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**ADSORPTION OF PYRIDINE FROM AQUEOUS SOLUTIONS ONTO
POLYALUMINIUM CHLORIDE AND ANIONIC POLYACRYLAMIDE WATER
TREATMENT RESIDUALS**

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Adsorption of pyridine from aqueous solutions onto polyaluminium chloride and anionic polyacrylamide water treatment residuals

Runbin Duan, Clifford B. Fedler and Xiaofei Jiao

ABSTRACT

The adsorption performance of pyridine onto polyaluminium chloride (PAC) and anionic polyacrylamide (APAM) water treatment residuals (WTRs) was investigated by batch experiments. This study confirmed the assumption that PAC–APAM WTRs had the ability to remove pyridine. The non-linear Dubinin–Radushkevich model and non-linear Freundlich model better described the isotherms, indicating that the adsorption was a chemically controlled multilayer process. The pyridine adsorption rate was simultaneously controlled by external film diffusion and intraparticle diffusion. The adsorption of pyridine was an endothermic reaction with randomness increase. The pyridine adsorption decreased with pH increase. Pyridine removal was observed to be a linear increase from 6.16% to 96.18%, with the increase of dosage from 2.5 g/L to 15 g/L. The Langmuir maximum adsorption capacity was 3.605 mg/g while the theoretical isotherm saturation capacity was 9.823 mg/g. Therefore, PAC–APAM WTRs recycled into contaminated soils for remediation is expected to be an innovative alternative disposal method. More research is recommended in the future to identify detailed adsorption mechanisms and the most appropriate mixing ratio of PAC–APAM WTRs to contaminated soils under various climatic conditions.

Key words | adsorption isotherms, anionic polyacrylamide, D–R model, polyaluminium chloride, pyridine, soil remediation

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HIGHLIGHTS

- The pyridine adsorption by PAC–APAM WTRs was investigated.
- The pyridine adsorption decreased with pH increase.
- The pyridine adsorption was a multilayer chemisorption process.
- The rate was controlled by external film diffusion and intraparticle diffusion.
- PAC–APAM WTRs recycling is an innovative alternative to disposal.

INTRODUCTION

Pyridine has been widely regarded as a typical and concerning pollutant found in surface water, soil water and groundwater around the world. Although it occurs naturally in the environment at extremely low concentrations, the

anthropogenic amounts of pyridine are more significant in various environmental systems due to the discharge found in industrial wastewater (Zhu *et al.* 2016a). Those industries include coal and coking processing, coal-fired power generating, shale oil processing, refinery, dye and paint production, agricultural chemicals manufacturing including insecticides, herbicides and fungicides, pharmaceuticals production, textile water repellent production, rubber

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production, and food additive production (Zhu *et al.* 2016a; Zhu *et al.* 2016b; Singh *et al.* 2016). As a typical aromatic N-heterocyclic compound, pyridine has strong toxicologic effects on aquatic and terrestrial ecological systems and also on humans, even at low concentrations because of the strong carcinogenic potential (Zhu *et al.* 2016b) and the harmful influence on the functioning of reproductive systems, immune systems, livers and kidneys (Singh *et al.* 2016). Because pyridine has a high solubility in water with a lasting persistence in the environment, it can easily enter nearby surface water bodies after the release by industrial wastewater discharge and infiltrate soils where it can leach downwards into underlying aquifers. Therefore, pyridine removal or immobilization is an important concern for minimizing the threat of organic pollutants to the health of human and ecological systems.

Water treatment residuals (WTRs) are wastes produced from municipal water treatment plants. The quantity of WTRs production has increased sharply in response to rapid urbanization, population increase, and life quality improvements. Currently, the main disposal method of WTRs is landfilling. However, the sustainability of landfilling WTRs is questioned from the current sustainable development and management context due to limited land resources, high cost for transporting WTRs from municipal water treatment plants to the remote landfilling sites, and the potential environmental and human health risks (Ahmad *et al.* 2016). Therefore, beneficial reuse of WTRs have become the primary interest for sustainable waste management in local and global water treatment industries (Duan & Fedler 2020). In addition, alternative disposal approaches for WTRs are being developed with an aim to replace landfilling. Due to the large particle surface area and strong absorption affinity to some pollutants, WTRs have been proposed as a low-cost sorbent for removing pollutants from wastewater (Ahmad *et al.* 2016) and remediating various contaminated soils (Tay *et al.* 2017; Zhao *et al.* 2018). High adsorption capacities of WTRs have been confirmed in previous studies for phosphorus, arsenate, heavy metals (Ahmad *et al.* 2016) and dye (Gadekar & Ahammed 2019).

Removal of pyridine from wastewater by adsorption processes has been considered because of its relatively lower operational cost with satisfying effects and it can be accomplished without the production of potentially dangerous by-products often produced in oxidative or reductive processes (Zhu *et al.* 2016a). Although previous studies have investigated the adsorption process for pyridine by using synthetic porous materials (Zhu *et al.* 2016b), there are no reports

available on pyridine adsorption by directly using wastes residuals without pre-processing by physico-chemical means. Our previous studies showed that WTRs had the ability to immobilize heavy metal ions in the contaminated soils (Duan & Fedler 2021). Moreover, more WTRs are produced by utilizing polyaluminium chloride (PAC) as the coagulant for clarifying raw water and anionic polyacrylamide (APAM) as the dewatering agent during sludge handling in water treatment plants worldwide (Duan & Fedler 2020). This type of WTR is typically called PAC-APAM WTR (Duan & Fedler 2020).

In this study, one hypothesis is that PAC-APAM WTRs have the ability to remove pyridine by adsorption, yet its adsorption performance for pyridine remains unknown. Therefore, the adsorption of pyridine onto PAC-APAM WTRs was investigated by batch experiments. The objectives of this study were: (1) to measure the adsorption capacity of PAC-APAM WTRs for pyridine by conducting an adsorption isotherm study, (2) to identify the critical process that controls the pyridine adsorption rate onto PAC-APAM WTRs by conducting adsorption kinetic study, and (3) to investigate the effects of temperature and pH on the pyridine adsorption by PAC-APAM WTRs. Overall, the study provides data about the remediation of pyridine contaminated soils for practicing engineers with an aim to recycling PAC-APAM WTRs in a sustainable manner.

METHODS

Collection and characterization of PAC-APAM WTRs

The air-dried PAC-APAM WTRs cakes were collected at the WTRs cake piling site of a municipal water treatment plant in the city of Taiyuan, Shanxi Province, China. The sampled cakes were meshed and dried overnight at 105 °C, finely ground, and screened through a 0.25-mm sieve ($0 < \text{particle size} < 0.25 \text{ mm}$). The obtained PAC-APAM WTR powder was stored in amber glass containers for use in the adsorption studies. Characteristics of PAC-APAM WTRs were determined by using the methods and instruments shown in Table 1. The metal elements were also measured and reported in Duan & Fedler (2021).

Study for effects of pH

Five standard pyridine solutions with pyridine concentrations between 10–50 mg/L were prepared by mixing pyridine ($\geq 99.5\%$) (Tianjin Kernel Chemical Reagent Co.

Table 1 | The methods and instruments used for determining the characteristics of PAC-APAM WTRs

Physical characteristics	Methods or instruments
Bulk density	The method provided by the Soil Science Society of America (Dane & Topp 2002)
Structure and micro-morphology	Scanning electron microscope (SEM) (JEOL-JSM-6700F, Japan)
Surface area, micropore area, external surface area, micropore volume, total volume of pores, and adsorption average pore width	Brunauer-Emmett-Teller (BET) surface area and porosimeter (ASAP2020C, Micromeritics Instrument Corporation, Norcross, Georgia, USA)
Chemical characteristics	Methods or instruments
pH (1:2) (m/v)	pH meter (PHS-3E, INESA Scientific Instrument Co. Ltd, Shanghai, China)
Electrical conductivity (EC) (1:2) (m/v)	EC meter (Mettler-Toledo FE38, Columbus, Ohio, USA)
The elements C, N, H, O, and S	Element analyzer (Vario EL cube, Elementar Analysensysteme GmbH, Langensfeld, German)
pH _{PZC}	The pH _{PZC} measurement method (Babić et al. 1999)

Ltd) with distilled deionized water (DDI water) for developing a calibration curve. Pyridine concentrations in aqueous solutions used in the adsorption studies were analyzed using an ultraviolet-visible spectrophotometer (UV-2601, Beijing Beifen-Ruili Analytical Instrument Co. Ltd) at a wavelength of 256 nm.

The effects of pH on pyridine adsorption were investigated over the pH range of 4–9, an initial pyridine concentration (C_0) of 30 mg/L, PAC-APAM WTRs dosage of 10 g/L, temperature (T) of 30 °C, and time (t) of 10 days. Two grams of PAC-APAM WTRs were put into 200 mL of the pyridine water solution, sealed in a 250-mL flask, and shaken at a speed of 2.33 Hz in a rotary shaker in darkness. The initial pH of the mixture was adjusted with 0.1 M hydrochloric acid or 0.1 M sodium hydroxide. Additionally, NaN_3 (200 mg/L) was added to the flask to inhibit the potential biodegradation of pyridine. After a 10-day adsorption period, the supernatant was withdrawn, separated by high-speed centrifugation at 50 Hz and filtered using a 0.45- μm syringe filter. The filtrate was then analyzed for the pyridine concentration.

The adsorbed pyridine by PAC-APAM WTRs (q_t , mg/g) at a given time was determined using Equation (1), where C_t (mg/L) is the pyridine concentration at t days, V (L) is the volume of the pyridine water solution and M (g) is the mass of PAC-APAM WTRs in the flask. The adsorption removal (AR , %) of pyridine by PAC-APAM WTRs was calculated using Equation (2).

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (1)$$

$$AR = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

For the requirements of quality assurance and quality control, blanks and standard solutions were used. All treatments in the batch adsorption study were replicated three times ($n=3$). The pH value was measured at the end of each adsorption test, and the difference of pH was in the range of -0.05 to 0.05 between the initial pH and the final pH in all tests.

Isotherms and the maximum adsorption capacity

Based on preliminary studies, 10 days was determined as the adsorption equilibrium time. The adsorption isotherm studies were performed under the conditions of C_0 of pyridine = 10, 30, 50, 80 and 100 mg/L, pH = 4, $T = 30$ °C, $t = 10$ days, and dosage of PAC-APAM WTRs = 2.0 g. The isotherm models in this study included non-linear Langmuir isotherm model, non-linear Freundlich isotherm model non-linear Dubinin-Radushkevich (D-R) isotherm model, and non-linear Temkin isotherm model (Foo & Hameed 2010). The obtained data were directly fitted into the four models using the software R (R Core Team 2019) to investigate the adsorption mechanisms of pyridine onto PAC-APAM WTRs. The maximum adsorption capacity, q_m (mg/g), of pyridine by PAC-APAM WTRs was acquired using the parameters of the Langmuir model.

Kinetics of pyridine adsorption onto and desorption from PAC-APAM WTRs

The kinetic study of pyridine adsorption was conducted at $C_0 = 30$ mg/L, pH = 4, $T = 30$ °C, dosage = 2.0 g PAC-APAM WTRs and $t = 0$ –10 days. The measured C_t (mg/L) and calculated q_t (mg/g) were fitted into a non-linear pseudo-first-order model, pseudo-second-order model and

an intraparticle diffusion (Weber–Morris) model using the software R.

Prior to the desorption study, all PAC-APAM WTRs used in each test in the kinetics study were collected, rinsed three times with DDI water and dried at 105 °C for 24 h. During the preparation of desorption study, a mass balance of PAC-APAM WTRs was executed. The mass loss of PAC-APAM WTRs in each test was less than 1% compared with the corresponding mass used in the kinetics study. The following desorption experiments were the same as those in the kinetics study, with DDI water replaced with the pyridine aqueous solutions.

Thermodynamic study

The effects of temperature on the adsorption of pyridine onto PAC-APAM WTRs were studied at $T = 20, 25$ and 30 °C. The other adsorption conditions were $C_0 = 30$ mg/L, $\text{pH} = 4$, dosage = 2.0 g PAC-APAM WTRs and $t = 10$ days. Three important values – free energy (ΔG° , kJ/mol), enthalpy (ΔH° , kJ/mol) and entropy (ΔS° , kJ/mol/K) – were determined from the batch experiments that were used to indicate the type of pyridine adsorption process onto PAC-APAM WTRs.

RESULTS AND DISCUSSION

Characterization of PAC-APAM WTRs

The PAC-APAM WTRs used in this study was the same as those in a previous study (Duan & Fedler 2020). The physical characteristics of PAC-APAM WTRs included bulk density of 1.144 g/cm³, particle size of less than 0.25 mm, Brunauer–Emmett–Teller surface area of 36.69 m²/g, t-plot micropore area of 1.89 m²/g, t-plot external surface area of 34.80 m²/g, t-plot micropore volume of 1.26×10^{-3} cm³/g, single point adsorption total pore volume of pores of 62.34×10^{-3} cm³/g and adsorption average pore width of 6.80 nm. The structure and micro-morphology of PAC-APAM WTRs are shown in the scanning electron microscope (SEM) image (Figure 1). The irregular surface comprising multiple micro-pores and macro-pores was regarded as one of the important factors in favour of the adsorption of various pollutants. Chemical characteristics of the PAC-APAM WTRs included pH (m/v = 1:2) of 7.64, electrical conductivity (EC) (m/v = 1:2) of 5.13 mS/cm, 11.38% carbon, 0.95% nitrogen, 2.90% hydrogen, 34.43% oxygen, and 0.35% sulfur.

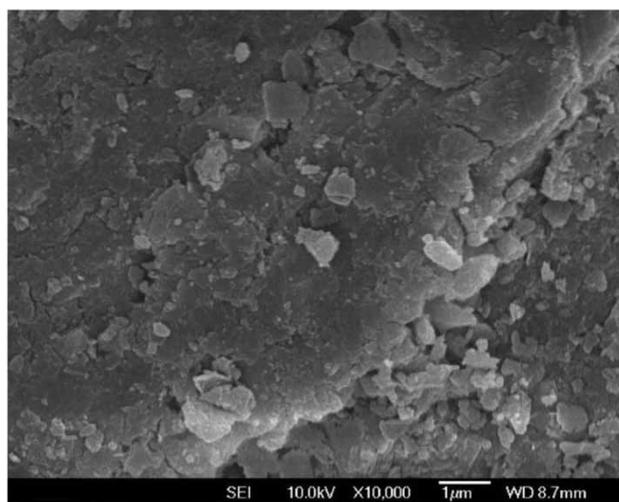


Figure 1 | An SEM image showing the structure and micro-morphology of the PAC-APAM WTRs used in this study.

Effects of pH

The uptake of pyridine at equilibrium by PAC-APAM WTRs (q_e , mg/g) and the adsorption removal (%) as a function of the initial solution pH are illustrated in Figure 2. Both values were calculated using Equations (1) and (2). It can be seen from Figure 2 that the equilibrium adsorption uptake of pyridine by PAC-APAM WTRs decreased with the increase in pH from 4 to 9. The significant drop (P -value < 0.05) occurred immediately after pH 7. This finding about pH effects is different from that reported on polymeric

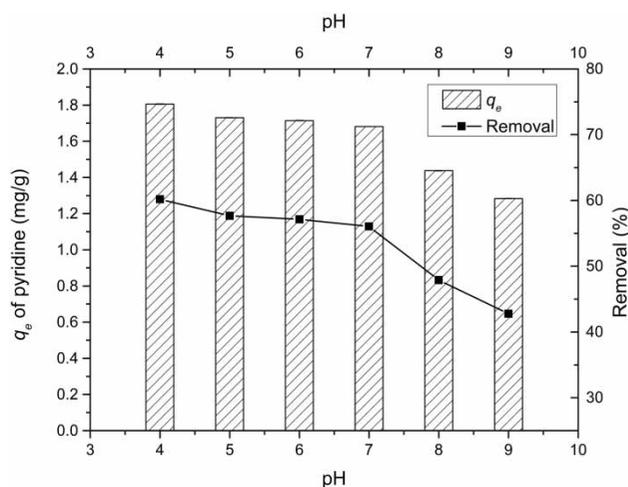
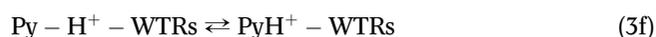
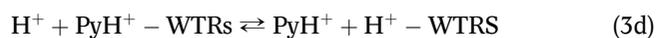
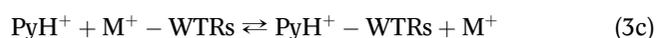


Figure 2 | pH effects on equilibrium adsorption uptake of pyridine onto PAC-APAM WTRs with the initial pyridine concentration of 30 mg/L and WTRs dosage of 10 g/L at 30 °C. All standard deviations ($n = 3$) were less than 2.65×10^{-3} mg/g for q_e , so the standard deviation bars approximately overlapped with the points of the average values.

adsorbents MN 200 and MN 500 (Zhu et al. 2016a), and activated carbon cloth (Alonso-Davila et al. 2012). It is reported that q_e of pyridine onto both MN 200 and MN 500 increased in acidic solutions with the increase of solution pH, but decreased at $\text{pH} > 7$ with the maximum q_e occurring under neutral conditions (Zhu et al. 2016a). The q_e of pyridine onto activated carbon cloth increased in acidic solutions with the increase of solution pH, but stayed approximately constant in alkaline solutions (Alonso-Davila et al. 2012).

The solution initial pH influenced the forms of pyridine and the surface properties of PAC-APAM WTRs (Alonso-Davila et al. 2012). The PAC-APAM WTRs exhibited the point of zero charge (pH_{pzc}) of approximately 9.1. This means that the surface of PAC-APAM WTRs is positively charged when the solution initial pH is < 9.1 . It indicated that the surface of PAC-APAM WTRs was positively charged in the pH range used in this study. In acidic aqueous solutions, pyridine has the remarkable protonating trend (the acid dissociation constant, $\text{pK}_a = 5.2$) (Zhu et al. 2016a). More positively charged pyridinium ions form in lower pH solutions and, conversely, less positively charged pyridinium ions exist in higher pH conditions.

The possible interactions occurring in the pyridine solutions with the addition of PAC-APAM WTRs are shown in Equations (3a)–(3f) based on the explanation provided by Weber (Weber 1966) and the following researchers (Singh et al. 2016). In Equations (3a)–(3f), Py means pyridine, H^+ means the hydronium ions, WTRs are the PAC-APAM WTRs and M^+ refers to the exchangeable cations on the PAC-APAM WTRs.



At $\text{pH} = 4$ and 5 that are lower than pK_a of pyridine, more pyridinium ions exist than neutral pyridine molecules in the solutions due to the reactions given by Equation (3a). The PAC-APAM WTRs are more positively charged at a lower pH because of the reactions given by Equation (3e) as well as possibly the reactions given by Equation (3d).

As a result, the pyridine adsorption should be higher at $\text{pH} = 5$ due to the weaker electrostatic repulsion which causes more reactions given by Equation (3c) if the exchangeable cations on the PAC-APAM WTRs are sufficient. However, it was observed that the pyridine adsorption was higher at $\text{pH} = 4$. The reactions described by Equation (3b) were the predominant adsorption mechanism, and they were negatively impacted by the pH increase. Singh et al. (2016) suggested that the adsorption decrease with the pH increase was because some neutral pyridine molecules might be negatively charged and, at lower pH, the surface of PAC-APAM WTRs was more positively charged, which was more suitable for the adsorption of the negatively charged pyridine molecules.

At $\text{pH} = 6$ and 7 that are higher than pK_a of pyridine, more neutral pyridine molecules than pyridinium ions are in the solutions. The main adsorption reactions should be those given by Equation (3b). At higher pH, the surface of PAC-APAM WTRs was less positively charged and there were possibly more OH^- competing with pyridine molecules for adsorption sites (Singh et al. 2016), resulting in the decrease of the pyridine adsorption. The competition of more OH^- with pyridine molecules could possibly explain the significant adsorption difference between $\text{pH} = 7$ and $\text{pH} = 8$.

In this study, with the increase of pH, pyridine adsorption became more difficult, but adsorption still took place. It might be due to π - π interactions (Mohan et al. 2004; Lataye et al. 2008; Alonso-Davila et al. 2012; Liao et al. 2013; Singh et al. 2016; Zhu et al. 2016a) occurring between pyridine and the surface of PAC-APAM WTRs at higher pH conditions. Further research should be performed to identify those compounds in PAC-APAM WTRs supplying π - π interactions with pyridine and identify those additional adsorption mechanisms to fully explain the findings in this study.

Dosage effects

The dosage effects on the pyridine adsorption by PAC-APAM WTRs for $C_0 = 30$ mg/L at $\text{pH} 4.0$ is shown in Figure 3. It can be seen that the pyridine removal (%) was observed to be a linear increase from 6.16% to 96.18% with the increase of WTRs dosage from 2.5 g/L to 15 g/L. The q_e of pyridine on PAC-APAM WTRs also increased approximately linearly from 0.185 mg/g to 2.885 mg/g. The increase of adsorption with the dosage increase could be attributed to the increase in the available adsorption sites resulting from the increase of adsorption surface area.

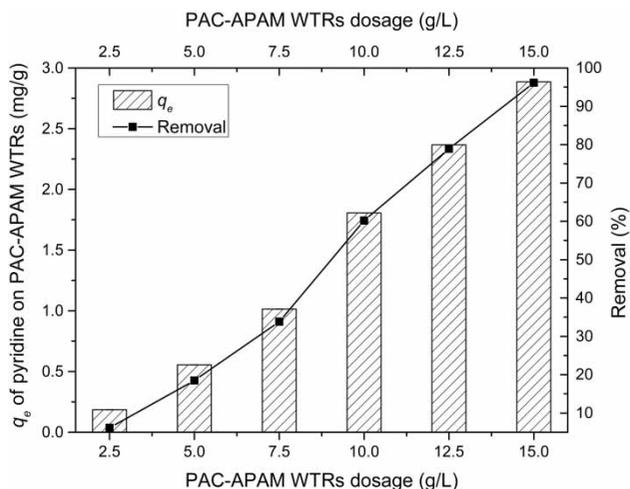


Figure 3 | Dosage effects on equilibrium adsorption uptake of pyridine onto PAC-APAM WTRs with the initial pyridine concentration of 30 mg/L and pH = 4.0 at 30 °C. All standard deviations ($n = 3$) were less than 3.06×10^{-3} mg/g for q_e , so the standard deviation bars approximately overlapped with the points of the average values.

Isotherms and the maximum adsorption capacity

Non-linear Langmuir isotherm model (Equation (4)), non-linear Freundlich isotherm model (Equation (5)), non-linear D-R isotherm model (Equations (6) and (7)) and non-linear Temkin isotherm model (Equation (8)) can describe the adsorption equilibrium between the concentration of pyridine in the bulk solution and the quantity of the adsorbed pyridine at the PAC-APAM WTRs interface. The Langmuir model is a classic isotherm model that assumes uniform adsorption energies are distributed on the adsorbent surface. One of advantages of the Langmuir model is that it provides a value of maximum adsorption capacity (q_m). As another of the earliest known adsorption isotherm model, the Freundlich isotherm model assumes multilayer adsorption with non-uniform affinities and adsorption energies on a heterogeneous adsorbent surface (Foo & Hameed 2010). The D-R isotherm model is an empirical model that is often used to identify the adsorption mechanism (Foo & Hameed 2010). The Temkin isotherm model assumes that the heat of adsorption is a function of temperature and will linearly decrease with the coverage (Foo & Hameed 2010).

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (4)$$

$$q_e = K_F C_e^{1/n} \quad (5)$$

$$q_e = (q_s) \exp(-k_{ad} \varepsilon^2) \quad (6)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \quad (8)$$

In Equations (4)–(8), q_e is the adsorption capacity of pyridine onto PAC-APAM WTRs at equilibrium (mg pyridine/g PAC-APAM WTRs); q_m is the Langmuir maximum monolayer adsorption capacity of pyridine by PAC-APAM WTRs (mg pyridine/g PAC-APAM WTRs); b is the Langmuir isotherm constant (L/mg); C_e is the equilibrium concentration of pyridine in bulk solutions (mg/L); K_F is the Freundlich isotherm constant ((mg/g)(L/mg)^{1/n}); n is the Freundlich dimensionless empirical parameter; q_s is the theoretical isotherm saturation capacity (mg pyridine/g PAC-APAM WTRs); k_{ad} is the D-R isotherm adsorption energy constant (mol²/J²); ε is Polanyi potential (J/mol), R is the gas constant (8.314 J/mol/K), T is the adsorption absolute temperature (K), b_T is the Temkin isotherm constant (J/mol) and A_T is the Temkin isotherm equilibrium binding constant (L/mg). To minimize the possible errors caused by linearization (Foo & Hameed 2010; Karri et al. 2017), these isotherm models were fitted with the obtained data from the batch experiments in the non-linearized forms rather than linearized forms.

The data fitting results are listed in Table 2. It can be clearly seen that the D-R isotherm model better describes

Table 2 | The parameters of the adsorption isotherm models for pyridine adsorption by PAC-APAM WTRs ($T = 30$ °C)

Isotherms	Parameters	
Langmuir	q_m (mg/g)	3.605
	b (L/mg)	0.085
	R^2	0.964
Freundlich	K_F ((mg/g)(L/mg) ^{1/n})	0.667
	n	2.663
	R^2	0.993
Dubinin–Radushkevich	q_s (mg/g)	9.823
	k_{ad} , mol ² kJ ⁻²	3.540×10^{-3}
	E , kJ/mol	11.855
	R^2	0.996
Temkin	b_T (J/mol)	3.899
	A_T (L/mg)	1.302
	R^2	0.983

the data of the isotherm adsorption batch experiments because the R^2 (0.996, the coefficient of determination) was higher than for the other isotherm models. However, no isotherm model tested was identified to be significantly superior in explaining the isotherm adsorption mechanisms.

Although the coefficient of determination (R^2) of the Langmuir model was lower than that of the others, the Langmuir model still provided an excellent fit to the data and the obtained parameters still provided useful information for the potential application of PAC-APAM WTRs for pyridine removal. The q_m was 3.605 mg pyridine/g PAC-APAM WTRs, which was comparable to the laboratory-measured maximum adsorption capacity, 3.253 mg pyridine/g PAC-APAM WTRs. In this study, the separation factor (R_L), which is defined as $1/(1 + b C_0)$, was always a positive number less than 1. These results indicate that the adsorption of pyridine onto PAC-APAM WTRs was inherently favourable. Although the q_m of PAC-APAM WTRs for pyridine adsorption was smaller than that of artificially synthesized materials such as MN 200 and MN 500 (Zhu et al. 2016a) or materials made by high energy inputs such as activated carbon from various raw materials (Lataye et al. 2008; Alonso-Davila et al. 2012; Zhu et al. 2016a), it was higher than other adsorbents such as sodium-montmorillonite and sodium-kaolinite (2.52 mg/g), rundle oil shale (0.26 mg/g) and granular activated carbon (1.20 mg/g) (Lataye et al. 2008). Compared to the processed or artificial synthesized adsorbents, one of the advantages of using PAC-APAM WTRs for pyridine adsorption over other adsorbents is that it requires minimal additional energy for pretreatment and does not require new raw materials because PAC-APAM WTRs are waste products.

Compared with the Langmuir model, the Freundlich model had a slightly higher coefficient of determination (P -value < 0.05). It shows that the Freundlich model described the isotherm adsorption experiments of pyridine onto PAC-APAM WTRs better than the Langmuir model. The value of $1/n$ was 0.38 and within the expected range of 0–1. This indicates that the adsorption of pyridine onto PAC-APAM WTRs is a chemisorption process and is favourable (Foo & Hameed 2010). The value of $1/n$ is indicative of the adsorption intensity or surface heterogeneity if it is in the range of 0–1 (Foo & Hameed 2010). If the value of $1/n$ is closer to 0, it means that the adsorption surface is more heterogeneous (Foo & Hameed 2010). This confirmed that the surface of PAC-APAM WTRs was more heterogeneous with respect to pyridine adsorption because this type of waste contains multiple complicated compounds for

pyridine adsorption and is not uniformly distributed on the adsorption surface. As a result, the adsorption sites for pyridine adsorption might be on the multiple layers with different adsorption energy and affinities.

The D-R model was also slightly better than the Langmuir model and the Temkin model because it had the highest R^2 fit (Table 2). The D-R model assumes that the energy distribution on the heterogeneous adsorption surface is a Gaussian energy distribution (Foo & Hameed 2010). The parameter, E , is the mean free energy of per molecule of adsorbate (Foo & Hameed 2010). A value of E in the range of 8–16 kJ/mol shows a chemical adsorption process, while if it is in the range of 1–8 kJ/mol, it would mean a physical adsorption process (Ozdes et al. 2011; Alberti et al. 2012). The E value (11.855 kJ/mol) in this study indicated that the adsorption of pyridine onto the PAC-APAM WTRs was a chemically controlled adsorption process. This was consistent with the Freundlich model with respect to chemisorption. The theoretical isotherm saturation capacity, q_s , was 9.823 mg pyridine/g PAC-APAM WTRs, which was higher than the laboratory-measured maximum adsorption capacity and the Langmuir model determined maximum adsorption capacity. This indicates that, given more time under favourable conditions, the PAC-APAM WTRs might have the ability to adsorb more pyridine than was found in this study on a per unit mass basis.

Kinetics and desorption

The adsorption kinetic models describe the relationship between adsorption time and the uptake of adsorbate under various specific adsorption conditions. They can provide information about the adsorption rate. Four adsorption kinetic models were used in this study to investigate the adsorption kinetic for pyridine adsorption onto PAC-APAM WTRs. Two of them were reaction order-based sorption kinetic models, including pseudo-first-order model (Equation (9)) and pseudo-second-order model (Equation (10)). The other two models were intra-particle diffusion models – the Weber-Morris model (Equation (11)) and the Elovich model (Equation (12)) (Alberti et al. 2012), which are based on reaction mechanisms. One of advantages of the reaction order-based sorption kinetic models is that they can describe the complete kinetic experimental data as well as the occurred discerned deviations (Alberti et al. 2012). The adsorption reaction mechanism-based kinetic models provide information about understanding the adsorption mechanisms

involved.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (9)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (10)$$

$$q_t = K_P t^{1/2} + C \quad (11)$$

$$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t) \quad (12)$$

In Equations (9)–(12), q_t (mg pyridine/g PAC-APAM WTRs) was the mass of pyridine uptake at time t per unit mass of PAC-APAM WTRs; k_1 (1/day), k_2 (g/(mg·day)), K_P (mg/(g·day^{1/2})), C (mg/g), α (mg/(g·day)) and β (g/mg) were the rate constants of the pseudo-first-order adsorption, the rate constant of pseudo-second-order adsorption, the Weber–Morris intraparticle diffusion rate, the Weber–Morris constant, the initial adsorption rate related to activation energy, and the desorption constant related to surface coverage (Alberti et al. 2012), respectively. Non-linear forms of all four kinetic models were utilized during data fitting. Similar to the data fitting for isotherms, it is recognized and reported that linearization of sorption kinetic models in some cases possibly causes a variation in the error structure and the error distribution (Alberti et al. 2012). This frequently results in different results and conclusions from non-linearized forms, even if different linearized forms are used for the same sorption kinetic model (Alberti et al. 2012). However, the data fitting for non-linearized forms requires a trial and error procedure (Alberti et al. 2012).

The data fitting results are shown in Table 3. It can be clearly seen that the pseudo-first-order, pseudo-second-order and Elovich kinetic models were consistent in describing the kinetic batch study data with similar values of the coefficient of determination (R^2). The Elovich model is mainly used to describe chemisorption. It assumes that the adsorption occurs on fairly heterogeneous adsorbents, and the adsorption is a multilayer process with each layer having different activation energies and adsorption sites exponentially increasing (Alberti et al. 2012). Since the Elovich model had a high correlation efficient in this study (Table 3), it can be inferred that the adsorption of pyridine onto PAC-APAM WTRs might be a multilayer chemisorption process. This inference from the kinetic study was in agreement with that from the isotherm study.

Non-linear Weber–Morris model was fitted in two cases: one for $C \geq 0$, and the other was $C < 0$ (Table 3).

Table 3 | Kinetic parameters for the adsorption of pyridine by PAC-APAM WTRs

Kinetics	Parameters		
Pseudo-first-order	k_1 /day	0.029	
	q_e (mg/g)	7.580	
	R^2	0.970	
Pseudo-second-order	k_2 (g/mg/day)	9.787×10^{-4}	
	q_e (mg/g)	14.929	
	R^2	0.970	
Intraparticle diffusion (Weber–Morris model)	K_P (mg/g/0.5 days)	0.879	Data fit, $C < 0$
	C (mg/g)	−0.910	
	R^2	0.991	
	K_P (mg/g/0.5 days)	0.508	Data fit, $C \geq 0$
	C (mg/g)	0.000	
	R^2	0.798	
Elovich	α (mg/g/day)	0.218	
	β (g/mg)	0.136	
	R^2	0.970	

Previous studies on adsorption have reported that C was not a negative number (Alberti et al. 2012). For $C = 0$, the adsorption rate limiting step is the intraparticle diffusion, while $C > 0$ means that both external mass transfer and intraparticle diffusion are the rate limiting steps (Alberti et al. 2012). In this study, when C was set as a non-negative number, the results showed that C was 5×10^{-15} mg/g and thus reported as zero with the coefficient of determination of (R^2) 0.798. In this case, the Weber–Morris model had a lower R^2 than the other three models. This means that the intraparticle diffusion was the rate limiting step because C was zero. However, in the other case, the Weber–Morris model described the batch study data quite well, with an $R^2 = 0.9914$ when C was set as a negative real number. The negative value of C was reported by previous adsorption studies and showed that external film diffusion limited the adsorption rate, in addition to intraparticle diffusion (Zhu et al. 2016b). The measured kinetic data and the Weber–Morris plots for these two cases of pyridine adsorption onto PAC-APAM WTRs are shown in Figure 4. It can be clearly seen that the prediction of the Weber–Morris model with $C < 0$ was much better than that with $C = 0$. The negative value of C (negative y-axis intercept in Figure 4) can be interpreted as an external film diffusion resistance that led to the time lag for the pyridine adsorption.

In the desorption study, no pyridine was detected in the liquid phase after a 10-day adsorption. It showed that the

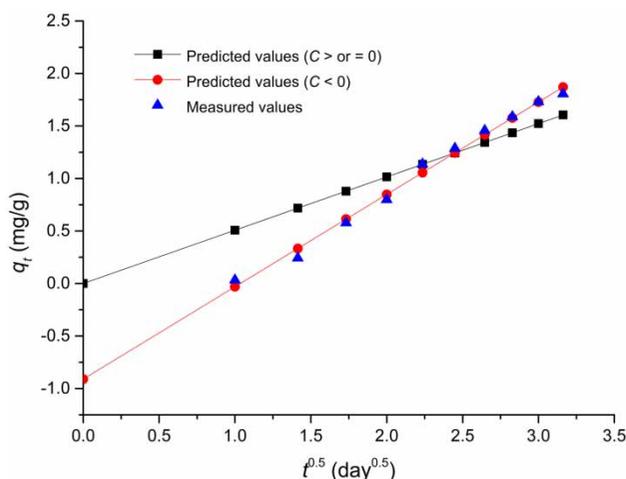


Figure 4 | Measured values of q_t (mg/g) and Weber–Morris intraparticle diffusion model predicted values with intercept $C \geq 0$ and $C < 0$ for pyridine adsorption onto PAC-APAM WTRs. Dosage = 10 g/L, $T = 30^\circ\text{C}$, $\text{pH} = 4$ and initial pyridine concentration = 30 mg/L. All standard deviations ($n = 3$) were less than 2.52×10^{-3} mg/g for measured q_t , so the standard deviation bars approximately overlapped with the points of the average values. All coefficients of variation for measured value were less than 1.79%.

adsorption of pyridine onto the PAC-APAM WTRs was relatively stable under the same adsorption conditions, and the leaching potential of pyridine is extremely low from PAC-APAM WTRs.

Thermodynamic parameters

The uptake of pyridine by PAC-APAM WTRs increased with an increase in temperature. Calculation of the Gibbs free energy change (ΔG° , kJ/mol) of pyridine adsorption by PAC-APAM WTRs is required to determine the adsorption equilibrium distribution coefficient (K_d , L/g). K_d was calculated by using Equation (13). ΔG° can be determined by the classical Van't Hoff equation (Equation (14)) (Lataye *et al.* 2008). Enthalpy change (ΔH° , kJ/mol) and entropy change (ΔS° , kJ/mol/K) were determined by fitting thermodynamic batch study data into Equation (15) (Lataye *et al.* 2008).

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{M} \quad (13)$$

$$\Delta G^\circ = -RT \ln K_d \quad (14)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (15)$$

In this study, the Gibbs free energy change for pyridine adsorption by the PAC-APAM WTRs was determined as 5.308 kJ/mol (20°C), 4.966 kJ/mol (25°C) and 4.759 kJ/mol

(30°C). The positive values of ΔG° showed that the pyridine adsorption by PAC-APAM WTRs was not a spontaneously process. In reality, although the pyridine adsorption rate onto PAC-APAM WTRs was lower than that onto reported artificial synthesized materials which have negative values of Gibbs free energy change (Zhu *et al.* 2016a), the batch experiments showed that the unprocessed PAC-APAM WTRs used in this study had the ability to adsorb pyridine.

The enthalpy change (ΔH°) and the entropy change (ΔS°) were 21.400 kJ/mol and 0.055 kJ/mol/K, respectively. The coefficient of determination (R^2) was 0.988. The positive value of ΔH° indicated that the pyridine adsorption by PAC-APAM WTRs was an endothermic adsorption process and was an activated process probably caused by the activation of some functional groups on the PAC-APAM WTRs which were available to interact with pyridine molecules.

The positive value of ΔS° implied that the pyridine adsorption by the PAC-APAM WTRs increased the randomness at the reaction interface. With the increase of temperature, some functional groups on the PAC-APAM WTRs favouring interaction with pyridine molecules were gradually activated and that caused the increase in the randomness at the liquid–solid interface (Zhu *et al.* 2016a). Also, it was possible that the temperature increase caused some structural changes in the PAC-APAM WTRs resulting in affinity changes between pyridine and the PAC-APAM WTRs which contributed to the randomness increase on the interface (Lataye *et al.* 2008).

Implications of engineering

This study proves that the low-cost PAC-APAM WTRs have the ability to remove one of the priority organic pollutants, pyridine. This finding provides information for engineers to comprehensively consider the technique by using PAC-APAM WTRs to remediate various pollutants in contaminated soils. Our studies have found that PAC-APAM WTRs can effectively remove phosphorus (Duan & Fedler 2020), copper(II), lead(II) (Ma *et al.* 2020), cadmium(II), zinc(II) (Duan & Fedler 2021) and phenol (Jiao *et al.* 2020). One concern for the application of PAC-APAM WTRs is the aluminium ion (Al^{3+}) leaching or being released from PAC-APAM WTRs, which may lead to possible Al^{3+} phytotoxicity (Zhao *et al.* 2018). However, our previous study did not find significant leaching. This study, plus our previous studies, demonstrated that PAC-APAM WTRs have the capability to be used as an adsorbent for the removal of

multiple organic and inorganic pollutants in soils. This study, as well as our other studies, also confirms that PAC-APAM WTRs recycling into contaminated soils is a sustainable disposal method for the municipal drinking water treatment industry by increasing the revenue and decreasing the cost on occupying land resources. More research is needed to understand the removal mechanisms and effects when PAC-APAM WTRs are used in the scenarios in which various pollutants simultaneously exist in the soils where there will be competition for adsorption sites. Also, when PAC-APAM WTRs is land-applied into contaminated soils, they are required to be mixed with the original contaminated soils rather than be entirely substituted for those soils (Hovsepyan & Bonzongo 2009). The appropriate ratio of PAC-APAM WTRs to the original contaminated soil should be investigated based on typical scenarios of contaminated soils under specific climate conditions.

CONCLUSIONS

This study investigated the adsorption of pyridine onto PAC-APAM WTRs and included an analysis of the adsorption isotherms, kinetics and thermodynamics of the adsorption in aqueous solutions. This study confirmed the assumption that PAC-APAM WTRs had the ability to remove pyridine. The D-R model and Freundlich model better described the pyridine adsorption isotherms. It indicated that pyridine adsorption by PAC-APAM WTRs was a chemically controlled multilayer adsorption process. An adsorption kinetic study showed that the pyridine adsorption rate was simultaneously controlled by external film diffusion and intraparticle diffusion. The pyridine adsorption was an endothermic process with randomness increase on the adsorption interface. The pyridine adsorption decreased with an increase in pH and increased with the increase in temperature and dosage of the PAC-APAM WTRs. Therefore, PAC-APAM WTRs recycled into contaminated soils for remediation is expected to be an innovative alternative disposal method for the WTRs produced from municipal drinking water treatment with an aim of achieving sustainability of the water industry. More research is recommended to identify the various compounds in PAC-APAM WTRs and their detailed adsorption mechanisms interacting with pyridine or other organic pollutants, and the proper mixing ratio of PAC-APAM WTRs to contaminated soils under various physical and climatic scenarios.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

- Ahmad, T., Ahmad, K. & Alam, M. 2016 Sustainable management of water treatment sludge through 3'R' concept. *Journal of Cleaner Production* **124**, 1–13. <http://dx.doi.org/10.1016/j.jclepro.2016.02.073>.
- Alberti, G., Amendola, V., Pesavento, M. & Biesuz, R. 2012 Beyond the synthesis of novel solid phases: review on modelling of sorption phenomena. *Coordination Chemistry Reviews* **256** (1–2), 28–45. <http://dx.doi.org/10.1016/j.ccr.2011.08.022>.
- Alonso-Davila, P., Torres-Rivera, O. L., Leyva-Ramos, R. & Ocampo-Perez, R. 2012 Removal of pyridine from aqueous solution by adsorption on an activated carbon cloth. *Clean – Soil, Air, Water* **40** (1), 45–55.
- Babić, B. M., Milonjić, S. K., Polovina, M. J. & Kaludierović, B. V. 1999 Point of zero charge and intrinsic equilibrium constants of activated carbon cloth. *Carbon* **37** (3), 477–481. <https://linkinghub.elsevier.com/retrieve/pii/S0008622398002164>.
- Dane, J. H. & Topp, G. C. 2002 *Methods of Soil Analysis, Part 4: Physical Methods*. Soil Science Society of America, Madison, Wisconsin, USA.
- Duan, R. & Fedler, C. B. 2020 Modeling phosphorus adsorption onto polyaluminium chloride water treatment residuals. *Water Supply*. <https://doi.org/10.2166/ws.2020.322>.
- Duan, R. & Fedler, C. B. 2021 Polyaluminium chloride and anionic polyacrylamide water treatment residuals as a sorbent for Cd²⁺ and Zn²⁺ in soils. *Water, Air, & Soil Pollution* **232** (1), 7. <http://link.springer.com/10.1007/s11270-020-04976-2>.
- Foo, K. Y. & Hameed, B. H. 2010 Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal* **156** (1), 2–10.
- Gadekar, M. R. & Ahammed, M. M. 2019 Modelling dye removal by adsorption onto water treatment residuals using combined response surface methodology-artificial neural network approach. *Journal of Environmental Management* **231**, 241–248. <https://linkinghub.elsevier.com/retrieve/pii/S0301479718311459>.
- Hovsepyan, A. & Bonzongo, J. J. 2009 Aluminum drinking water treatment residuals (Al-WTRs) as sorbent for mercury: implications for soil remediation. *Journal of Hazardous Materials* **164** (1), 73–80. <https://linkinghub.elsevier.com/retrieve/pii/S0304389408011709>.

- Jiao, X., Duan, R. & Du, Z. 2020 Adsorption study of dried alum-sludge from a water treatment plant towards phenol water. *Journal of Taiyuan University of Technology* **51** (5), 717–723.
- Karri, R. R., Sahu, J. N. & Jayakumar, N. S. 2017 Optimal isotherm parameters for phenol adsorption from aqueous solutions onto coconut shell based activated carbon: error analysis of linear and non-linear methods. *Journal of the Taiwan Institute of Chemical Engineers* **80**, 472–487.
- Lataye, D. H., Mishra, I. M. & Mall, I. D. 2008 Pyridine sorption from aqueous solution by rice husk ash (RHA) and granular activated carbon (GAC): parametric, kinetic, equilibrium and thermodynamic aspects. *Journal of Hazardous Materials* **154** (1–3), 858–870.
- Liao, P., Yuan, S., Xie, W., Zhang, W., Tong, M. & Wang, K. 2013 Adsorption of nitrogen-heterocyclic compounds on bamboo charcoal: kinetics, thermodynamics, and microwave regeneration. *Journal of Colloid and Interface Science* **390** (1), 189–195. <http://dx.doi.org/10.1016/j.jcis.2012.09.037>.
- Ma, C., Duan, R. & Du, Z. 2020 Adsorption of Pb²⁺ and Cu²⁺ in water by dried alum-sludge from a water treatment plant. *Industrial Water Treatment* **40** (2), 59–62.
- Mohan, D., Singh, K. P., Sinha, S. & Gosh, D. 2004 Removal of pyridine from aqueous solution using low cost activated carbons derived from agricultural waste materials. *Carbon* **42** (12–13), 2409–2421.
- Ozdes, D., Duran, C. & Senturk, H. B. 2011 Adsorptive removal of Cd(II) and Pb(II) ions from aqueous solutions by using Turkish illitic clay. *Journal of Environmental Management* **92**, 3082–3090.
- Singh, K., Chandra, B., Rhyman, L. & Ramasami, P. 2016 Effective adsorption of pyridine (Py) onto mesoporous silica derived from de-oiled mustard cake (DOMC): experimental and theoretical study. *Journal of Environmental Chemical Engineering* **4** (1), 1383–1392. <https://linkinghub.elsevier.com/retrieve/pii/S2213343716300331>.
- Tay, D. Y. Y., Fujinuma, R. & Wendling, L. A. 2017 Drinking water treatment residual use in urban soils: balancing metal immobilization and phosphorus availability. *Geoderma* **305**, 113–121. <https://linkinghub.elsevier.com/retrieve/pii/S0016706116309168>.
- Team, R. C. 2019 *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing. <https://www.r-project.org/>
- Weber, J. B. 1966 Molecular structure and pH effects on the adsorption of 1,3,5-triazine compounds on montmorillonite clay. *American Mineralogist* **51**, 1657–1690.
- Zhao, Y., Liu, R., Wesley, O., Yang, Y. & Shen, C. 2018 Acceptability of land application of alum-based water treatment residuals – an explicit and comprehensive review. *Chemical Engineering Journal* **353** (July), 717–726. <https://doi.org/10.1016/j.cej.2018.07.143>.
- Zhu, Q., Moggridge, G. D., Ainte, M., Mantle, M. D., Gladden, L. F. & D'Agostino, C. 2016a Adsorption of pyridine from aqueous solutions by polymeric adsorbents MN 200 and MN 500. Part 1: adsorption performance and PFG-NMR studies. *Chemical Engineering Journal* **306**, 67–76.
- Zhu, Q., Moggridge, G. D. & D'Agostino, C. 2016b Adsorption of pyridine from aqueous solutions by polymeric adsorbents MN 200 and MN 500. Part 2: kinetics and diffusion analysis. *Chemical Engineering Journal* **306**, 1223–1233. <http://dx.doi.org/10.1016/j.cej.2016.07.087>.

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