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Removal of cyanide from wastewater by adsorption onto pistachio hull wastes: Parametric experiments, kinetics and equilibrium analysis

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ABSTRACT

Many waste materials have been evaluated for their efficacy in removing different classes of contaminants from water and wastewater in order to improve the cost-effectiveness of adsorption. In the present study, pistachio green hull wastes were investigated as a potential adsorbent for the removal of cyanide from a synthetic wastewater. The effects of a selection of the most significant parameters (pH, adsorbent dose, cyanide concentration and contact time) were initially evaluated based on the percentage of cyanide removed from the wastewater. At an optimum pH of 10, over 99% removal of 100 mg/L cyanide was obtained for an adsorbent dose of 1.5 g/L after a 60 min contact time. Kinetic evaluation indicated that the adsorption of cyanide ions onto the pistachio hulls clearly followed the pseudo-second order rate reaction. The equilibrium assessment illustrated that the Langmuir model is the best fit for the experimental data, which attains a maximum adsorption capacity of 156.2 mg/g. The sorption of cyanide ions onto the introduced adsorbent was inferred to be a chemosorption process with intraparticle diffusion as the most important step controlling the overall process rate. Accordingly, the pistachio hull waste is introduced as an efficient and low-cost adsorbent for removal of different concentrations of cyanide from water and wastewater.

1. Introduction

Cyanide is a very toxic compound that is released into the environment through the effluents of industrial activities such as metal plating, electronics, photography, coal coking, plastics, chemical-fertilizer and mining [1,2]. Cyanide is included in the CERCLA priority list of hazardous substances [3] and has adverse health effects on people as well as other living organisms [4]. Exposure to small amounts of cyanide can be deadly irrespective of the route of exposure [5]. Therefore, environmental regulations require reducing the cyanide concentration in wastewater to below 0.2 mg/L prior to discharge into the environment. Dash et al. [2] have recently reviewed and compared methods that have been investigated for the removal of cyanide from wastewater. Although biodegradation is usually the preferred technique for treating wastewater due to its cost-effectiveness and environmental friendliness, there is little information on the use of bioprocesses for treatment of cyanide-laden wastewater (e.g., [6–8]). Cyanide is toxic to microorganisms, particularly in high concentrations [1], which leads to a low biodegradation rate and restricts the potential of bioprocesses for efficiently removing cyanide and its compounds.

Chemical processes are another option for cyanide removal and are currently the conventional method most often used for the treatment of cyanide-containing wastewaters [9,10]. However, this technique is unattractive from both economic and environmental perspectives because it requires the use of chemical compounds and does not degrade the full range of cyanide compounds [10]. Adsorption is also used for cyanide removal. Adsorption systems are simple to operate, are not affected by the toxicity of the target compound(s) and do not require hazardous chemicals. Moreover, adsorption facilitates concentrating and then recovering the adsorbed compounds if desired. Table 1 summarizes some published literature on cyanide removal by adsorption. As shown, the most common adsorbent is plain or modified activated carbon, which has a relatively low cyanide adsorption capacity between 0.4 and 29.6 mg/g. In addition to its low capacity for cyanide removal, production and regeneration of the activated carbon is very expensive, making it impractical for full-scale applications. To make the adsorption process attractive and feasible, novel low-cost adsorbents with higher adsorption capacities are required.

Recently, agricultural waste materials have been extensively investigated for their ability to remove different contaminants from water and wastewater. Cyanide adsorption by waste materials has been reported only rarely; for instance, Yazici et al. [11] reported a low cyanide adsorption capacity of 0.401 mg/g onto rice husk. Therefore, testing the performance of other waste materials that

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Nomenclature

C_0	initial Cr(VI) concentrations (mg/L)
C_t	Cr(VI) concentrations at time t of reaction (mg/L)
C_e	Cr(VI) concentrations at equilibrium time (mg/L)
E	mean of adsorption free energy (kJ/mol)
k_{id}	constant of intraparticle diffusion ($mg/g\,min^{0.5}$)
k_1	pseudo-first order rate constant (1/min)
k_2	pseudo-second order rate constant (mg/g min)
K_{DR}	D–R constant (mol^2/kJ^2)
k_L	Langmuir constant (L/mg)
K_F	Freundlich adsorbent capacity ($mg/g(L/mg)^{1/n}$)
M	mass of PHP added to the solution (g)
n	the reciprocal of reaction order
q_t	adsorption capacity at time t (mg/g)
q_e	adsorption capacity at equilibrium conditions ($mg_{Cr(VI)}/g_{PHP}$)
q_{max}	maximum adsorption capacity (mg/g)
R	gas constant (8.314 J/mol K)
T	absolute temperature (K)
V	volume of the Cr(VI) solution (L)
ε	Polanyi potential (J/mol)

are available in high quantities to find a low-cost and efficient alternative adsorbent is necessary.

This work aimed to pursue this subject with pistachio hulls, an agricultural waste that is abundantly and easily available at no cost in Iran, to adsorb cyanide from wastewater. Thus, a set of experiments was carried out to study the capacity of pistachio hull powder (PHP) to remove cyanide under varying conditions. The influences of solution pH, adsorbent dose, cyanide concentration and contact time as well as zinc availability on cyanide adsorption were evaluated. The kinetics and isotherm of the cyanide adsorption process were also analyzed.

2. Materials and methods

2.1. Materials

PHP was prepared from green pistachio hull wastes taken from a local farm in Kerman, Iran. Prior to use, the pistachio green hull waste was dried in sunny ambient air for 3 days. The dried materials were then powdered in a grinder and sieved (size 200). Cyanide solution was prepared by diluting aliquots of 1 g/L stock cyanide solution into distilled water. The stock solution was made by dissolving NaCN in distilled water. All chemicals used were analytical grade and purchased from Merck Co.

2.2. Experimental procedure

All adsorption experiments were carried out over several runs in a jar test instrument (ZAG Chemie Co.) equipped with a paddle-type mixer using 100 mL synthetic cyanide wastewater. Table 2 presents the experimental runs and conditions. For each experiment, 100 mL cyanide solution was added to the vessel placed in the jar test instrument, and the test conditions were adjusted to the designated level (Table 2). Then, a given mass of PHP was added to the solution and the suspension was immediately stirred at 100 rpm. Upon reaching the preset contact time for each test, the suspension was clarified using a 0.2 μm pore size filter, and the filtrate was analyzed for residual cyanide. The cyanide adsorption efficiency (RE) and equilibrium adsorption capacity (q_e) were then calculated from Eqs. (1) and (2). The pH of wastewater was adjusted to the desired level using a 0.1 N NaOH or HCl solution. All experiments were carried out at a constant room temperature of $24 \pm 3\,^{\circ}C$.

$$RE = \frac{(C_i - C_t)}{C_i} \times 100 \quad (1)$$

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

Table 1
Summary of recently published literature on cyanide removal by adsorption.

Adsorbent	pH	Kinetic order	Fitted isotherm model	Adsorption capacity (mg/g)	Reference
Activated carbon	11	–	–	3.516	[11]
Rice husks	11	–	–	0.401	[11]
Cu(II) impregnated AC	10.5	–	–	16.6	[12]
Cu-impregnated AC	10.5–11	Pseudo-second order	Langmuir	19.7	[13]
Ag-impregnated AC	10.5–11	Pseudo-second order	Langmuir	22.4	[13]
Plain impregnated AC	10.5–11	Pseudo-second order	Langmuir	29.6	[13]
TiO_2	7	–	–	13	[14]
Plain carbon	–	–	–	6.6	[15]
TBA-carbon	–	–	–	29.2	[15]
Ag-impregnated AC	>11	–	–	26.5	[16]
Ni-impregnated AC	>11	–	–	15.4	[16]
Plain AC	>11	–	–	7	[16]
Pyrophyllite	7	–	Langmuir and Freundlich	72.4	[17]

Table 2
Experimental runs and conditions for cyanide adsorption onto PHP.

Run	Purpose	Conditions			
		pH	PHP dose, g/L	C_{CN^-}, mg/L	C_t, min
1	Effect of pH	2–10	2	50	60
2	Effect of PHP dose	10	0.5–2.5	100	60
3	Effect of C_{CN^-} and contact time	10	1.5	50, 100, 200	3–60
6	Equilibrium tests	10	1.5	50–400	180

2.3. Kinetic and isotherm analysis

To evaluate the efficiency of cyanide mass transfer to PHP, the kinetics of adsorption were evaluated based on data obtained during experimental run four (Table 2) using pseudo-first and second order models. Linear forms of these models are given in Eqs. (3) and (4). Also, to determine if intraparticle diffusion was the rate-limiting step for cyanide adsorption onto PHP, the experimental data were fitted to the Weber–Morriss model shown as Eq. (5).

- Pseudo-first order equation : $\ln(q_e - q_t) = \ln q_e - k_1 t$ (3)
- Pseudo-second order equation : $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ (4)
- Weber–Morriss equation : $q_t = k_{id} t^{0.5} + C$ (5)

The equilibrium experimental data were fitted with several available models to describe the interaction between cyanide molecules and the surfaces of the PHP particles [18] as well as to analyze the distribution type of chromium in the liquid and solid phases. Identifying the best-fit isotherm is critical for optimizing the adsorption process design. Linear forms of the selected models are as follows:

- Langmuir : $\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}}$ (6)
- Freundlich : $\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$ (7)
- Temkin : $q_e = B \ln A + B \ln C_e$ (8)
- Dubinin–Radushkevich (D–R) : $\ln q_e = \ln q_m - K_{DR}\varepsilon^2$ (9)

Refer to "Nomenclature" for descriptions of the parameters and constants in the presented models.

2.4. Adsorbent characterization and analytical methods

At the beginning of the experiment, the prepared powder was characterized by evaluating the pH of zero point charge (pHzpc), specific surface area, pore volume and size, surface morphology, and surface functional groups. The specific surface area (based on the BET method) and pore volume were determined by nitrogen gas adsorption analyzer (Micromeretics/Gemini-2372). The mean pore diameter was calculated using BET, and total pore volume was based on the equation reported by Altenor et al. [19]. The surface structure of PHP particles was analyzed by scanning electron microscopy (SEM, Philips XL-30) at different image magnifications. To illustrate the functional groups present on the surface of the adsorbent, Fourier transform infrared (FTIR) spectra were collected between 450 and 4000 cm^{-1} using a Nicolet spectrometer. The concentration of cyanide ions in solution was measured by the titrimetric method as described in section 4500-CN^- D. of the Standard Methods [20].

3. Results and discussion

3.1. Adsorbent characteristics

An SEM micrograph of surface PHP particles is shown in Fig. 1, which displays flask-type amorphous particles with smooth surfaces and pores. BET specific surface and total pore volume on the adsorbent were 1.04 m^2/g and 0.0002 cm^3/g, respectively. Because the specific surface area of PHP is low, the functional groups likely have a more pronounced role than particle surface area [18] in adsorbing cyanide ions from liquid. The mean pore diameter was calculated to be 0.77 nm, indicating that PHP is a micropore adsorbent. The pHzpc of PHP was determined to be 4.9, signifying a positive surface charge for a solution pH below 4.9 and a negative surface charge for a solution pH greater than 4.9. Fig. 2 depicts the FTIR spectrum of PHP, including the peak wave numbers and the corresponding assigned groups. As shown in Fig. 2, there are hydroxyl, carboxylic, phenolic, and amino groups on the surface of the tested adsorbent. This result implies that a complex PHP particle surface is involved in adsorbing cyanide ions [21].

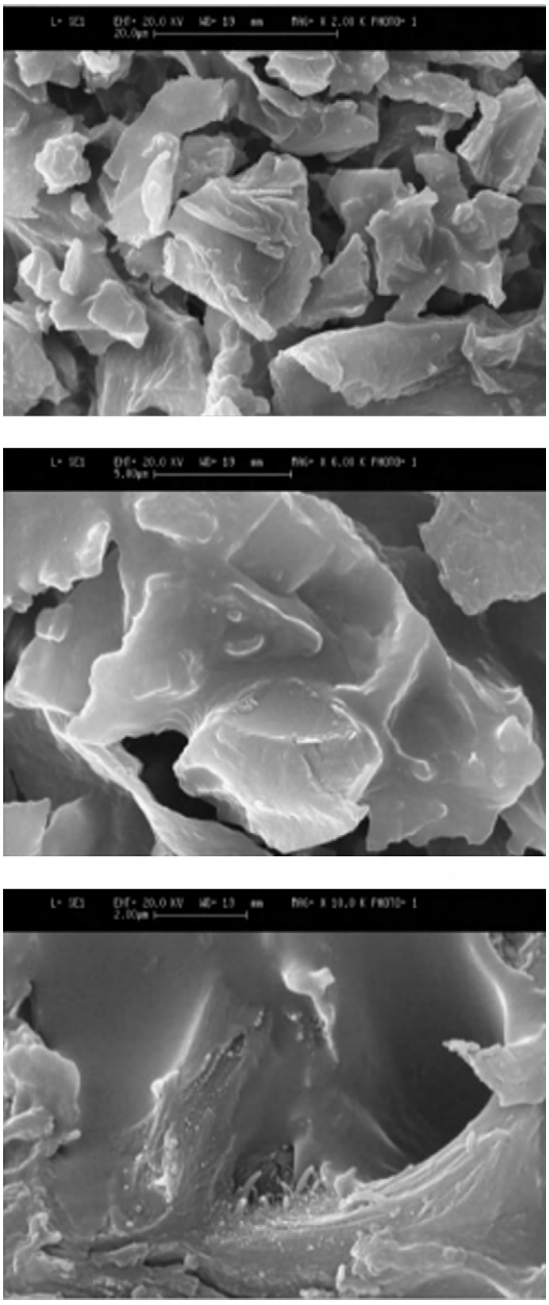

Fig. 1. SEM micrographs of PHP at different magnifications.

3.2. Influence of solution pH and the mechanism of adsorption

In the first run of adsorption experiments (Table 2), cyanide adsorption onto PHP was studied as a function of pH; results are given in Fig. 3. As shown in Fig. 3, the highest cyanide removal of 99% obtained at pH 10. Peak cyanide adsorption at pH 10 can be explained by considering the fact that the pH of the solution influences both the surface charge of the PHP particles and the

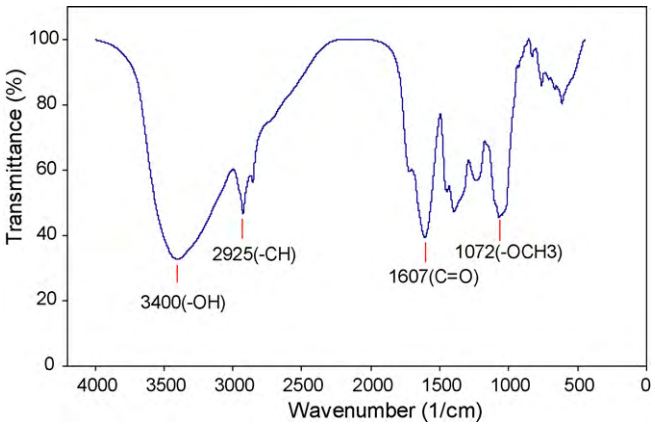

Fig. 2. FTIR spectrum of PHP at wave numbers from 450 to 4000 cm^{-1}.

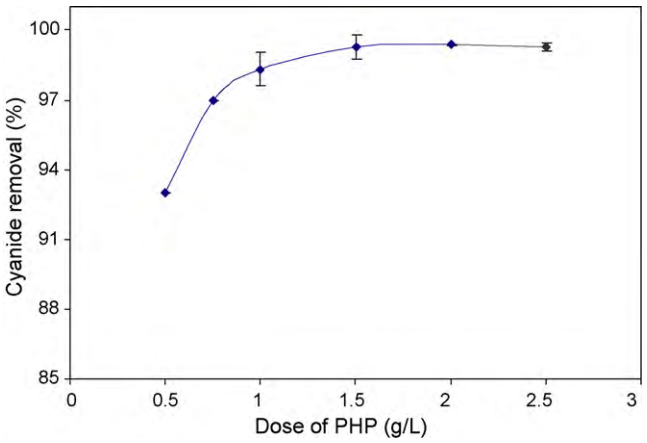

Fig. 4. Influence of PHP dose (0.5–2.5) on cyanide removal by PHP (pH 10, C_{CN^-} = 100 mg/L, contact time = 60 min).

dominant species of cyanide in the solution. The p*K*a of HCN is 9.0 [14] and the pHzpc of the PHP surface is 4.9, implying that HCN is completely dissociated to CN^- at a solution pH of 10, whereas the PHP particle surfaces are negatively charged for a pH over 4.9 (pHzpc). Because CN^- is a nucleophilic ion, when in contact with the negatively charged adsorbent, it binds with the anionic functional groups present on the surface of adsorbent (Fig. 2) and thereby improves adsorption [2]. Therefore, chemical ion exchange is determined to be the prevailing mechanism for the adsorption of cyanide ions onto PHP. Moreover, some removal may occur through surface precipitations and chemical reactions with surface sites, complexation of CN^- with functional groups, and physical adsorption [21]. According to information provided in Table 1, most researchers have similarly reported attaining maximum cyanide adsorption onto different adsorbents in the pH range of 9–11.

3.3. Influence of PHP dosage

Because adsorption is mainly a surface phenomenon, the amount of surface available for adsorption and thus the mass of adsorbent can significantly affect adsorption efficiency. Therefore, the effect of PHP dosage on cyanide removal was investigated at an optimum pH of 10 under the conditions given in Table 2. Fig. 4 represents the removal percentages of cyanide as a function of PHP dosage. As illustrated in Fig. 4, the removal of cyanide at a dose of 0.5 g/L was 93%; removal improved to 99.3% when the PHP dosage was increased to 1.5 g/L and remained almost unchanged thereafter. A dose of 1.5 g/L was thus selected as an optimum value for the remaining adsorbent experiments. Achievement of a high cyanide removal percentage with a relatively low adsorbent dose indicates the high affinity and suitability of PHP for removal of cyanide from wastewater. The increasing adsorption efficiency with increasing PHP dose can be attributed to the increase in surface area and by extension the greater number of exchangeable sites available for interaction with cyanide ions. In comparison, for instance, Ref. [13] reported 14.3, 35.4 and 92.3% removal of 100 mg/L cyanide for 4.5 g/L plain, copper- and silver-impregnated GAC, respectively, after around 24 h contact time. Considering the low adsorption capacity of GAC (plain and modified), which is the most conventional industrial adsorbent, as well as its high production cost, PHP is certainly much more efficient and cost effective and is therefore a promising adsorbent for treating cyanide-laden wastewaters.

3.4. Influence of cyanide concentration and contact time

The influence of varying initial cyanide concentration from 50 to 200 mg/L on adsorption was investigated under the conditions provided in Table 2. Fig. 5 depicts the average results of duplicated tests. Based on data plotted in Fig. 5, at least 85.1% cyanide uptake was achieved for concentrations as high as 200 mg/L cyanide at a very short contact time of 1 min. Overall, the rate of cyanide uptake was higher within first 30 min contact time. This result implies high affinity and thus favorability of PHP for adsorbing cyanide from industrial wastewaters. A further increasing in the mixing time led to improved removal percentages for all three cyanide concen-

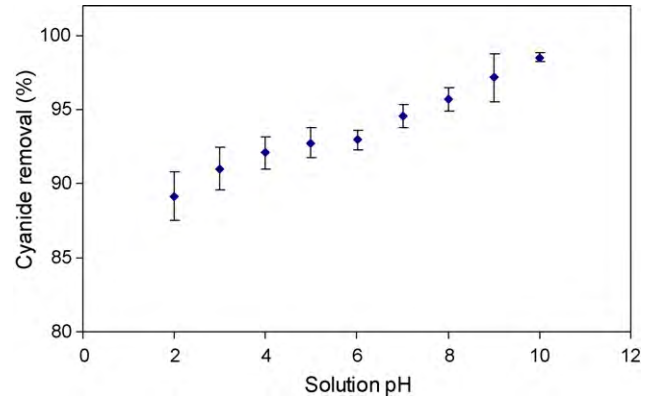

Fig. 3. Influence of solution pH (2–10) on cyanide removal by PHP (PHP dose = 2 g/L, C_{CN^-} = 50 mg/L, contact time = 60 min).

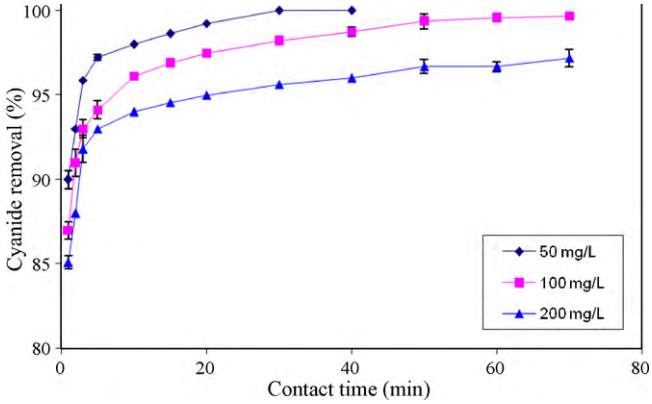

Fig. 5. Influence of initial cyanide concentration (50–200 mg/L) and contact time (3–60 min) at pH 10.

Table 3
Kinetic details of cyanide adsorption onto PHP.

Kinetic model	Pseudo-first order	Pseudo-second order	Weber–Morriss
Equation	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$t/q_t = (1/k_2 q_e^2) + t/q_e$	$q_t = k_{id}\, t^{0.5} + C$
Plot	$\ln(q_e - q_t)$ vs. t	t/q_t vs. t	q_t vs. $t^{0.5}$
Concentration (50 mg/L)			
Fitted model	$\ln(q_e - q_t) = 0.859 - 0.122\, t$	$t/q_t = 0.003 + 0.03\, t$	$q_t = 0.614\, t^{0.5} + 30.40$
R^2	0.891	1	0.856
Constant	$k_1 = -0.122$ L/min	$k_2 = 0.30$ mg/g min	$k_{id} = 0.614$
Calculated q_e ($q_{e,cal}$)	2.36 mg/g	33.3 mg/g	–
Experimental q_e ($q_{e,exp}$)	33.2 mg/g	33.2 mg/g	–
Δq	104.6%	2.2%	–
Concentration (100 mg/L)			
Fitted model	$\ln(q_e - q_t) = 1.816 - 0.066\, t$	$t/q_t = 0.004 + 0.015\, t$	$q_t = 0.914\, t^{0.5} + 59.94$
R^2	0.865	1	0.797
Constant	$k_1 = -0.066$ L/min	$k_2 = 0.056$ mg/g min	$k_{id} = 0.914$
Calculated q_e ($q_{e,cal}$)	6.15 mg/g	66.7 mg/g	–
Experimental q_e ($q_{e,exp}$)	66.5 mg/g	66.5 mg/g	–
Δq	96.6%	3.8%	–
Concentration (200 mg/L)			
Fitted model	$\ln(q_e - q_t) = 2.518 - 0.067\, t$	$t/q_t = 0.002 + 0.0075\, t$	$q_t = 1.627\, t^{0.5} + 117.6$
R^2	0.813	0.999	0.819
Constant	$k_1 = -0.067$ 1/min	$k_2 = 0.028$ mg/g min	$k_{id} = 1.627$
Calculated q_e ($q_{e,cal}$)	12.4 mg/g	133.4 mg/g	–
Experimental q_e ($q_{e,exp}$)	129.9 mg/g	129.6 mg/g	–
Δq	96.3%	3.2%	–

trations, which attained equilibrium times of 30, 60 and 80 min. The equilibrium removal efficiencies of cyanide at concentrations of 50, 100 and 200 mg/L were 100, 99.7 and 97%, respectively, demonstrating a reduction in removal efficiency with increasing concentration. The reduction of cyanide removal as a function of its concentration can be explained by the limitation of available free sites for adsorption of CN^- with increased cyanide concentration in bulk solution for a fixed mass of adsorbent, as well as by the increase in intraparticle diffusion.

3.5. Kinetics of cyanide adsorption onto PHP

Information on adsorption kinetics is needed to select optimum operating conditions for industrial applications [22] and is helpful for determining the adsorbate uptake rate and thus the time needed to attain equilibrium. To provide this information for cyanide adsorption onto PHP, the experimental data from run three of the study was fitted with three of most conventional kinetic models proposed in Section 2.3. A summary of the models used and

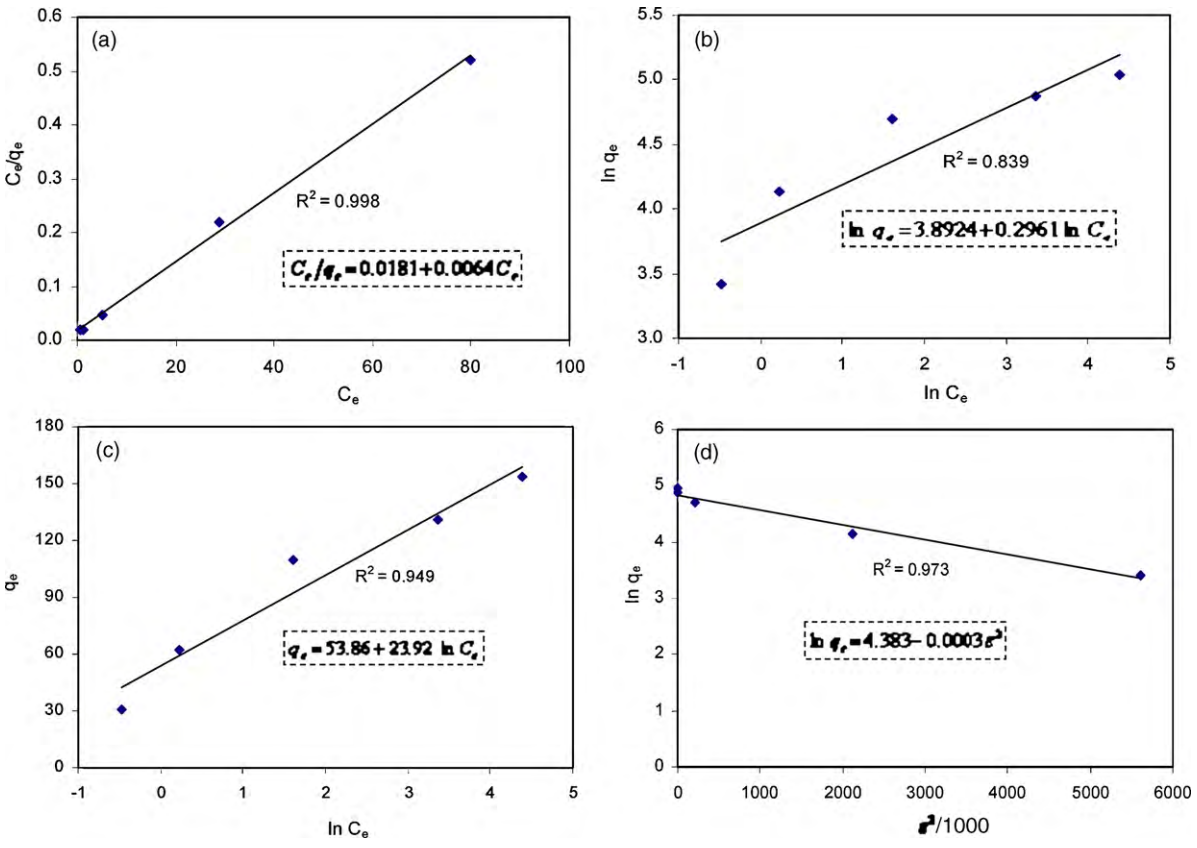

Fig. 6. Linear plots of isotherm models of (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) Dubinin–Radushkevich for adsorption of cyanide onto PHP.

the kinetic information obtained is presented in Table 3. Based on Table 3, a complete correlation was attained between the pseudo-second order kinetic model and the experimental data from three tested concentrations, and R^2 values were higher than for the pseudo-second order model. Therefore, cyanide adsorption onto PHP is favored by pseudo-second order model. The validity of the pseudo-first and second order models was assessed by calculating the standard deviation between model-predicted and experimental adsorption capacities. As shown in Table 3, the values of Δq for all three concentrations were very low for the pseudo-second order model in comparison to those for the pseudo-first order model, confirming the applicability of the former. Hence, adsorption under the studied conditions most likely depends on both PHP and cyanide, and chemosorption likely controls the overall adsorption rate [23,24] of cyanide onto PHP.

The pseudo-second order adsorption rate constants, k_2, for three concentrations of 50, 100 and 200 mg/L cyanide are also given in Table 3; k_2 is reduced with increasing adsorbate concentration. This finding can be attributed to the enhanced mass transfer rate with an increased concentration gradient. In the literature of cyanide adsorption, information regarding adsorption kinetics is very limited. Nevertheless, the available literature reports pseudo-second order models (Table 1), which complies with the findings of the present work.

The adsorption of an adsorbent usually takes place through several consecutive steps: bulk solution transport, film diffusion, pore diffusion, and adsorption on the surface or pores [25]. The lowest step limits the overall adsorption rate. According to the literature, film diffusion and diffusion into particle pores (intraparticle diffusion) often control an adsorption process. To identify the step possibly controlling the adsorption of cyanide onto PHP under the selected conditions, the experimental data were fitted with the Weber–Morriss equation, which is the most commonly tested model [25]. Table 3 summarizes details of the fitted model. As shown in Table 3, a relatively high R^2 was obtained by fitting the Weber–Morriss model with the experimental data at all three concentration levels, suggesting that the intraparticle diffusion step is involved in controlling cyanide adsorption onto PHP. However, because the intercepts, C, which is indicative of liquid film around the PHP particles, had positive values, it is presumed that film diffusion also played a role in the adsorption [26] of cyanide onto PHP particles.

The intraparticle diffusion constant increased with increasing cyanide ion concentration (Table 3), revealing a reduced contribution from pore diffusion limitation with higher adsorbate concentration. This result reconfirms the enhancement of adsorption capacity with increased cyanide concentration (Table 3). On the other hand, according to data provided in Table 3, the values of the model intercepts, C, increased with increasing cyanide concentration. Therefore, the effect of film diffusion on cyanide adsorption is probably more considerable at higher adsorbate concentrations [25,27].

3.6. Isotherm of cyanide adsorption onto PHP

An isotherm represents the relationship between the amount of cyanide adsorbed onto PHP at given experimental conditions and the equilibrium concentration of cyanide in the liquid phase. Therefore, an isotherm would be informative for determining the maximum capacity of PHP for adsorbing cyanide and useful for designing an optimized adsorption process. In this regard, the conformity of experimental data with four of the most used isotherm models (Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R)) was evaluated. Fig. 6 shows the plotted models, including the fitted models and correlation factors (R^2), and the extracted isotherm information is consolidated in Table 4.

Table 4
Fitted isotherm models for cyanide adsorption onto PHP.

Isotherm	Parameters	Values
Langmuir		
	q_{max}	156.2
	k_L	0.35
	R^2	0.998
	R_L	0.21–0.03
Freundlich		
	K_F	49
	n	3.38
	R^2	0.839
Temkin		
	B	23.92
	A	2.25
	R^2	0.949
Dubinin–Radushkevich		
	K_{DR}	0.0003
	q_{max}	80.1
	$E = 1/\sqrt{2K_{DR}}$	40.8
	R^2	0.973

Referring to Fig. 6 as well as Table 4, it is clear that the R^2 of the Langmuir plot is higher than the others, suggesting that the equilibrium adsorption of cyanide onto PHP could be best described with the Langmuir isotherm. Therefore, cyanide ions are presumed to have been adsorbed as a monolayer on adsorption sites that are homogeneously distributed [28] on the surface of PHP with no interaction between the adsorbed cyanide ions, i.e., all molecules had equal activation energy [25]. The favorability of the Langmuir model was further assessed using the equilibrium dimensionless parameter, R_L, written as $R_L = 1/bC_i$. Considering the obtained Langmuir constant, the calculated value for R_L falls between 0 and 1 (Table 4), confirming the favorability of cyanide adsorption onto PHP. For higher cyanide concentrations, R_L values are lower and adsorption is therefore more favorable [23]. Moreover, the constant n in the plot of the Freundlich isotherm is greater than unity (between 1 and 10), which proves that PHP is an appropriate and beneficial adsorbent [29] for cyanide. No information could be found in the available literature on the isotherm of cyanide adsorption by agricultural waste materials to compare with our findings. Nonetheless, Deveci et al. [13] have also obtained a better fit using the Langmuir isotherm for experimental data for cyanide adsorption onto plain and impregnated activated carbon. The maximum capacity of PHP for adsorbing cyanide ions was found to be 156.2 mg/g, which is much higher than the maximum value so far reported in the literature for cyanide ion adsorption by different adsorbents (Table 1). Accordingly, PHP is a very efficient adsorbent with a high capacity to adsorb cyanide in aqueous solutions. In addition to having an excellent adsorption capacity, PHP is easily prepared from green hull wastes which are abundantly available at no cost. These unique features along with the simplicity of its use present PHP as a very promising alternative adsorbent for cyanide removal in a technically and economically feasible and thus appropriate adsorption process.

Table 4 depicts further that the experimental data had also a good correlation with the Temkin isotherm ($R^2 = 0.949$). Therefore, the adsorption of cyanide by PHP is described by an even distribution of binding energies up to some maximum binding energy [23]. Also, according to Fig. 6c, the Temkin adsorption potential ($B \ln A$) of PHP is 53.86 kJ/mol, illustrating that the bond between cyanide ions and the PHP surface is very strong [30]. Moreover, based on information given in Table 4, the value of E in the D–R isotherm was found to be 40.8 kJ/mol. E depicts the mean adsorption free energy per molecule of the adsorbate when it is transferred from the infinity solution to the surface of the adsorbent, and thereby describes the type of adsorption [31,32]. This finding reconfirms

the conclusion made above that the adsorption of cyanide onto PHP is a chemical process controlled by intraparticle diffusion [33].

4. Conclusion

Cyanide is a very toxic compound that is released into the environment through industrial effluents; therefore, it needs to be removed prior to wastewater discharge. Adsorption is one of the most widely used treatment methods for removing contaminants from water and wastewater. This work introduced a new adsorbent, pistachio hull powder (PHP), which is available as an agricultural waste material at no cost. The experimental evaluation revealed that PHP was capable of removing a high concentration of cyanide ions (up to 200 mg/L) in a relatively short contact time with a low amount of adsorbent. The maximum capacity of PHP adsorption of cyanide was determined to be 156.2 mg/g, which is much higher than the maximum value reported in the literature for cyanide ion adsorption by other adsorbents. Therefore, PHP is an efficient, cost effective and thus promising adsorbent for treating cyanide-containing liquid streams.

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