Activated Carbon Impregnated by Zero-Valent Iron Nanoparticles (AC/nZVI) Optimized for Simultaneous Adsorption Furfural: Green Synthesis, Regeneration, Characterization, and Adsorption-Desorption Studies

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**Activated carbon impregnated by zero-valent iron nanoparticles (AC/nZVI)
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Abstract

Furfural is an organic aromatic compound that has attracted considerable interest as a potential
chemical for the production of biochemical and biofuels. However, furfural has proved to
possess ecotoxic effect on the environment and to humans, therefore measures are required to

prevent these effects. One of the most widely used methods for eliminating furfural is the surface adsorption process. The present study focused on the structure and morphology of the composite nanoparticles, investigated using FTIR, XRD, BET and FE-SEM techniques. Furthermore, the variables of time, solution pH, dosage composite and initial furfural were evaluated. Furfural adsorption was performed by spectrophotometer at a wavelength of 227 nm. The removal efficiency under optimal conditions for furfural (Furfural concentration of 250 mg/L, the composite dose of 4 g/L, the reaction time of 60 min and pH = 7) was 81.46%. In addition, the study of isotherm and adsorption kinetics for furfural showed that the adsorption process follows the Langmuir isotherm and quasi-quadratic kinetics. The $q_{\max}$ of the composite was determined by the Langmuir model of 222.22 mg/g. Therefore, the present study exclusively showed that the activated carbon coated with nZVI nanoparticles used as an effective and environmentally friendly adsorbent for furfural removal from aqueous solutions. Furthermore, this study could possibly have applied for the adsorption of other chemical compounds such as dyes, metronidazole, aniline.

Keywords Environmental pollutants. Green synthesis. nanoparticles. furfural adsorption. activated carbon. nZVI

Introduction

The presence of resistant and toxic materials and substances in water sources that can cause complex problems (USEPA 1998). Complex chemical compounds of various industries such as petrochemicals, oil refineries, process units and chemical production have entered the environment and these industries have always been considered as a major source of environmental pollutants, especially soil and water resources. Among the wide range of elements present in the environment, furfural is used on a large scale in refineries and petrochemical industries, paper and cardboard, oil refining and is present in their wastewater in the range of 100-1200 mg/L (Borghei & Hosseini 2008, Elaheh et al. 2011, Hoydonckx et al. 2000, Li et al. 2011, Shu 2006, Singh et al. 2009, Yang et al. 2012). Furfural is one of the types of aromatic aldehydes. Furfural is a bi-furfural liquid and oil that has an almond odour and rapidly turns to yellow furfural upon contact with air (OSHA. Washington 1992). Furfural is soluble in water and has a boiling point of 161.8 °C (EPA 2006, Zeitsch 2000). Human exposure can occur through inhalation, swallowing, skin or eye contact, or absorption through the skin. Exposure to concentrations of 1.9-14 ppm from furfural has caused headaches, redness of the eyes, and tearing

in some workers exposed to it. Exposure to higher concentrations causes pulmonary edema (Anbia & Mohammadi 2009, Faramarzpour et al. 2009, OSHA. Washington 1992).

Several methods have been studied in furfural removal, the most important of which are biological methods and adsorption process. Catalytic and photocatalytic methods, extraction from nanofiltration solvents are other methods that have been studied and reported by various researchers in furfural removal (Anbia & Mohammadi 2009, Faramarzpour et al. 2009, Mao et al. 2012, Singh et al. 2009, Zhang et al. 2011). Studies have shown that the furfural biodegradation includes both aerobic and anaerobic approaches, which are expensive. Furthermore, under the influence of various parameters and toxicity of furfural at high concentrations, as well as difficulties in degradability and toxicity of most compounds in the petrochemical industry effluent, the use of this method has made furfural removal practically impossible (Fahmi et al. 2011, Mebrek & Derriche 2010, Sahu et al. 2008). Other advantages of this method are production and high-quality effluents (Iram et al. 2010, Shen et al. 2011).

Nanotechnology is the study of the materials that are < 100 nm in size, and their physical, chemical and biological properties are fundamentally different from their origin. Multiple methods have been proposed so far for the synthesis of nanoparticles (Shen et al. 2011). Many of these methods are not efficient enough (Iram et al. 2010). A chemical reducing agent (e.g. sodium borohydride) is efficiency metal ions and a stabilizing agent (e.g., polyvinylpyrrolidone) is used to control the growth of particles and prevent them from accumulating (Fazlzadeh et al. 2017). Several methods are environmental friendly as well (Ramezani et al. 2013). However, there is a considerable interest in the biosynthesis of metal nanoparticles using organisms such as plant and microbial extracts (Iram et al. 2010). Among these organisms, plant extract synthesis or the green synthesis of nanoparticles have been prioritized because of the stability imparted to the nanoparticles.

During the green synthesis, a redox reaction occurs in the saline solutions in which the plant extracts (reducing agents) transfer electrons to metal ions and eventually metal nanoparticles are produced. In this method, no pressure, energy, high temperature and toxic chemicals are involved, therefore, pose lower risks to humans and ecosystems and is cost-effective (Fazlzadeh et al. 2017). Today, materials nature (plant extracts) such as grape residue, grapefruit and eucalyptus leaves, black tea extract, have been used to synthesize Zn nanoparticles (Fazlzadeh et al. 2017, Ramezani et al. 2013). Recently, accelerate the separation of nanomaterials from

aqueous media to stabilize nanoparticles on materials such as oxides, polymers, Fibers, activated carbon, etc. are required. Among the above, the use of passive carbon has driven economic benefits and environmental considerations (Fazlzadeh et al. 2017, Ghaedi et al. 2013).

Activated carbon has high availability, low cost, high surface area, reusability, properties of surface chemistry and high pore volume and therefore has involved enormous consideration (Bhatia et al. 2018). However, commercial activated carbon (AC) has been proved expensive. Therefore, there is an essence for economically affordable materials that could be an alternative for the commercially available activated carbon. At the other end, AC can be obtained extensively from materials such as Algae, coconut shell, corn, lignin, etc (Mohan & Pittman 2006). However, there are limited studies that have reported on the performance of AC prepared from pomegranate peel and the stabilization effect of nanoparticles using plant extracts on activated carbon for furfural removal, evaluation of its efficiency in the removal under the influence of various variables on the process such as pH, reaction time, adsorbent dose and initial furfural concentration in synthetic solutions. Therefore, the present study has assessed the use of activated carbon prepared from the pomegranate peels coated with nZVI nanoparticles, as an effective and ecologically friendly adsorbent for furfural elimination from aqueous solutions.

Materials and methods

Material

The furfural (Chemical formula: $C_5H_4O_2$ and Molecular weight: 96.08 g/mol) and all the chemicals such as H_2SO_4 and $NaOH$ were procured from Merck, Germany. H_2SO_4 and $NaOH$ were to adjust the pH of the furfural solution. The water was used twice in all stages of the experiments.

Characterization of the furfural

The specific surface area was determined based on BET analysis and pore volume by nitrogen gas adsorption analysis. The average diameter of the cavities and the total volume of the cavities were also determined. The surface structure of the adsorbent was analyzed by field emission scanning electron microscopy (FESEM) at the same magnification. FTIR analysis in the range of $450-4000\text{ cm}^{-1}$ was used to identify the functional groups on the nanocomposite surface by Perkin Elmer Spectrum Two. X-ray diffraction of the composite was determined at an angle in

the range of $2\theta = 10-80$ by XRD (Philips PNA-analytical diffractometer). The residual furfural concentration was measured by DR5000HACH spectrophotometer at 277 nm (Singh et al. 2009).

Preparation of the active carbon

In this study, pomegranate peel was used to prepare activated carbon. In the first stage, the pomegranate skin was sliced into 0.5 cm pieces and impregnated with phosphoric acid. The impregnated skins were transferred to the reactor and placed at 800 °C for 2 h. Following the removal from the reactor, the carbon was rinsed with distilled water and placed in an oven at 110°C for 2 h to dry. Finally, AC was separated by a sieve with a mesh between 20-30 and ready for use (Fazlzadeh et al. 2017).

NZVI preparation using green synthesis technique

Pomegranate peel extract was prepared by boiling for 60 minutes. The obtained extract was then filtered by vacuum pump, filtered to form nanoparticles, FeCl₂ solution with specified normality is added to 250 cc of distilled water and FeCl₂ solution is added to the pomegranate peel extract. The appearance of a darker colour indicates the formation of zero-capacity iron particles. The nanoparticles were then placed in the oven at 70 ° C for 24 h to dry (Leili et al. 2018).

Loading nZVI on AC

The composite was synthesized by adding 0.05 g of nZVI-NPs to 200 cc of distilled water and was stirred for 10 min to obtain a uniform solution. Following this, 5 g of AC was added to the solution (250 rpm for 2 h). The composite was put in the oven (at 95°C temperature for 10 h) (Rashtbari et al. 2020b).

Batch furfural adsorption studies.

In the present study, Sulfuric acid and sodium hydroxide 0.1 M were used to adjust the pH. The furfural stock solution was prepared by diluting. The adsorption study was performed with a pH change from (3-5-7-9-11) amount of adsorbent (0.5-1-2-3-5-6 g/L), furfural concentration (100-150-250-350 mgL⁻¹) and contact time (5 to 120 min). The removal efficiency and the amount of furfural adsorption in the adsorbent mass unit after the adsorption process were determined through Eqs 1 and 2, respectively (Rashtbari et al. 2020a, Shokoohi et al. 2018)

$$\%R = \frac{(C_0 - C_f)}{C_0} 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

where, C_0 and C_e are the initial furfural concentration and equilibrium liquid phase concentration of furfural (mg/L) respectively, C_f is the final furfural concentration, M is the amount of adsorbent and V is the volume of the solution (L), AC-nZVI nanoparticles (g).

Evaluation of zero charge point (pH_{pzc})

Fifty milliliters of 0.1 M NaCl solution was poured into 150 mL Erlenmeyer flasks with a pH adjusted with sulfuric acid and sodium hydroxide in the range of 2-12. An amount of 0.04 g of nanocomposite was added to the solutions (stirred for 48 h). The final pH was measured and its curve was plotted against the initial pH. The point on the curve that intersects the bisector was identified as the pH_{pzc} nanocomposite (Ali et al. 2020, Rivera-Utrilla et al. 2010).

Results and discussion

Composite characteristics analysis

The FTIR analysis of activated carbon and AC-nZVI composite is shown in Fig. 1(a). The adsorption peak 900-1300 cm^{-1} belongs to the phosphorus-containing functional groups, which are the activation of phosphoric acid used during the preparation process (Ghaedi et al. 2013) and the peaks used. The wavelengths generated between 400-1800 cm^{-1} are related to the vibrations of Fe-O bonds. The presence of nZVI nanoparticles can be proved by the appearance of an absorption band at 506 cm^{-1} (Bhatia et al. 2018). The 3000-2800 band with a peak of 2850 cm^{-1} in the AC-nZVI composite is related to the presence of the C-H alkanes band (EPA 2006). The peak observed for AC and AC-nZVI in the band 13432 cm^{-1} can be related to the O-H vibration in the H_2O molecule (Mohan & Pittman 2006). Also, the peaks observed in bands 2925 and 2850 as indicated (EPA 2006) involvement of C-H and O-H (acidic group) of pomegranate peel extract in the formation of particles (Leili et al. 2018). Absorption peaks appear at the absorption wavelengths in 1030, 1456, 1634, 2932 and 3426 corresponding to the functional groups of polyphenol compounds. Therefore, it can be claimed that the polyphenols in the extract play a double role as reducing the metal ion and converting it to nanoparticles and as a stabilizing

nanoparticle (Sun et al. 2014). Some peaks disappeared after nZVI coverage in AC and decreased irregularity in the AC-nZVI spectrum. Overall, nZVI coverage on AC has been successful.

The XRD result shows that the AC-nZVI-NPs owns a crystalline structure that improves the process of adsorption through physical adsorption. The maximum peak of around $2\theta = 32$ (with very high intensity) was also observed on the XRD image (Fig. 1(b)). Fig. 2 shows the results of the morphology of the adsorbent surface. According to Fig. 2 (a), the surface of activated carbon has a favourable porosity. These cavities provide a good opportunity for nZVI nanoparticles to be trapped inside. In Fig. 2(b), nZVI nanoparticles can also be seen as white particles. These nanoparticles are dispersed and evenly distributed on the activated carbon surface. Stabilization of nanoparticles on activated carbon partially blocks surface porosity, probably because zero-capacity iron nanoparticles cannot enter the internal cavities of activated carbon tissue and therefore remain on the outer surface of activated carbon. The FE-SEM image of the stabilized nanoparticles indicates that the porosity composite has a suitable specific surface area and the zero-capacity iron nanoparticles are well stabilized on the activated carbon (Rashtbari et al. 2020b, Sun et al. 2014).

BET analysis was performed based on measuring the volume of nitrogen gas absorbed and desorbed by the material surface at a constant temperature of liquid nitrogen (77 K) to calculate the pore volume and surface area. This analysis was performed by BET device (Quanta chrome Instruments, CHEMBET 3000). Fig. 3 shows the results of the BET analysis of AC-nZVI nanocomposite. Table 1, it can be seen that the porosity of nanocomposite is more than activated carbon. The area of specific surface area of activated carbon and nanocomposite is calculated as 731.12 and 821.74 m^2g^{-1} , respectively. This result shows that by adding nZVI nanoparticles to the activated carbon, the adsorbent surface area increased. The maximum amount of adsorbent pores was in the range of 3.08 nm, which indicates the microscopic structure.

The effect of pH on process efficiency

pH is the most important parameter in the adsorption process. The effect of pH of 3, 5, 7, 9 and 11 with a reaction time of 60 minutes at a concentration of 250 mg/L. Results obtained by studying the pH effect on the adsorption efficiency of furfural on Nano-composites are presented in Figs. 4 (A,B). The presented data in Fig. 4 (b) indicated that with increasing of the pH from 3 to 7, the adsorption of furfural on Nano-composites surface has also increased. According to the

experimental results, it was observed that the removal efficiency under neutral pH conditions is slightly higher than the alkaline and acidic conditions. At this stage, pH 7 was selected as the optimal pH. At $\text{pH} < \text{pH}_{\text{pzc}}$, the AC-nZVI had a positive charge and in $\text{pH} > \text{pH}_{\text{pzc}}$, it had a negative charge. As a result, in solutions with a $\text{pH} < 6.76$, the nanocomposite had a positive charge at its surface, while the furfural dye molecules were negatively charged. As the pH decreases due to the increase of H^+ ions in the solution, the formation of electrostatic attraction between the H^+ ion and the dye increases that ultimately increases the adsorption rate as well. On the other hand, nanocomposite had a negative charge due to $\text{pH} > 6.76$, so the anionic dye and the adsorbent repelled (Fazlzadeh et al. 2018, Sun et al. 2014) as reported earlier (Sahu et al. 2008).

Examining the effect of adsorbent dose

The adsorbent dose determines the adsorbent capacity for a given initial concentration of furfural, Fig. 5 shows the changes in the furfural adsorption process by the composite. In experiments performed on 100 mL samples with a concentration of 250 mg/L of paint, the contact time was 60 minutes, pH was 7 and doses of 0.5, 1, 2, 3, 4, 5 and 6 g/L were performed. It was found that the removal rate in furfural increases with increasing the amount of adsorption. The furfural removal increased from 22.28% to 83.32% by increasing the dose from 0.5 to 6 g/L. The $q_{\max}$ decreased with increasing dose therefore the $q_{\max}$ of furfural decreased from 111.42 mg/g to 34.72 mg/g; therefore, the optimal dose of 4 g/L was selected. The results show that with increasing the adsorbent dose, the furfural removal efficiency increases, which changes faster in the adsorbent dose to 4 g/L. After 4g/L, the removal efficiency has been a gentle and almost constant process. Increased furfural uptake occurs to increase the adsorbent dose due to the increase in the number of positive sites, the increase in the adsorbent surface and the presence of a strong driving force. At low doses of adsorbent, fewer active sites are provided to the furfural molecules, which leads to a decrease in removal efficiency (Mebrek &Derriche 2010). These findings were found to be consistent with a previous study for the furfural removal by active carbon(Mouni et al. 2018).

Effect of time andthe initial concentration

Fig. 6 shows the effect of contact time on furfural uptake. Another influential factor in furfural removal is contact time. In order to evaluate the optimal contact time for experiments in the range of 350-100 mg/L under optimal conditions of pH = 7 and the amount of adsorbent 4 g/L, was evaluated at times from 0 to 120 minutes. The stirrer speed was 250 rpm and the experiments were performed at a temperature of 25°C. As shown in Fig. 6, the adsorbent removal efficiency was performed at high speed in 60 minutes and then increased with a gentle slope to 120 minutes and reached almost equilibrium. Therefore, the optimal contact time for the adsorbent was chosen to be 60 minutes. The rate of pollutant diffusion into the pores decreases, followed by the rate of adsorption. On the other hand, initially, the surfaces available to absorb the contaminant on the adsorbent are completely free and as a result, the adsorbent is in contact with the contaminant with all surfaces and over time the available surfaces become less and thus the adsorption rate decreases (Fazlzadeh et al. 2018). Similar results were also reported in

previous studies (Fazlzadeh et al. 2018, Sahu et al. 2008, Zhang et al. 2019). Fig. 6 shows the effect of the initial concentration of furfural on the removal efficiency of AC-nZVI from the furfural aqueous solution. It was observed that the removal efficiency was declined with increasing furfural concentration at the equilibrium time of 60 min. As the initial concentration of furfural increased from 100 to 250 mg/L, the furfural removal efficiency by AC-nZVI increased from 85.9% to 90.93%, respectively. This may be owed to the finite number of active sites on the adsorbent that becomes saturated at higher concentrations of furfural. In other words, at low concentrations, the availability of the active AC-nZVI sites to the furfural molecules is more than when high concentrations of furfural are involved (Fang & Yang 2021).

Isotherm studies

Isotherm plots for furfural adsorption are shown in Fig. 7 (pH 7, AC-nZVI dose of 4 g/L and $25 \pm 2^\circ\text{C}$). Table 2 displays the isotherm parameters at ideal conditions. Providing the r^2 values obtained for the tested theoretical models (Table 2), it can be observed that the two isotherm models (Langmuir, Freundlich) conform firmly to the experimental result. As the paradigm, Freundlich describes a method of chemical adsorption. An adsorption intensity (n) of 1.74 within 1 to 10 ($1 < n < 10$) for furfural adsorption indicates a desirable adsorption process on AC-nZVI (Shu et al. 2020, Zhang et al. 2019). The isotherm parameters and R^2 values for Langmuir, Freundlich models are calculated from slopes and intercepts by plotting $1/C_e$ versus $1/q_e$ (Fig. 7a), $\log C_e$ versus $\log q_e$ (Fig. 7b), respectively. The isotherm plots for furfural adsorption by AC-nZVI-NPs at the optimum conditions of pH 7, a dose of 4 g/L and temperature of $25 \pm 2^\circ\text{C}$ as shown in Fig. 8.

Kinetic studies

Kinetic experiments are conducted to track the mechanism that governs an adsorption process (Shu et al. 2020). To test the kinetic data, kinetic adsorption models (pseudo-first-order, pseudo-second-order, and intraparticle diffusion models) were used. The equations of linear kinetic models with kinetic parameter definition are given in Table 3. pseudo-first-order are estimated from the intercepts and slopes of plots between $\text{Log}(q_e - q_t)$ versus t (Fig. 9a), q_e and k_2 for pseudo-second-order are estimated from slopes and intercepts of plots between t/q_t versus t (Fig. 9b). The findings obtained on linear adsorption kinetics are summarized in Table 3. The kinetic

parameters were derived from the kinetic models' plots at maximum pH 7 conditions and 4 g/L doses of nanoparticles. The regression coefficients (r^2) verified the correlation between the predicted kinetic model values and the experimental results. The pseudo-second-order kinetic model is found to fit characterize the kinetic experimental data with its values of r^2 closer to unity. This means that adsorption of furfural to AC-nZVI is a chemical adsorption form (Fazlzadeh et al. 2018).

Adsorbent reclamation

The adsorbent recovery process is considered to get their economic value and solve operational problems. AC-nZVI was recovered using 0.1 M NaOH solution. As seen in Fig. 10, the performance was 93.44%, which decreased to 81.74% (five recovery cycles), suggesting that the restored adsorbent already has a high potential to adsorb the AC-nZVI and can be used regularly. The NaOH and the furfural in the active AC-nZVI sites interact, and the furfural is isolated from the active sites. Therefore, nanocomposite has a high potential for wastewater treatment in the pharmaceutical industry. Because it can be reused after five consecutive periods by recovering the adsorbent and by its ability to maintain the removal efficiency. It is also cost-effective and therefore very necessary for industrial applications to prevent secondary pollution in the treatment of wastewater (De Gisi et al. 2016).

Comparison of AC-nZVI nanocomposite for furfural

The deposition of on the composite AC-nZVI was compared. The performance of furfural removal obtained using AC-nZVI shows that furfural removal from its aqueous solution can be implemented. The deposition of furfural (for an initial concentration of 250 mg/L, pH = 7, dose = 4 g/L, T_{im} =60 min, stirring speed = 250 rpm and T_{em} = $25 \pm 2^\circ\text{C}$) was compared in the presence of AC-nZVI (Fig11) using AC as an adsorbent under same condition. A furfural adsorption of 81.87% and 62.06% were obtained using adsorption AC-nZVI and AC, respectively. Using AC-nZVI, a furfural adsorption of 81.87% was achieved within 60 min. This improvement was associated with the combination AC and nZVI nanoparticles which increased surface adsorption (Fazlzadeh et al. 2018). Presently, from various methods, adsorption are considered auspicious treatments to remove various recalcitrant furfural. Based on Table 4, numerous researchers have examined furfural removal in aqueous environments via several adsorbent. At the other end, desorption process is a favourable method for the removal of

furfural. In addition to suitable removal efficiency, other benefits include its moderate costs and non-toxicity. However, the majority of the results in Table 4 are better than that of the present study. In addition, a new composite that can be used for adsorption processes was obtained but more studies are required in order to make this process a feasible option.

Conclusions

The adsorption of furfural onto AC-nZVI nanoparticles was examined in this report. The findings of this analysis show that furfural can be extracted in a very short time by the process of adsorbing on AC-nZVI nanoparticles. The effects of various operating parameters such as pH (3 - 11), dosage (0.5 – 6 g/L), contact time (5 - 120 min), temperature (298K), and initial concentration of fluoride (100 – 350 mg/L) on fluoride adsorption were studied. Furthermore, the removal efficiency of 81.46% was observed at the best conditions (furfural: 250 mg/L, pH of 7, and AC-nZVI dosage of 4 g/L and contact time of 60 min). The process of furfural adsorption on AC-nZVI was found to depend on the Freundlich adsorption isotherm models. Monolayer adsorption capacity of AC-nZVI was 222.22 mg/g. The kinetic data fitted best into the pseudo-second-order model considering the values of the regression coefficients (r^2). AC-nZVI with a very high capability is nevertheless convenient economically to remove various contaminants from water. It could be concluded that the synthesized AC-nZVI can be used as an effective adsorbent for furfural ions removal from aqueous solutions.

Appendix

The crude data extracted from literature included.

Author contribution Yousef Poureshgh and Yousef Rashtbari participated in the conceptualization and design of the research and supervised the work. Shirin Afshin and Asghar Hamzezhadeh are responsible for experimental analysis and interpretation of data. Ayoob Rastegar contributed to literature search and quality assessment, Shahin Ahmadi, Farooq Sher and Soumya Ghosh wrote the first draft of manuscript. All authors have read and approved the final paper as submitted.

Ethical Approval: The authors of this article have covered all the ethical points, including non-plagiarism, duplicate publishing, data distortion, and data creation in this article. This project has been registered in Ardabil University of Medical Sciences with the code of ethics of IR.ARUMS.REC.1398.018

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Declarations

Competing interest The authors declare no competing interests.

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Table 1. Adsorption properties of AC-nZVI at 77 K.

Material	S _{BET} (m ² /g)	S _{micro} (m ² /g)	S _{meso} (m ² g ⁻¹)	V _{Total} (cm ³ /g)	V _{micro} (cm ³ /g)	V _{meso} (cm ³ /g)	D _p (nm)
AC	731.12	524.13	213.26	0.549	0.2236	0.3142	3.0136
AC-Fe	821.74	591.29	234.52	0.629	0.2564	0.3561	3.0867

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Table 2. Equilibrium parameters for Langmuir and Freundlich.

Langmuir				Freundlich			
Equation	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}$				$q_e = K_F C_e^{\frac{1}{n}}$		
	$q_m(\text{mg/g})$	$K_L(\text{L/mg})$	R^2	R_L	$K_f[(\text{mg/g}) (\text{mg/L})^{1/n}]$	n	R^2
furfural	222.22	0.002	0.9707	0.571	3.10	1.74	0.985

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Table 3. Kinetics parameters for pseudo first and pseudo second.

C_0 mg/L	Pseudo first order				Pseudo second order		
	$Log(q_e - q_t) = Log q_e - \frac{k_1 t}{2.303}$				$t/q_t = 1/k_{2p} q_e^2 + t/q_e$		
	q_e, epx (mg g ⁻¹)	q_{e1}, cal (mg g ⁻¹)	k_1 (min ⁻¹)	R^2	q_{e2}, cal (mg g ⁻¹)	K_2 (gmg ⁻¹ min ⁻¹)	R^2
100	24.25	20.62	0.0304	0.8589	24.51	0.0116	0.9984
150	34.5	20.93	0.0295	0.9437	36.63	0.0029	0.9848
250	58.75	44.86	0.0189	0.8526	60.98	0.0009	0.9506
350	69.34	52.47	0.0122	0.7555	70.92	0.0004	0.8497

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484 **Table 4.** Comparison of the Adsorption of Furfural onto Various Adsorbents

Adsorbent material	Maximum removal (%)	Maximum $q_{\max}$ (mg/g)	Conditions	Reference
Activated Carbon	60	0.053	pH = 5.9 Adsorbent dosage = 10 g/L Initial concentration = 50 mg/L Time = 60 min Temperature = 303 K	(Sahu et al. 2008)
torrefied biomass	60	80	pH = 2 Adsorbent dosage = 250 g/L Initial concentration = 50 mg/L Time = 30 min	(Doddapaneni et al. 2018)
MCM-48	-	196.1	pH = 6 Adsorbent dosage = 0.1 g/L Initial concentration = 1000 mg/L Time = 1 h Temperature=298 K	(Anbia & Mohammadi 2009)
AC-nZVI	81.3	222.22	pH = 7 Adsorbent dosage = 4 g/L Initial concentration = 250 mg/L Time = 60 min Temperature = $25 \pm 2^{\circ}\text{C}$	This study
synthesize zero valent iron nanoparticles (NZVI)	87	454.4	pH = 2 Adsorbent dosage = 0.5g/L Initial concentration=100 mg/L Time = 60 min Temperature = 298 K Speed = 200 rpm	(Fazlzadeh et al. 2018)
Organobentonite	-	536.3	pH = 7 Adsorbent dose = 2 g/L Contact time = 6 h Temperature = 30 $^{\circ}\text{C}$ Initial fluoride concentration = 100 mg/L	(Mebrek & Derriche 2010)

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Fig. 1FTIR spectra (a) XRD patterns (b) of the AC and AC- nZVI- NPs.

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Fig.2 FE-SEM images of AC (a) and AC-nZVI –NPs (b, c).

Fig. 3BET of AC and AC-n nZVI-NPs.

Fig.4Effect pH improves on the efficiency of removal of furfural, pHpzc (a) and pH (b)($C_0=200$ mg/L, Tim=60 min, stirring speed = 250 rpm, Temp = $25 \pm 2^\circ\text{C}$).

Fig. 5 The effect of the AC-nZVI dosage varies on the removal efficiency of furfural ($C_0 = 200$ mg/L, $T_{im} = 60$ min, stirring speed = 250 rpm, Temp = $25 \pm 2^\circ\text{C}$ and pH = 7).

Fig. 6 Effect of contact time and initial furfural Concentration for the adsorption of furfural onto AC-nZVI-NPs (dose = 4 g/L, stirring speed = 250 rpm, Temp = $25 \pm 2^\circ\text{C}$ and pH = 7).

Fig.7 Langmuir (a) and Freundlich (b) models for adsorption of furfural by AC-nZVI-NPs.

Fig. 8 Isotherm plots for furfural adsorption by AC-nZVI-NPs (pH = 7, dose = 4 g/L, C_0 = 250 mg/L, T_{im} = 60 min stirring speed = 250 rpm and Temp = $25 \pm 2^\circ\text{C}$).

Fig. 9 Pseudo first order (A) and second-order (B) kinetics models for the adsorption of furfural by AC-nZVI-NPs.

Fig. 10The AC-nZVI-NPs recovery in four stages.

Fig. 11 Comparison of different processes on the adsorption of furfural (pH = 7, dose = 4 g/L, C_0 = 250 mg/L, T_{im} = 60 min, stirring speed = 250 rpm and $T_{em} = 25 \pm 2^\circ\text{C}$).

Figures

Figure 1

FTIR spectra (a) XRD patterns (b) of the AC and AC- nZVI- NPs.

Figure 2

FE-SEM images of AC (a) and AC-nZVI –NPs (b, c).

Figure 3

BET of AC and AC-n nZVI-NPs.

Figure 4

Effect pH improves on the efficiency of removal of furfural, pHpzc (a) and pH (b) ($C_0 = 200\ mg/L$, $T_{im} = 60\ min$, stirring speed = 250 rpm, Temp = $25 \pm 20^\circ C$).

Figure 5

The effect of the AC-nZVI dosage varies on the removal efficiency of furfural ($C_0 = 200 \text{ mg/L}$, $T_{im} = 60 \text{ min}$, stirring speed = 250 rpm, Temp = $25 \pm 2^\circ\text{C}$ and pH = 7).

Figure 6

Effect of contact time and initial furfural Concentration for the adsorption of furfural onto AC-nZVI-NPs (dose = 4 g/L, stirring speed = 250 rpm, Temp = $25 \pm 2^\circ\text{C}$ and pH = 7).

Figure 7

Langmuir (a) and Freundlich (b) models for adsorption of furfural by AC-nZVI-NPs.

Figure 8

Isotherm plots for furfural adsorption by AC-nZVI-NPs (pH = 7, dose = 4 g/L, C_0 = 250 mg/L, T_{im} = 60 min, stirring speed = 250 rpm and Temp = $25 \pm 2^\circ\text{C}$).

Figure 9

Pseudo first order (A) and second-order (B) kinetics models for the adsorption of furfural by AC-nZVI-NPs.

Figure 10

The AC-nZVI-NPs recovery in four stages.

Figure 11

Comparison of different processes on the adsorption of furfural (pH = 7, dose = 4 g/L, C₀ = 250 mg/L, T_{im} = 60 min, stirring speed = 250 rpm and T_{em} = 25 ± 20°C).