9019	–	–
	n	–	1.78	–	–
	β (mol² kJ⁻²)	–	–	–	2·10⁻³
	RMSE	0.002	0.197	1.04	0.233
	R^2	0.9997	0.9419	0.9967	0.9354
E1	q_{max} (ng g⁻¹)	56.82	–	–	38.89
	b	0.212 L ng⁻¹	–	11.66 kJ mol⁻¹	–
	a (L g⁻¹)	–	–	2.5908	–
	K_f (ng g⁻¹)(L g⁻¹)$^{1/n}$	–	9.4820	–	–
	n	–	1.78	–	–
	β (mol² kJ⁻²)	–	–	–	4·10⁻³
	RMSE	0.011	0.234	1.79	0.194
	R^2	0.9961	0.9149	0.9877	0.9459

separate adsorbent from the solution[27]. Hence, the desorption efficiencies of E2 and E1 hormones from the adsorbent surface in three consecutive cycles of adsorption and desorption were obtained. They amounted to 51.8, 37.6, and 19 % for E2, and 54.7, 42.1, and 23 % for E1, respectively, which shows that rice husk silica adsorbent tends to keep E2 and

E1 hormones adsorbed during the desorption process. Results showed that, the removal efficiency of E2 and E1 hormones in the three consecutive cycles of repeated adsorption using the same batch of adsorbent, gradually decreased to the values of 49.4, 18.5, and 3.5 % for E2, and 50.9, 21.4, and 5 % for E1, respectively.
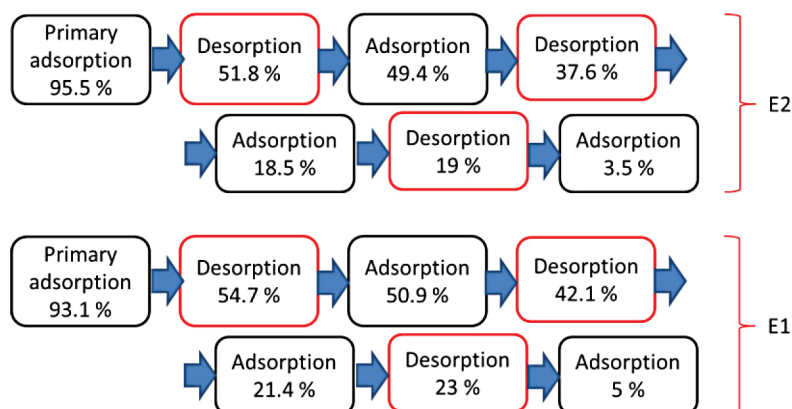

Fig. 8 – *Desorption/adsorption modeling of E2 and E1 hormones on rice husk silica*

Raw rice husk study

Finally, the efficiency of raw rice husk for the adsorption of estrogen hormones under previously determined optimal conditions was investigated. The removal efficiency of E2 and E1 hormones was 13 and 9 %, respectively. Such a large difference in removal efficiency of hormones when using silica against raw rice husk is due to the difference between their structural characteristics, which was expressed in the first part of the results. Adsorption is a surface phenomenon; upon production of silica, the specific surface area increases, resulting in better adsorption of hormones.

For the sake of comparison, the mechanism, isotherms, and kinetics of removal of two endocrine disrupting chemicals, 17β-estradiol (E2) and 17α-ethinyloestradiol (EE2) by activated carbon adsorption were investigated by Ifelebuegu[58]. Mathematical models were used to describe the adsorption phenomenon with the kinetic and thermodynamic parameters evaluated using the adsorption equilibrium data at varying temperatures. Higher adsorption rates were achieved in an acidic pH range (such as in this study), with the sorption kinetics data showing a good fit to the pseudo-second-order rate equation and the Langmuir adsorption isotherm model (such as in this study) for both E2 and EE2. The values of enthalpy for both E2 (84.50 kJ mol^{-1}) and EE2 (90 kJ mol^{-1}) indicated a chemical nature of the sorption process[58] (such as in this study, but at a much higher enthalpies).

Braga *et al.* investigated the adsorption of the endocrine disruptor 17ß-estradiol (E2) on pine bark and almond shell[59]. These traditional Portuguese agro-forestry by-products were milled, sieved into different particle size fractions, and submitted to two different kinds of treatment. Adsorption experiments were conducted in batch system at room temperature and at pH 4.75 and 6.80, respectively for pine bark and almond shell. E2 was more effectively adsorbed on 100 to 150 μm particles of both sorbents. Pine bark washed with hot water and pine bark treated with formaldehyde showed higher percentage of adsorption than any other material tested at doses of 5.0 g L^{-1}. The adsorption was of comparable efficiency in case of almond shells at doses of around 20 g L^{-1}. In this case, the percentage of adsorption was found to be 88 and 90 % for the sorbents treated with formaldehyde or washed with hot water. The adsorption isotherms were found to fit Freundlich equation, with correlation coefficients (R^2) between 0.904 and 0.998.

Conclusions

In studies on the presence of hormones, especially estrogens in the environment, these compounds have been observed at low concentrations (ng L^{-1}) in surface water, ground water, urban and hospital wastewaters, and livestock sewage, and yet they are capable of exerting intensive hormonal activity. Although advanced treatment processes are able to remove the hormones effectively in most cases, such as in treatment with activated carbon, advanced oxidation, etc., there are limitations in their use due to the high cost and production of harmful by-products. The results of this study showed that rice husk silica could be considered as an effective and accessible adsorbent for the removal of estrogenic hormones with high adsorption efficiency. The maximum removal efficiency of estrone and 17β-estradiol hormones was obtained at the level of 93.1 and 95.5 %, respectively, at pH 4, 10 ng L^{-1} initial concentration of hormones, contact time of 60 minutes, and 1.5 g L^{-1} adsorbent dosage. By applying nonlinear regression procedure, the pseudo-first-order kinetic model and Langmuir adsorption isotherm produced the best fit with experimental data for both estrogen hormones. It is very important to remove estrogens from water prior to it being supplied to the community; otherwise, the estrogens may disturb the human endocrine system and cause cancer. Therefore, the results of this paper are very promising, and supplemental studies in pilot and full scale are required to make the process applicable as a technology. Future research can focus on thermodynamics of adsorption and use of the investigated adsorbent for removal of other hormones.
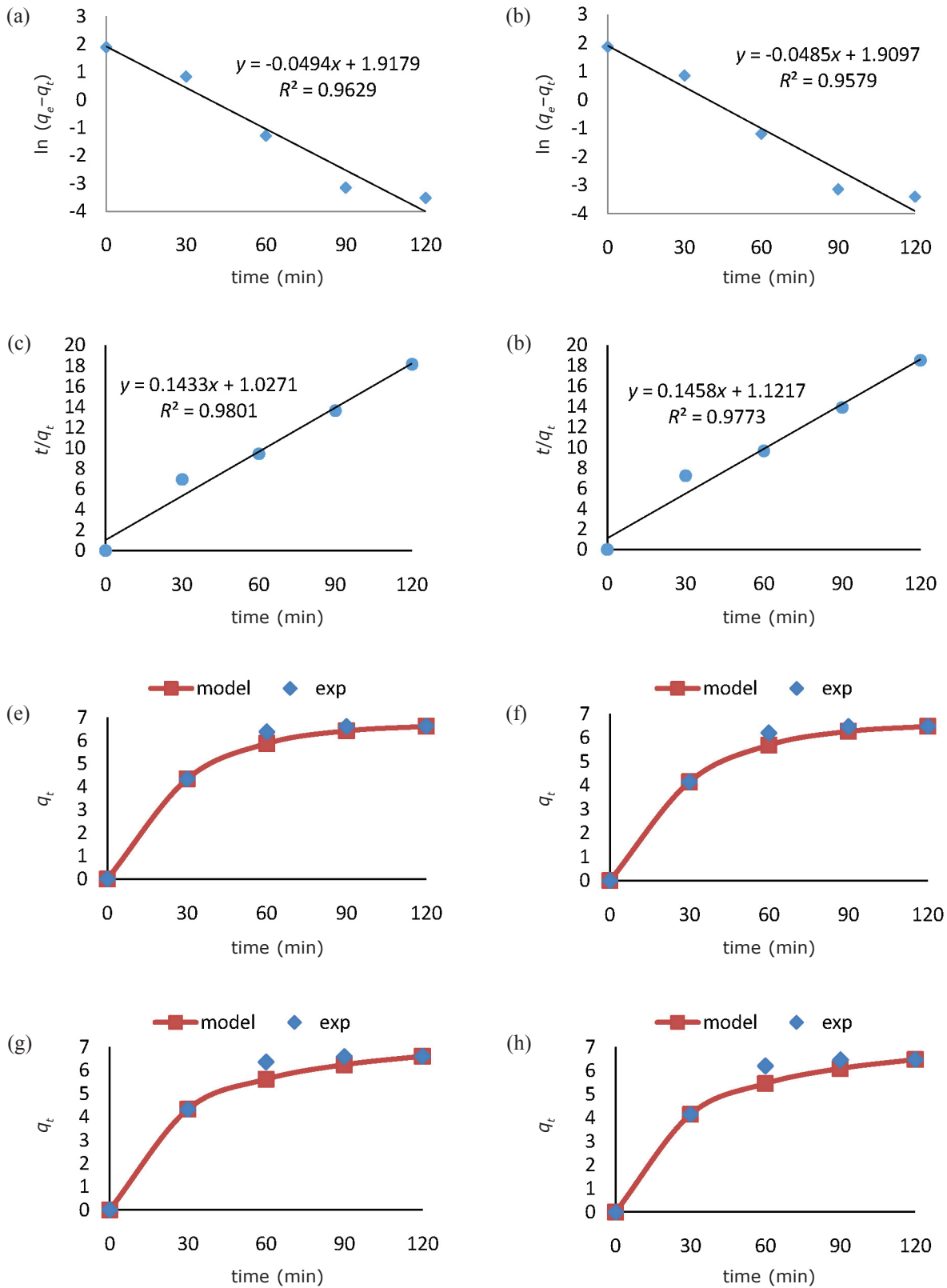
Supplementary materials

Fig. 9 – *Adsorption kinetics modeling of E2 and E1 hormones on rice husk silica. Linear pseudo-first-order kinetic for E2 (a), linear pseudo-first-order kinetic for E1 (b), linear pseudo-second-order kinetic for E2 (c), linear pseudo-second-order kinetic for E1 (d), non-linear pseudo-first-order kinetic for E2 (e), non-linear pseudo-first-order kinetic for E1 (f), non-linear pseudo-second-order kinetic for E2 (g), non-linear pseudo-second-order kinetic for E1 (h).*
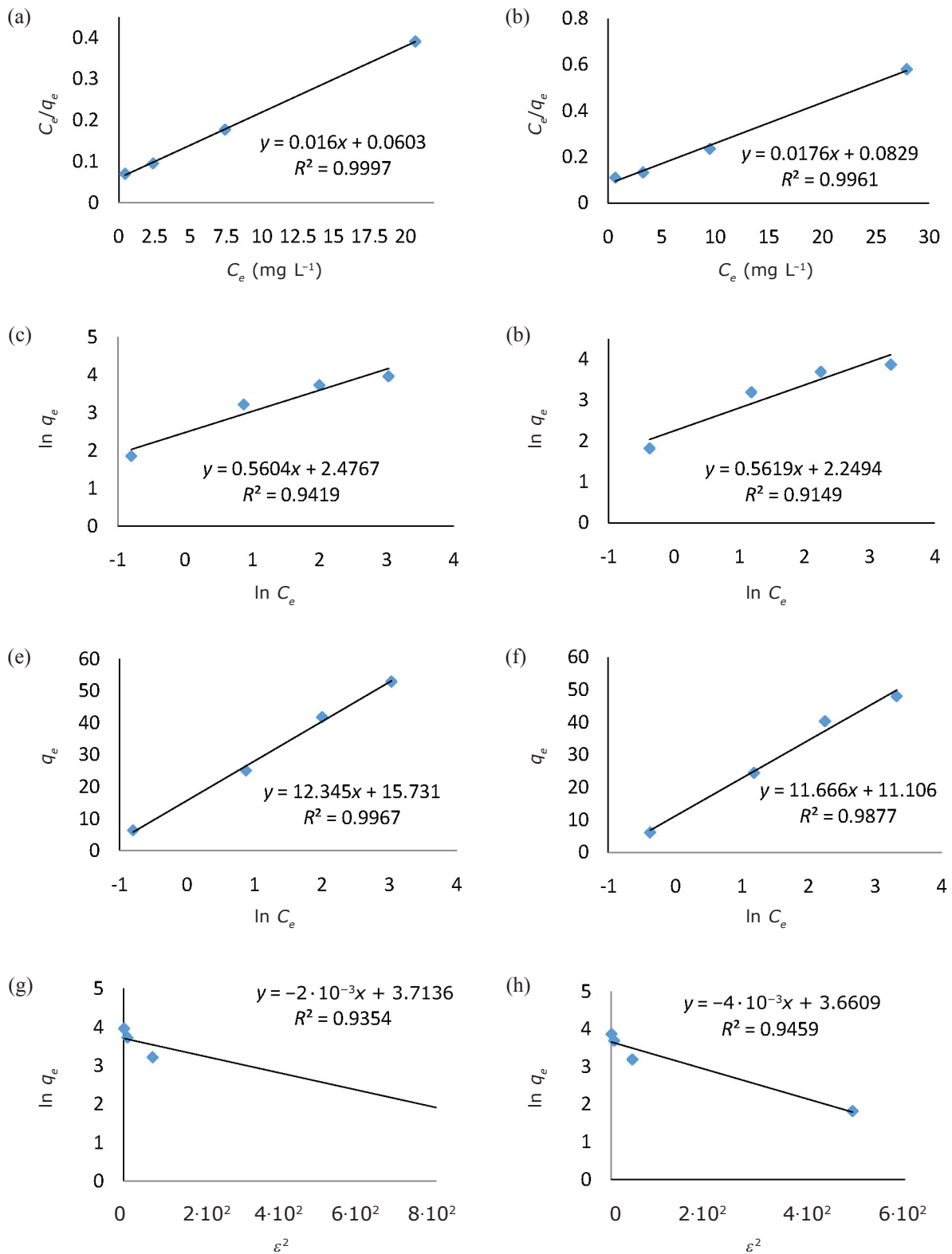
Fig. 10 – *Adsorption isotherm modeling of E2 and E1 hormones on rice husk silica (adsorbent dosage of 1.5 g L⁻¹, pH of 4 and contact time of 60 min). Langmuir adsorption isotherm for E2 (a), Langmuir adsorption isotherm for E1 (b), Freundlich adsorption isotherm for E2 (c), Freundlich adsorption isotherm for E1 (d), Temkin adsorption isotherm for E2 (e), Temkin adsorption isotherm for E1 (f), Dubinin-Radushkevich isotherm for E2 (g), Dubinin-Radushkevich isotherm for E1 (h).*

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