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Isotherm, Kinetic and Thermodynamic Terms of Adsorption of Pyrimethamine from Binary Aqueous Solution

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Abstract
The processing of under-utilized sawdust as adsorbent for removing contaminants like pharmaceuticals from aqueous solutions is a sustainable environmental management strategy. In this study, sawdust was carbonized, activated with $ZnCl_2$ and code-named Z-AC. Binary aqueous solutions of pyrimethamine containing paracetamol were treated with Z-AC; and effects of contact time, pH, temperature, adsorbent dose and adsorbate concentration were determined in batch adsorption experiments. The isotherm, kinetic and thermodynamic studies were conducted. The equilibrium was attained at 100 minutes. At pH 2.0 and 7.6, pyrimethamine load on Z-AC were 5.20 and 2.68 mg/g respectively. At 30 ^oC and 50 ^oC, pyrimethamine adsorbed were 1.68 and 2.52 mg/g respectively. Z-AC has monolayer adsorption capacity of 4.76 mg/g for pyrimethamine in binary solution. Load of pyrimethamine per unit mass of Z-AC decreased with increased dose of Z-AC. The best isotherm and kinetic fitting were Langmuir (0.98) and pseudo-first order (0.98) respectively. The process was endothermic (+18.5 kJ/mol/K) with increased degree of randomness (+48.52 J/mol/K). The process was feasible at higher temperatures. Higher pH and adsorbent doses de-enhanced the process while increased temperatures enhanced adsorption of pyrimethamine in binary aqueous media. Therefore, Z-AC could be utilized in adsorption process for remediating pharmaceutical contaminated aqueous media.
Keywords: pyrimethamine, binary solution, paracetamol, pharmaceuticals, isotherm, thermodynamics

Introduction

The availability of usable and potable water is on decline across the world. This is due to discharge of substances with range of sources into water bodies (Adesokan et al., 2022). These substances constitute contaminants and pollutants that impact water resources with negative attributes. These water contaminants and pollutants could be toxic at low concentration, persistent, bio-accumulate or alter the standard characteristics (colour, odour, taste, density, biological oxygen demand, chemical oxygen demand and pH) of water (Manisalidis et al., 2020). Human exposure to these pollutants in the environment could be primary where there would be direct contact through water. Pollutants in portable water could impair human health or worsen condition of vulnerable populations like sick and persons with compromised immune system. Also, presence of contaminants and pollutants could hinder direct usage of water resource for agricultural, e.g. irrigation, and industrial, e.g. cooling, purposes. Human could made secondary contact with pollutants in water through consumption of aquatic food resources. Some persistent, bio-accumulative, bio-magnified and transformed pollutants could enter food chains and wreck havocs (Fuller et al., 2022).

Some of the contaminants and pollutants are heavy metals, dyes, organic chemicals, detergents, pesticides, herbicides, hydrocarbons, flame retardants and industrial additives, plasticizers and pharmaceuticals and personal care products. These substances are generated by pharmaceutical, medical/health, agrochemicals, petrochemical, dyeing and agricultural industries/facilities (Akhtar et al., 2021). Drugs are neurological and physiological compounds administered to facilitate, maintain and sustain wellbeing. Pharmaceuticals/drugs are endocrine disruptive substances. Involuntary exposure to pharmaceuticals could lead to cancer, renal failure and other health infractions, especially among aged, children and ailing populations (Kusturica et al., 2022; Wilkinson et al., 2022).

Extensive profiling of levels of contaminants and pollutants in environment has been done, as well as their effects on ecosystem. However, pharmaceuticals are substances of emerging concerns. Methods of determining pharmaceuticals in the environment are emerging as well as their impacts. The contaminants from these sources enter into the environment through, majorly, discharge of effluents. Many wastewater treatment plants were not designed to deteriorate/remove emerging contaminants (Patel et al., 2019). One of the promising methods for treatment of pharmaceutical-bearing water/wastewater is adsorption. Adsorption, using low cost adsorbent, is comparatively cheap and effective (Vinayagam et al., 2022).

Pyrimethamine, a pharmaceutical, is a substance in anti-malarial drugs. Anti-malarial drugs are among most produced and dispensed in Nigeria and many global south countries, because of prevalence of malarial disease. The propensity of pyrimethamine in pharmaceutical wastewater is expected to be high. Therefore, in this study pyrimethamine was removed from aqueous solution using sawdust-based adsorbent.

Materials and Methods

Material and equipment

Sawdust was collected from a wood processing factory in Ogbomoso, Nigeria. $ZnCl_2$ HCl and NaOH of analytical grades were purchased from chemical store outlets in Ibadan. Pyrimethamine and paracetamol were donated by Bond Chemical Industry Limited, Awe, Oyo State for research purpose. Some of the equipment used were spectrometer (Pelkinlmer Spectrum BX), oven (Carbolite), ultraviolet-visible (UV) (B-UV 1800PC) spectrophotometer, furnace (Carbolite AAF 1100) and pH meter (Jenway 3520).

Preparation of Z-AC

A 300 g of sawdust was soaked in 300 mL of 1 M $ZnCl_2$ for 30 minutes in a clean crucible. The mixture was put in the furnace, the temperature rose to and maintained at 800 ^{0}C for 5 minutes. The sample was removed with the help of a probe, poured into cold (iced) water; excess water drained and allowed to stand at room temperature. The activated carbon generated was washed with warm distilled water to remove residual acid until pH of the supernatant was neutral. The sample was then dried in an oven at 110 ^{O}C overnight and sieved, 0.4 mm sizes retained and stored in air tight containers as Z-AC (Adesokan et al., 2021).

Batch adsorption experiments

The batch adsorption was conducted in 100 mL adsorption bottles containing 20 mL of equal concentrations of pyrimethamine and paracetamol. The adsorbent-adsorbate systems were oscillated on a mechanical shaker. The effects of adsorbent dosage (0.1– 1.0 g), pH (2.8, 3.8, 4.9, 7.6), contact time (0–200 min), initial adsorbate concentration (30 – 70 mg/L), and temperatures (30, 40, 50 ^{o}C) were evaluated. After the adsorption, the mixtures were filtered and the filtrates analysed with the ultraviolet-visible (UV) spectrometer to determine the amount of un-adsorbed adsorbates in solutions. The amount of adsorbate uptake at equilibrium was determined using:

$$q = \frac{V(C_i - C_e)}{m}$$

Where, q is amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), V is the volume of solution (L), m is the amount of adsorbent (g), and C_i and C_e (mg/L) are the initial and equilibrium adsorbate concentrations in the solution, respectively.

Adsorption Isotherms

Table 1 contains selected isotherms used to process experimental data and then described the adsorption processes.

Table 1: Adsorption isotherm parameters

Model	Linearised Formulae	Reference
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K.Q_o} + \frac{C_e}{Q_o}$	(Langmuir, 1918)
Freundlich	$lnq_e = lnK_F + \frac{1}{n} lnC_e$	(Freundlich, 1906)
Temkin	$q_e = BlnK_T + BlnC_e$	(Tempkin and Pyzhev, 1940)
Dubinin–Radushkevich	$\ln q_e = \ln(q_s) - (K_{ad}\varepsilon^2)$	(Rieman and Walton, 1974)

In Langmuir Model plot, C_e/q_e versus C_e gives a straight line with intercept: $1/K.Q_o$; and slope: $1/Q_0$. Langmuir isotherm equilibrium parameter, R_L: $R_L = \frac{1}{1+K_L C_i}$. (Rieman and Walton, 1974). C_i = highest initial adsorbate concentration (mg/L); R_L>1 = unfavourable; R_L=1=linear; favorable 0<R_L<1=favourable and R_L = 0 = irreversible. In Freundlich Model plot, lnq_e vs ln C_e yields an intercept of log K_F and a slope of 1/n. n defines isotherm shape; 1/n = 0 = irreversible; (0<1/n<1) = favourable; unfavourable (1/n>1); n = 1=linear; n > 1 = physical process and n < 1= chemical process. In Temkin Model, q_e was ploted against ln C_e. K_T =Temkin isotherm equilibrium binding constant (L/g); b_T (B) = Temkin isotherm constant; R= universal gas constant (8.314J/mol/K); T= Temperature at 298K; B = Constant related to heat of sorption (J/mol). In Dubinin–Radushkevich Model, ln qe was plotted against ε^2: $\varepsilon = RT\ln[1 + \frac{1}{C_e}]$; $E = [\frac{1}{\sqrt{2B_{DR}}}]$; K_{ad} = B_{DR}; E<8 kJ/mol (physical adsorption); E = 20–40 kJ/mol (chemical adsorption) (Tempkin and Pyzhev, 1940); E = 8–16 kJ/mol (ion-exchange) (Helfferich, 1962); q_e = amount of adsorbate on the adsorbent at equilibrium(mg/g); q_s = theoretical isotherm saturation capacity (mg/g); K_{ad} = Dubinin–Radushkevich isotherm constant (mol^2/kJ^2).

The Kinetic Study

Samples were taken from adsorption bottles at time intervals and the amounts of adsorbates were measured. The amount of adsorbed adsorbate at time, *t*, q_t (mg/g), was calculated using Equation:

$$q_t = \frac{(C_o - C_t)V}{m}$$

The kinetic parameters were calculated using kinetic equations presented in Table 2.

Table 2: Adsorption kinetic parameters

Kinetic	Equation	Reference
Pseudo-First Order	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} . t$	(Lagergren, 1898)
Pseudo-Second Order	$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$	(Ho & G. McKay, 1998)
Elovich	$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln t$	(Okiemen and Onyega, 1989; Sparks, 1986)
Intra-Particle Diffusion	$Q_t = k_{id}t^{0.5} + C_i$	(Weber and Morris, 1962)

In Pseudo-First Order equation, q_e and q_t are the amounts of the pyrimethamine adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the rate constant adsorption (min^{-1}). A plot of $\log(q_e - q_t)$ versus t gives a slope of $(-\frac{k_1}{2.303})$ and intercept of $\log q_e$. In Pseudo-Second Order equation, $h = (k_2\ q_e^2)$; q_e is the amount of the solute adsorbed at equilibrium per unit mass of adsorbent ($mg\ g^{-1}$) , q_t is the amount of solute adsorbed ($mg\ g^{-1}$) at any given time, *t* (min) and k_2 is the rate constant for pseudo-second-order adsorption ($g\ mg^{-1}min^{-1}$) and *h,* known as the initial sorption rate. In Elovich equation, plot of q_t vs *ln t* gives a straight line with intercept $\frac{1}{\beta}\ln(\alpha\beta)$ and slope $\left(\frac{1}{\beta}\right)$. α is the initial adsorption rate (mg/g. min), β is the desorption constant (g/mg) and q_t is the amount of solute adsorbed (mg/g) at any given time, t (min). In Intra-Particle Diffusion equation, graph of Q_t versus $t^{0.5}$ gives a straight line with slope, k_{id}, and intercept, C_i. C_i defines the thickness of the boundary layer. Q_t (mg/g) = quantity of adsorbate adsorbed at time, t and k_{id} ($mg/gh^{0.5}$) = intra-particle diffusion constant.

Thermodynamic Study

A series of experiments were performed at 30, 40 and 50 °C to establish the effect of temperature on the adsorption capacities of Z-AC for the pyrimethamine in binary solution. The thermodynamic parameters of the adsorption were determined using the equations:

$$log(\frac{C_{Ae}}{C_e}) = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT}$$

$C_{Ae} = (C_i - C_e)$ (mg/L) = amount of adsorbate adsorbed on adsorbent at equilibrium; C_e (mg/L) = amount of adsorbate in solution at equilibrium; R = gas constant (8.314 J/mol/K); T = temperature (K). The enthalpy change (ΔH), the entropy change (ΔS) and the change in standard free energy (ΔG) were calculated. The spontaneity of the processes was thereby determined using van't Hoff graph which is a plot of $log(\frac{C_{Ae}}{C_e})$ vs $\frac{1}{T}$.

Results and Discussion

Effect of Z-AC dose on adsorption of PYR from binary solution

In binary solution of PYR and paracetamol, at 0.1, 0.2, 0.3, 0.4 and 0.5 g of Z-AC, the q_e were 1.91, 1.34, 1.04, 0.68, 2.22 mg/g respectively (Figure 1). These q_e were comparable to those for single system (Giwa et al., 2021). As Z-AC dose increased, the q_e (mg/g) decreased (dose α $1/q_e$). As Z-AC dose increased, the adsorption sites per molecule of PYR in binary solution increased. The competition among the molecules in solution thereby reduced and there was dropped in repulsive drift towards the Z-AC surface.

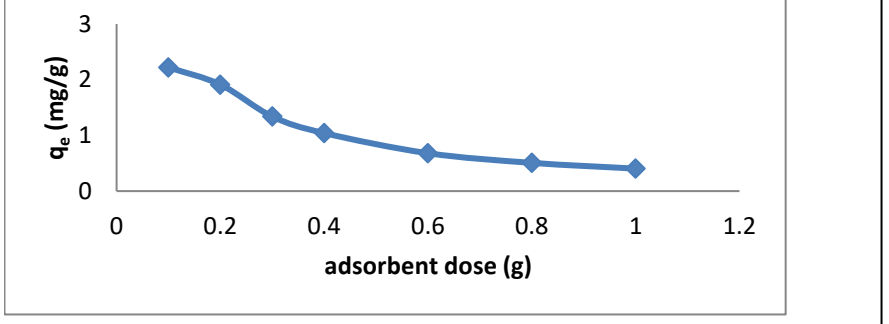

Figure 1: Effect of Z-AC dose on adsorption of PYR from binary solution

Effect of pH on the adsorption of PYR from binary solution

At pH 2.8, 3.8, 4.9 and 7.6 respectively, 5.14, 3.41, 2.14 and 2.68 mg/g of PYR were adsorbed from PYR and paracetamol binary solution (Figure 2). These values were higher than those reported for adsorption of PYR from single solution (Giwa et al., 2021). This indicated that pH enhanced adsorption of PYR in binary system as q_e reached 5 mg/g. At acidic pH, the solution was protonated. The nucleophilic centers on already adsorbed PARA picked up the electrophile (H^+) and became charged. The adsorbed and charged PARA provided adsorptive sites for PYR. However, as pH changed from acidic to basic, adsorption of PYR was de-enhanced and q_e reduced. This might due to electrostatic repulsion among PARA (OH^-, CO^-, N), adsorbents (negative at pH above pzc), PYR (N^-) and OH^- of solution.

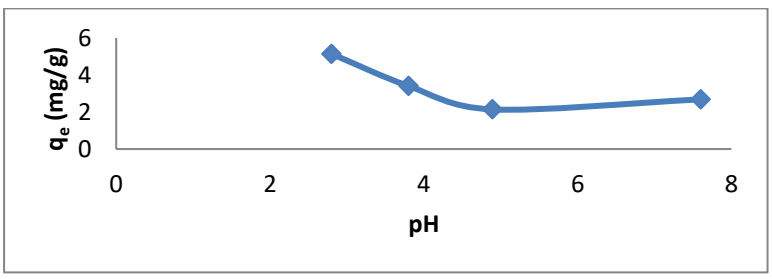

Figure 2: Effect of pH on adsorption of PYR from binary solution

Isotherm Study of the Adsorption of PYR from Binary Solution

At 30, 40, 50, 60 and 70 mg/L respectively, 3.09, 3.86, 3.84, 3.81 and 4.25 mg/g of PYR (in mixture with paracetamol) were adsorbed (Figure 3). As concentration increased from 30 to 40 mg/L, the bulk solution driving force (mutual repulsion among PYR and paracetamol molecules) increased. This could lead to increase drift towards the adsorptive sites of Z-AC. The adsorption capacity of Z-AC was thereby improved. However, between 40 and 60 mg/L, there was dropped in the capacity of Z-AC; paracetamol molecules could have had competitive adsorption edge over PYR molecules. At 70 mg/L, the capacity of Z-AC increased again for PYR. As initial PYR binary solution concentration increased, the available adsorptive active sites were completely occupied. Therefore excess adsorbate molecules remained in solution.

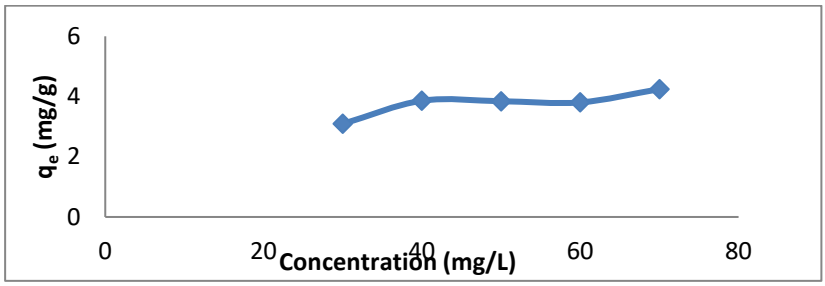

Figure 3: Effect of initial PYR binary solution concentration on PYR adsorption

In binary system of PYR+PARA, the model that best fit the adsorption of PYR by Z-AC was Langumuir (R^2 =0.976) (Figure 4, Table 3) which indicated monolayer adsorption. The maximum monolayer adsorption capacity of Z-AC for PYR (q_{max}) was 4.76 mg/g. This was bigger than q_{max} of Z-AC for PYR in single system (Giwa et al., 2021). This showed that presence of PARA in the system aided adsorption of PYR by Z-AC. R_L value of 0.105 showed that the process was favourable. The value n parameter calculated from Freundlich model was 4.525 L/g and activation energy (E_a kJL/mol/mg), 0.158, defined adsorption of PYR in binary solution as physical process.

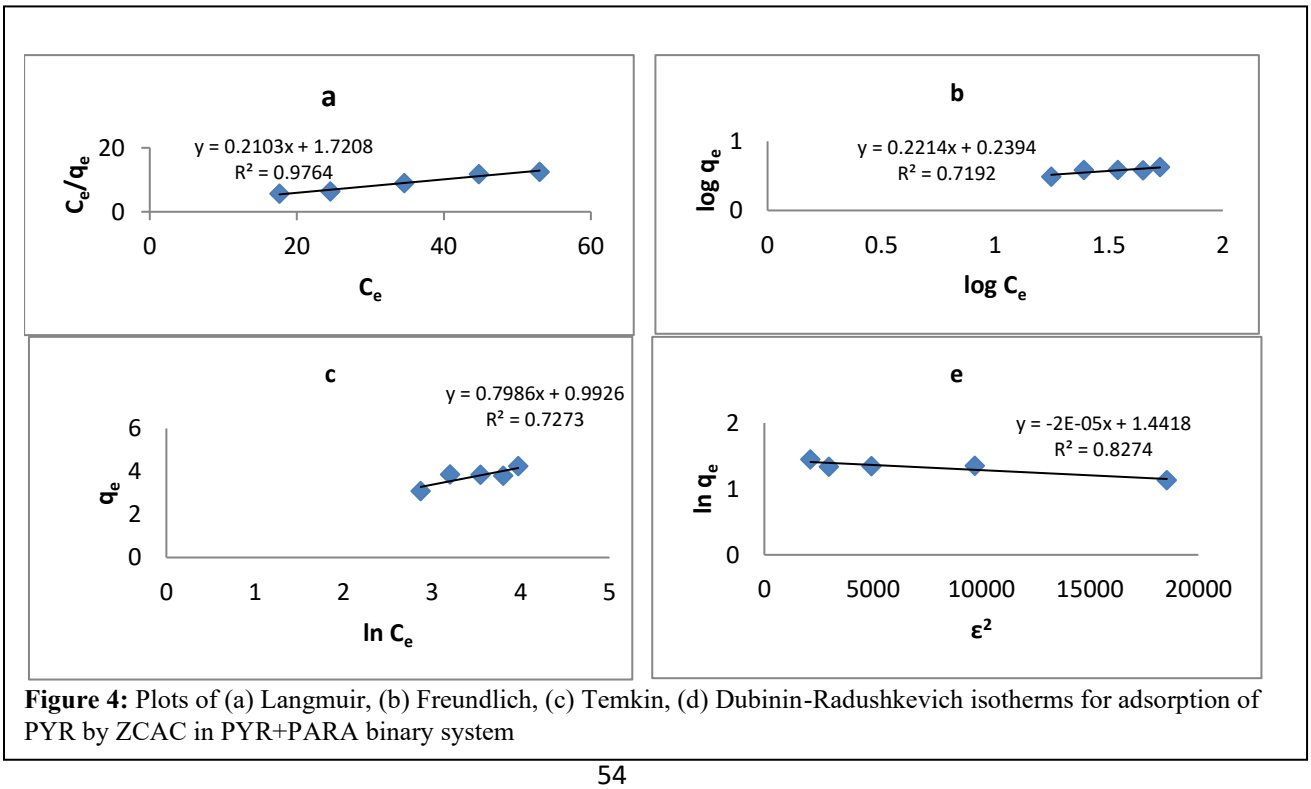

Figure 4: Plots of (a) Langmuir, (b) Freundlich, (c) Temkin, (d) Dubinin-Radushkevich isotherms for adsorption of PYR by ZCAC in PYR+PARA binary system

Table 3: Isotherm Parameters of Adsorption of pyrimethamine in binary solution by ZCAC

Langmuir				Freundlich				Temkin				D-R			
q_{max} (mg/g)	k_L (L/mg)	R_L	R^2	K_F (mg/g)	n (L/g)	1/n	R^2	K_T	b_T (kJ/mol/gL)	β (L/g)	R^2	q_s (mg/g)	K_{ad} (JL/mol/mg)	E_a (KJL/Mol/mg)	R2
4.76	0.122	0.105	0.98	1.73	4.53	0.22	0.72	3.47	3.16	0.80	0.73	4.23	2×10^{-5}	0.158	0.70

Kinetic Study of the Adsorption of PYR in Binary Solution

The q_e at 30, 90, 120 and 200 minutes were 0.77, 1.77, 1.97 and 1.86 mg/g respectively (Figure 5). The adsorption reached equilibrium around 100 minutes as against the single adsorption at 240 mintues (Giwa et al., 2021). The adsorption of PYR in binary system by Z-AC might be influenced in a number of ways. Paracetamol molecules were suspected to diffuse faster competitively into the available pores and also might interact with Z-AC surface through its nucleophilic centers. Therefore adsorption of PYR by Z-AC in binary system was de-enhanced and q_e (binary aystem) smaller than q_e (single system) (Giwa et al., 2021). Also, bulk solution repulsive force created by paracetamol and PYR molecules in solution might generate high drift (enhanced mobility) of molecules and therefore equilibrium was attained earlier than in single solution.

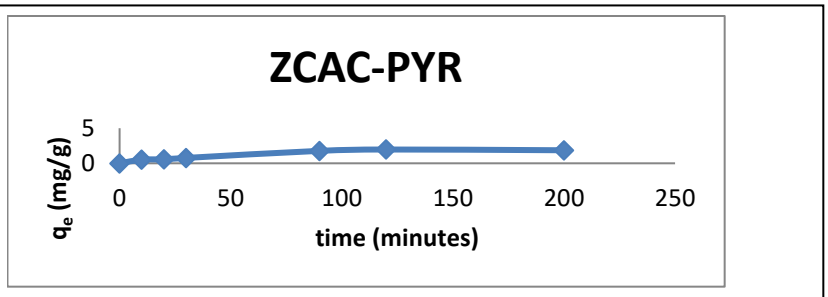

Figure 5: Effect of contact time on adsorption of PYR in binary solution

The data of adsorption of PYR by Z-AC from the mixture with paracetamol fitted best pseudo-first order kinetics (PFO). The PFO kinetic regression coeffiecient (R^2 = 0.977) (Figure 6) was the highest, together with lower SSE value, followed by that of intraparticle diffusion (R^2 = 0.964), and the values of pseudo-first-order q_{cal} (2.25 mg/g) was the closest to q_{exp} (1.97 mg/g) (Table 4). The rate of removal (K_1) of PYR from binary solution by 1 mg of Z-AC per 1 minute was 0.025 mg. The high R^2 of Intraparticle diffusion model suggested that diffusion of PYR into the pores of Z-AC play role in rate determining step of the process.

Table 4: Kinetics parameters for pyrimethamine adsorption onto Z-AC

Kinetic	ZCAC (binary system)
$q_{e,\ exp}$	1.966
Pseudo-first order	
q_e (mg/g)	2.254
K_1 (mg/g/min)	0.0253
R^2	0.977
SSE (%)	0.144
Pseudo-second order	
q_e (mg/g)	3.155
h (mg/g/min)	0.0415
K_2	0.0042
R^2	0.778
SSE (%)	0.594
Elovich	

A	0.100
β (min.g/mg)	1.672
R^2	0.879
Intraparticle	
C_i (mg/g)	-0.285
K_{id}(mg/g/$min^{1/2}$)	0.211
R^2	0.964

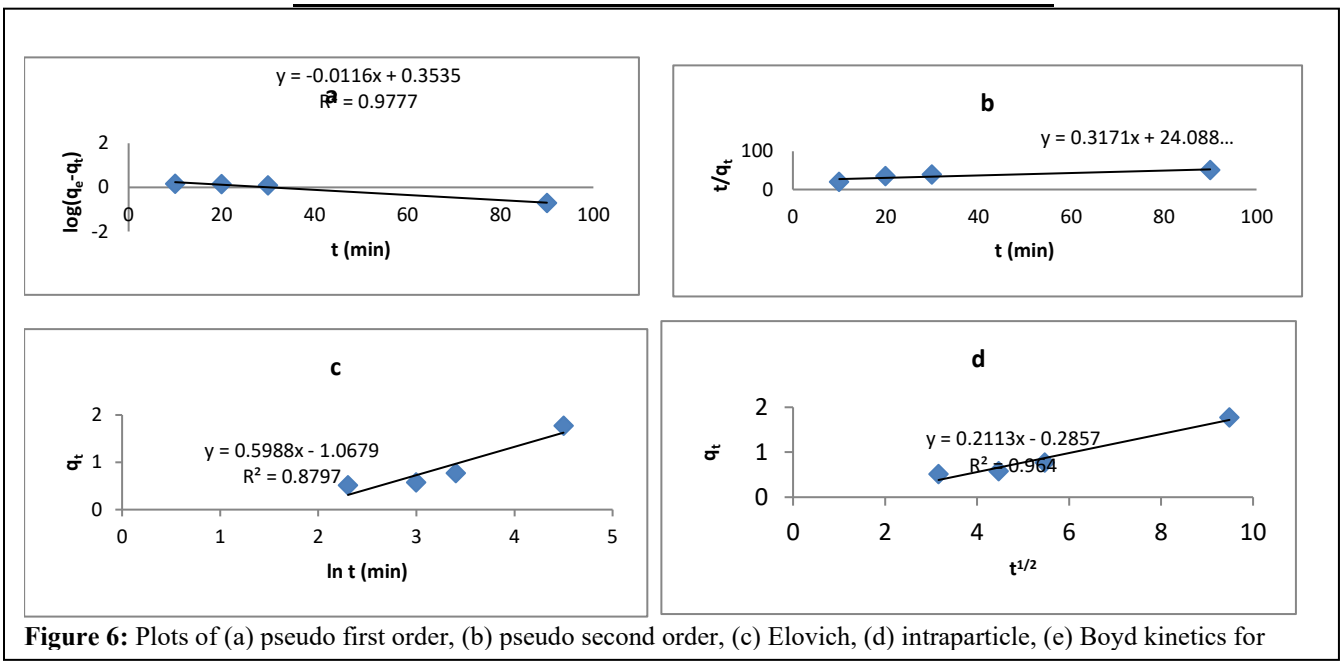

Figure 6: Plots of (a) pseudo first order, (b) pseudo second order, (c) Elovich, (d) intraparticle, (e) Boyd kinetics for

Thermodynamic Study of the Adsorption of PYR in Binary Solution

The capacities of Z-AC for PYR in binary solution were 1.68, 2.31 and 2.52 mg/g at 30, 40 and 50 °C (Figure 7). As temperature increased, the capacity of Z-AC for PYR increased. As temperature increased, the PYR molecules acquired energy and migrated faster onto the Z-AC surface and the adsorption sites. High temperature could soften the pore openings and pore walls and made them more receptive to migrating adsorbate molecules. The q (mg/g) of ZCAC-PYR in binary system was higher than those of single system at the tested temperatures (Giwa et al., 2021). The presence of paracetamol enhanced the adsorption of PYR from binary solution. Paracetamol could have specific interaction with the Z-AC and at the same time served as bonding surface for PYR.

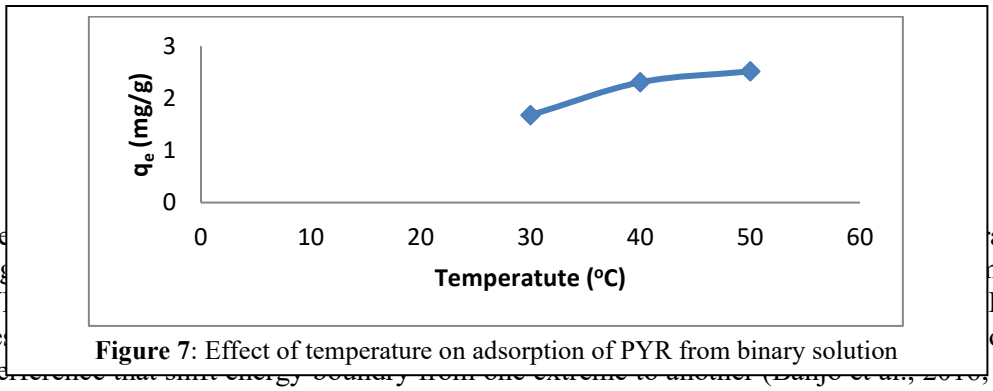

Figure 7: Effect of temperature on adsorption of PYR from binary solution

The randomness (+ΔS°) (Fig mean the affinity of PY R by ZCAC in the pre occur as a result of inte Ozcan and Ozcan, 2004).

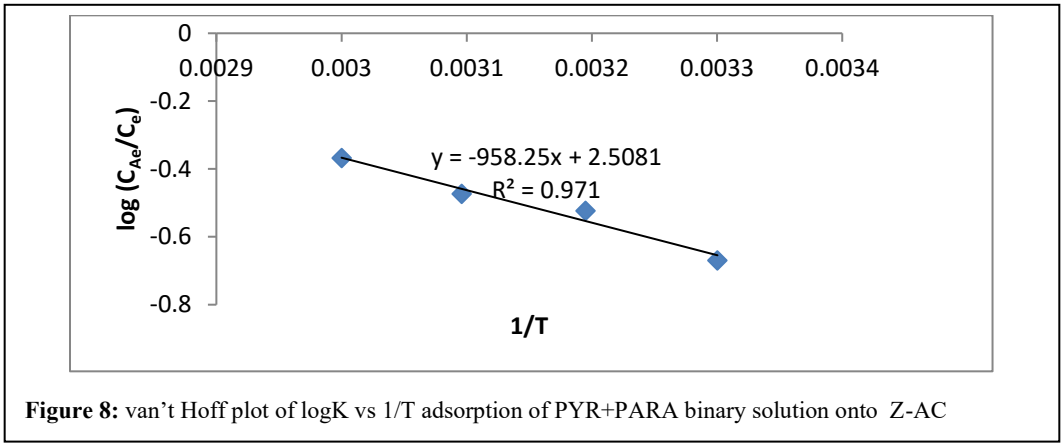

Figure 8: van't Hoff plot of logK vs 1/T adsorption of PYR+PARA binary solution onto Z-AC

Table 5: Thermodynamics parameters of adsorption of pyrimethamine onto the Z-AC from binary solution

Thermodynamic Parameters	Temperatute (K)	Z-AC
	302	+3.798
	313	+3.313
ΔG^0 (kJ/mol/K)	323	+2.828
	333	+2.343
ΔS^0 (kJ/mol/K)		+0.049
ΔH^0 (kJ/mol/K)		+18.500

Conclusion

Presence of paracetamol in the solution enhanced capacity of Z-AC for pyrimethamine. Also, increase in temperature and decrease in pH enhanced adsorption of pyrimethamine in binary solution. Z-AC showed good capacity for adsorption of pyrimethamine from binary aqueous solution which contained paracetamol.

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