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Spent Silica Gel as an Adsorbent for Ciprofloxacin and Tinidazole Removal from Aqueous Solutions

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ABSTRACT

The study investigated the adsorption of ciprofloxacin (CIP) and tinidazole (TIN) from aqueous solutions using spent silica gel (SSG) as an adsorbent. The physicochemical characterization of SSG was conducted by following standard methods. The adsorption experiments assessed the effects of pH (3–11), adsorbent dosage (0.25–1.5 g), initial concentrations (40–240 mg/L), contact time (0–60 min), and temperature (298–328 K). The results of physicochemical characterization revealed favourable pH (6.93), bulk density (0.99 g/cm³), iodine adsorption number (1.03×10^{-3} mol/g), and surface area (198.42 m²/g). Maximum uptake was observed at pH 5–7 and an adsorbent dose of 0.25 g. The Freundlich isotherm best described adsorption (R^2 = 0.9611 for CIP, 0.9925 for TIN), suggesting multilayer coverage, while kinetic modeling followed the pseudo-first-order model ($R^2 > 0.96$). Thermodynamic parameters indicated spontaneous, exothermic, and physisorption, with $\Delta G°$ values ranging from -16.19 to -18.30 kJ/mol. These findings highlight the efficiency of SSG as a low-cost adsorbent for removing pharmaceutical contaminants from wastewater.

Keywords: Adsorption isotherms, adsorption kinetics, ciprofloxacin, pharmaceutical/healthcare waste, Spent silica gel, tinidazole, Wastewater treatment

INTRODUCTION

Developing countries like Nigeria face substantial challenges in managing pharmaceutical waste due to inadequate waste treatment infrastructure and poor disposal practices, exacerbating environmental and health risks [1-3]. In recent years, environmental researchers have increasingly focused on emerging contaminants such as pharmaceuticals and personal care products (PPCPs), recognizing them as significant threats to environmental and public health [4-6]. The global surge in the consumption of pharmaceuticals and personal care products is evident

in the steady rise in prescription rates, contributing to widespread environmental contamination [7]. Pharmaceuticals such as antibiotics, analgesics, contraceptives, steroids, and antidepressants are frequently detected in wastewater and aquatic ecosystems, raising concerns about their adverse effects on non-target organisms and human health.

Beyond their direct biological impacts, pharmaceutical waste particularly antibiotics contributes to unpleasant odors, skin disorders, and microbial resistance, complicating wastewater treatment processes and increasing the risk of untreatable infections [8, 9]. The World Health Organization (WHO) and the United Nations Children's Fund (UNICEF) emphasize the need for proper management of healthcare waste to mitigate these risks [10]. Healthcare waste, which varies from non-hazardous to hazardous materials, requires diverse treatment and disposal strategies to ensure environmental safety [11].

Biological effects on non-target organisms and human health have raised serious concerns regarding the persistence of pharmaceuticals in the environment [12, 13]. Their low biodegradability often leads to their persistence and bioaccumulation in aquatic systems, further exacerbating ecological risks [14]**.** Particularly, steroids and antibiotics have been identified as endocrine disruptors, causing physiological disturbances in biological systems [15, 16]. Among pharmaceuticals, antibiotics are of special concern due to their extensive use in human medicine, veterinary applications, and agriculture, leading to their widespread release into the environment [17, 18]. The indiscriminate disposal of antibiotics contributes to the development of antimicrobial resistance (AMR), a growing global health crisis [19, 20]. Ciprofloxacin, a broad-spectrum fluoroquinolone antibiotic, and tinidazole, a nitroimidazole derivative used to treat anaerobic bacterial and protozoan infections, are commonly detected in surface waters, posing risks to aquatic ecosystems and human health [21, 22].

Various techniques have been explored for removing pharmaceuticals and personal care products (PPCPs) from wastewater, including membrane filtration, advanced oxidation processes, biological degradation, and adsorption. Among these, adsorption has gained prominence due to its efficiency, cost-effectiveness, and operational simplicity. While activated carbon has been widely used for its high adsorption capacity, the search for alternative, sustainable, and low-cost adsorbents has intensified.

Silica-based adsorbents have emerged as a promising alternative for the removal of pharmaceutical pollutants, including antibiotics, from wastewater. Functionalized silica materials

have demonstrated notable efficiency in adsorbing fluoroquinolones from aqueous solutions [5], while silica nanoparticles modified with organic functional groups have exhibited high adsorption capacities for antibiotics, steroids, and endocrine-disrupting compounds [16, 23]. However, most studies focus on synthetic modifications, which, although effective, can be costly and may generate secondary waste, highlighting the need for more economical and environmentally friendly alternatives.

Despite the promising adsorption capabilities of silica-based materials, limited studies have explored the use of spent silica gel (SSG), a non-hazardous pharmaceutical waste, as a low-cost and sustainable alternative for antibiotic removal. Additionally, previous research has not extensively investigated the thermodynamic and kinetic aspects of CIP and TIN adsorption on SSG, particularly under varying environmental conditions such as pH, adsorbent dosage, and temperature. This study, therefore, bridges this gap by assessing the feasibility of SSG as an economical and environmentally friendly adsorbent, evaluating its adsorption behavior, and elucidating the governing mechanisms.

MATERIALS AND METHODS

Adsorbent precursor, chemicals and apparatus

Spent silica gel obtained from pharmaceutical stores in Makurdi, Benue State, Nigeria was cleaned dried and pulverized.

Chemicals

Ciprofloxacin and tinidazole tablets were obtained from chemical and pharmaceutical stores in Makurdi Benue State. Hydrochloric acid (HCl), Sodium hydroxide (NaOH), and deionized water were used for pH adjustments. Ciprofloxacin is a broad-spectrum antibiotic of fluoroquinolone group CIP ($C_{17}H_{18}FN_3O_3$, molecular weight = 331.34 g/mol). Tinidazole, a prominent member of the nitroimidazole antibiotics, a derivative of 2-methylimidazole, IUPAC name 1-methyl-5-nitro-imidazole, chemical formula $C_8H1_3N_3O_4S$ and molecular weight = 247.27g/mol. Both have chemical structures below:

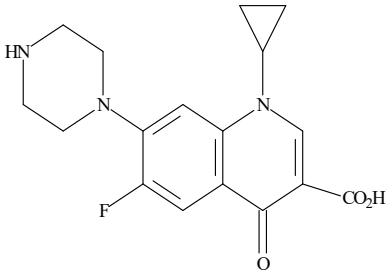

Figure 1: Chemical structure of Ciprofloxacin (1-cyclopropyl-6-floro-4-oxo-7-(piperazin-1-yl)-quinolone-3-carboxylic acid)

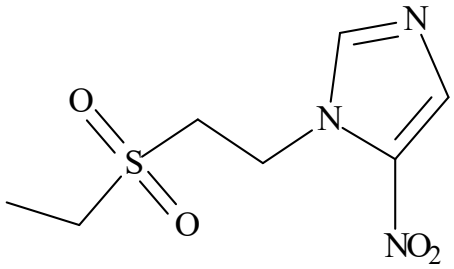

Figure 2: Chemical structure of Tinidazole (1-methyl-5-nitro-imidazole)

Instruments

UV-Visible spectrophotometer (Shimadzu UV-1800), pH meter (Hanna Instruments), SEM (JEOL JSM-5600LV), FT-IR spectrometer (Agilent Cary 630), and analytical balance (±0.0001 g precision) were used for characterization and analysis.

Preparation of adsorbent

Spent silica gel was collected from pharmaceutical waste, washed thoroughly with deionized water, and oven-dried at 105 °C for 6 hours. The dried SSG was ground using a mortar and pestle, then sieved through a 2 mm mesh to obtain uniform particle sizes. The processed SSG was stored in airtight containers for further use.

The adsorbents were further characterized physicochemically. Adsorbent pH was determined by dispersing 1.0 g triplicate samples of the adsorbent in distilled water for 1 hour and measuring the pH of the resulting filtrate [5]. Bulk density was determined using the tamping procedure as described in recent studies [24]. Attrition resistance was measured following a standardized mechanical durability test, ensuring minimal material loss during handling [16].

Adsorbent surface area was evaluated using the iodine adsorption method, where a 0.5-g portion of the adsorbent was dispersed in an excess of standard iodine solution, followed by back-titration of the unreacted iodine with standard sodium thiosulfate solution [25]. A blank titration was also performed on an aliquot of iodine solution not treated with the adsorbent. The iodine number (i.e. moles of iodine adsorbed per gram of adsorbent) was calculated using Eq. (1), while the adsorbent surface area (m^2/g) was determined using Eq. (2), a modified method based on contemporary adsorption studies [2].

$$n_{I_2}(\text{mol.g}^{-1}) = \frac{C_{S_2O_3{}^{2-}}(V_b - V_s)}{2x10^3 m_a} \quad (1)$$

$$A\ (m^2.\text{g}) = N_o \left[\frac{C_{S_2O_3{}^{2-}}(V_b - V_s)}{2x10^3 m_a}\right] \sigma_{I_2} \quad (2)$$

where $C_{S_2O_3{}^{2-}}$ is the concentration of the thiosulphate (mol/L); Vb and Vs are respectively, the titre values of the blank and adsorbent-treated iodine solutions (L); ma is mass of the adsorbent (0.5 g); No is the Avogadro's number; and σ is the cross-sectional area of an iodine molecule (m^2), given as 3.2 × 10-19 m^2. Titratable surface charge was determined using the Boehm titrimetric method, a widely accepted technique for quantifying acidic and basic functional groups on adsorbent surfaces [14]. Fourier transform infrared (FTIR) and SEM analysis were performed according to the manufacturer's specifications.

Formation of calibration curve for UV/Vis-spectrophotometric determination

Stock solutions of ciprofloxacin and tinidazole were prepared, by dissolving in distilled water a single tablet of each drug separately in 1 L volumetric flask and making up to the mark. Standard working concentrations: 40, 80, 120, 160, 200, and 240 mg/L were obtained by serial dilution of appropriate volumes of the stock. Each dilution was measured in a UV-visible spectrophotometer at the wavelength ciprofloxacin and tinidazole absorbed the highest amount of UV radiation λmax (CIP) = 271 nm and λmax (TIN) = 308 nm. The linearity range of 0 -240 mg/L was obtained and used for constructing the calibration curve. The calibration curve (Fig. 3) was constructed so that the absorbance results collected through experimentation could be directly converted into concentration by extrapolating through the linearity range.

The simultaneous equation method was used to determine ciprofloxacin and tinidazole concentrations in a mixture where each drug absorbs at the maximum wavelength of the other. Absorbances of single standard solutions (240 mg/L) were measured at their respective wavelengths to obtain molar absorptivities. These values were used in the simultaneous equation to calculate individual drug concentrations in the binary mixtures.

$$(A_{MIX})_{\lambda CIP} = \varepsilon_{CIP(\lambda CIP)} C_{CIP} + \varepsilon_{TIN(\lambda CIP)} C_{TIN} \quad (3)$$

$$(A_{MIX\lambda_{TIN}} = \varepsilon_{CIP(\lambda TIN)} C_{CIP} + \varepsilon_{TIN(\lambda_{TIN}} C_{TIN} \quad (4)$$

where:

$(A_{mix})\lambda cip$ is the absorbance of the mixture at the wavelength of maximum adsorption of ciprofloxacin, $(A_{mix})\ \lambda tin$ is the absorbance of mixture at the wavelength of maximum adsorption of tinidazole, C_{cip} is the concentration of ciprofloxacin, C_{TIN} is the concentration of tinidazole, $\varepsilon(cip)\lambda cip$ is the molar absorptivity of ciprofloxacin at wavelength maximum of tiprofloxacin, $\varepsilon(TIN)\lambda cip$ is the molar absorptivity of tinidazole at the wavelength maximum of CIP, $\varepsilon(cip)\lambda TIN$ molar absorptivity of ciprofloxacin at wavelength maximum of tinidazole, $(\varepsilon TIN)\lambda TIN$ molar absorptivity of tinidazole at wavelength maximum of tinidazole.

Batch adsorption experiments

Batch adsorption experiments were designed to investigate the effect of operational variables such as initial solution pH, concentration, adsorbent dose, contact time and temperature on aqueous phase removal of single and binary solutions of ciprofloxacin and tinidazole by spent silica gel. Meanwhile, the chemical stability of ciprofloxacin and tinidazole were tested at 298 K, wherein separate aliquots (50 mL) of ciprofloxacin and tinidazole standards (40, 80 and 120 mg/L) with or without SSG samples (0.5 g) were equilibrated for 0, 12, 24, 48 and 72 h, followed by residual ciprofloxacin and tinidazole assay by UV-Visible spectrophotometry. The range of ciprofloxacin and tinidazole recoveries was 97.80-101.40%, and so, it was possible to confirm that the standard single and binary ciprofloxacin and tinidazole solutions and adsorbent-treated samples were stable for four consecutive days at 298 K. Consequently, a maximum ciprofloxacin and tinidazole -adsorbent contact time of 4 h was chosen throughout this study to

minimize possible antibiotic losses especially at the higher temperatures (308 - 328 K) investigated.

In order to check the effect of initial solution pH on aqueous phase removal of ciprofloxacin and tinidazole in single and binary solutions, 0.5 g portions of SSG were dispersed in separate 50 mL aliquots of 240 mg/L ciprofloxacin and tinidazole in single and binary solutions, which were previously adjusted to pH 2, 5, 7, 9 and 11 by drop-wise addition of 0.1 M NaOH or 0.1 M HCl, with the aid of a pre-calibrated pH meter. After 4 h equilibration with the aid of a mechanical shaker, the slurries were filtered and the filtrate assayed for residual ciprofloxacin and tinidazole.

The effect of adsorbent dose on aqueous phase removal of ciprofloxacin and tinidazole was studied by contacting different portions (0.5, 1.0, 1.5, 2.0 and 2.5 g) of SSG with 50-mL aliquots of 240-mg/L ciprofloxacin and tinidazole solution on a mechanical shaker. The slurries were filtered after 4 h equilibration and the residual ciprofloxacin and tinidazole concentrations in the filtrate were determined.

Adsorption isotherms for aqueous phase removal of ciprofloxacin and tinidazole were developed at different temperatures by contacting 0.5 g portions of SSG with separate 240 mL portions of each of the ciprofloxacin and tinidazole solutions prepared to furnish different initial concentrations, Co (mg/L) in the range ($40 \leq Co \leq 240$) at 298, 308, 318 and 328 K on a thermostatic water bath. The slurries were filtered after 4-h equilibration and the filtrate assayed for residual ciprofloxacin and tinidazole.

Adsorption thermodynamic parameters were generated from the isothermal data recorded at different temperatures. Finally, the effect of contact time on aqueous phase removal of ciprofloxacin and tinidazole (i.e., adsorption kinetics) was investigated by contacting separate 50-mL aliquots of 240-mg/L ciprofloxacin and tinidazole solutions with 0.5 g of SSG for 0, 10, 30, 60, 120, 180, and 240 min at 298 K on a thermostatic water bath. At the elapse of each specified time interval, the slurry was filtered and the filtrate assayed for residual ciprofloxacin and tinidazole.

This procedure was repeated at 308, 318 and 328 K. In all batch adsorption experiments, residual ciprofloxacin and tinidazole concentrations in the filtrates were determined by measurement with a UV-visible spectrophotometer at 294 nm. The amount of ciprofloxacin and tinidazole adsorbed (mg/g adsorbent) was calculated by the mass balance equation

$$Q(\text{mg.g}^{-1}) = \frac{(C_o - Cres)V}{m_a} \quad (5)$$

where C_o and C_{res} are the initial and residual concentrations of Ciprofloxacin and Tinidazole for the single and binary concentrations (mgL^{-1}), respectively; V, volume of the aliquot used of the single and binary concentrations (50 mL = 0.05 L); and m_a is the mass of SSG (0.5 g) used for the batch treatment.

Quality control/assurance was achieved through good laboratory practices. All glass wares and plastics were properly washed and rinsed with distilled water and oven dried. Procedural blank samples were subjected to similar treatments using the same amounts of reagents. In all cases, measurements were made in triplicates.

RESULTS AND DISCUSSION

Physicochemical attributes SSG adsorbents

The physicochemical attributes of SSG are recorded in Table 1. SSG pH 6.9. Adsorbent pH 6-8 are acceptable for applicability for water and wastewater treatment [5]. Bulk densities of 99 kg/cm³ were recorded for SSG. This parameter gives an estimate of the packing volume of an adsorbent and is important during adsorbate uptake. An adsorbent with high bulk density gives an idea of volume activity and suggests better quality performance. SSG showed 34.10% attrition. These values are high compared with 1.50-2.5% and 7.40-10.38% reported for banana empty fruit bunch and Delonix regia fruit pod, respectively [16]. Attrition measures the adsorbent's ability to withstand frictional forces by stirring and washing and is an important parameter in understanding loss of adsorbent during handling and regeneration.

SSG had iodine number ((× 10^{-3} mol/g)) and surface area (m^2/g) of 1.03 and 198.42, respectively. These values are higher than those reported for *Hemidesmus indicus* [26], base-treated and carbonized rice husks [5], banana empty fruit bunch and Delonix regia fruit pod [16]. The iodine number gives an idea of the total surface area of an adsorbent. Adsorbents with high iodine number/surface area perform better in the removal of small-sized contaminants.

The titratable surface charge (mmol H^+ eq/g) gives a measure of the acidic and basic functional groups on the adsorbent's surface. The titratable surface acidic groups were determined by selective neutralization with a series of bases of varying strength: $NaHCO_3$, Na_2CO_3, and NaOH.

Table 1: Selected physicochemical attributes of Spent silica gel

Attribute		Value
pH water (solid:liquid = 1:100)		6.93 ± 1.0
Bulk density (g/cm^3)		0.99 ± 0.1
Attrition (%)		34.10 ±0.1
Iodine number (× 10^{-3} mol/g)		1.03 ± 0.2
Surface area (m^2/g)		198.42~200 ± 2.0
Surface charge (mmol H^+ eq/g)		
NaOH		0.95 ± 0.1
$NaHCO_3$		0.85 ± 0.1
Na_2CO_3		1.17 ± 0.1
	Wave number (cm^{-1})	Functional group
FT-IR Analysis	1062	Si-O-Si asymmetric stretch
	1613.9	H-O-H bending [27]
	797	Si-O-Si symmetric stretch [22]

The titratable surface charge (mmol H^+eq/g) gives a measure of the acidic and basic functional groups on the adsorbent's surface. The titratable surface acidic groups were determined by selective neutralization with a series of bases of varying strength: $NaHCO_3$, NaOH and Na_2CO_3

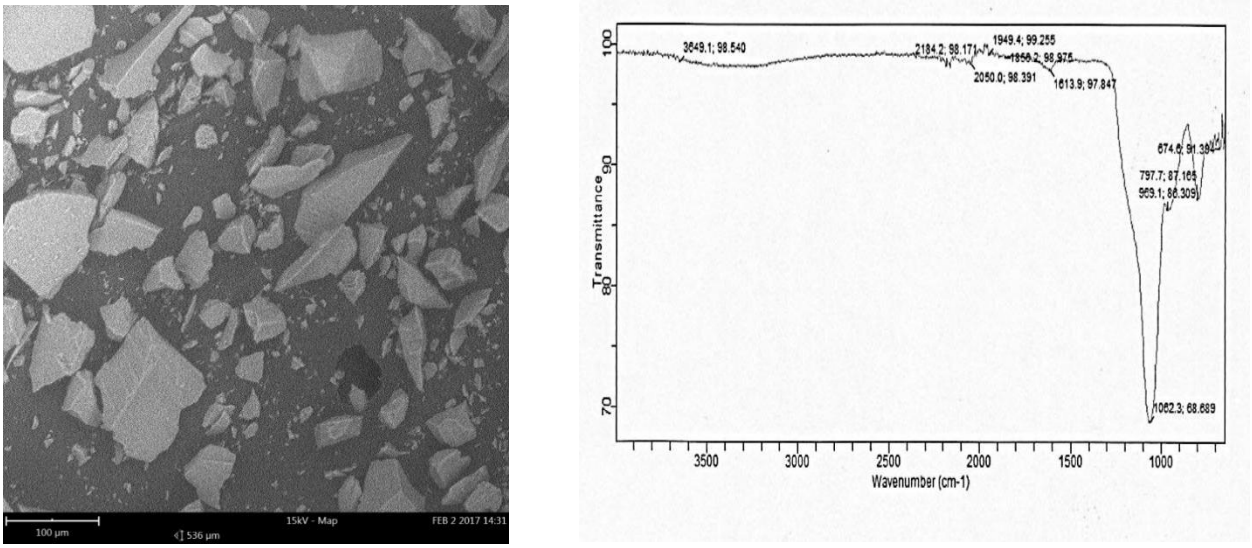

Figure 3: Surface Morphology of Spent Silica Gel Obtained from Scanning Electron Microscope (100 um resolution) and FT-IR Spectrum of Spent Silica Gel

FT-IR analysis identified the individual functional groups present; the major functional groups present in spent show silica gel can be seen in the FT-IR spectrum. The FT-IR spectrum of the SSG before adsorption is presented in Figure 3. The broad band centered at 1062 /cm was

attributed to the asymmetric stretching frequency of Si-O-Si, the band centered at 797 /cm was due to the symmetric stretching of Si-OH. The small peak at 1613.9 /cm is attributed to the H-O-H bending vibrations of the adsorbed water molecules. Overall, the FTIR frequency shifts indicate that Ciprofloxacin and Tinidazole were bound to SSG via silanol, siloxane and hydroxyl groups.

The SEM images of spent silica gel showed that the particles are irregular in shape with a size that was generally in micron order. This image was compared to that reported in literature for wheat hull and wheat hull ash as a potential source of SiO_2 [22].

Adsorption studies

Batch adsorption experiments were designed to investigate the effect of operational variables concentration, adsorbent dose, contact time and temperature on aqueous phase removal of single solutions and binary solutions of ciprofloxacin and tinidazole at specified concentration using spent silica gel.

Formation of calibration curve for UV-Visible spectrophotometric determination of ciprofloxacin and tinidazole

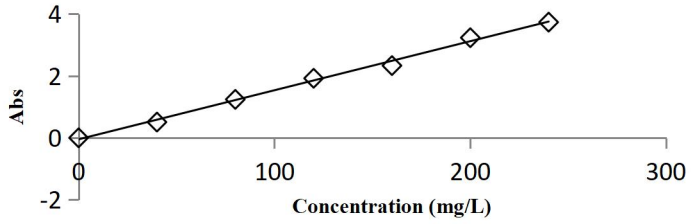

Figure 4A: Calibration curve for UV-Visible spectrophotometric determination of ciprofloxacin in single solution (λmax = 271 nm)

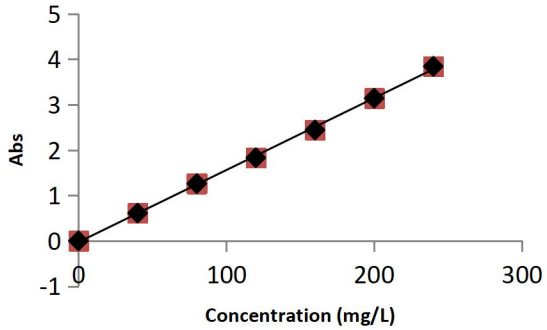

Figure 4B: Calibration curve for UV-Visible spectrophotometric determination of tinidazole in single solution (λmax = 308 nm)

Effect of initial solution pH on aqueous phase removal of ciprofloxacin and tinidazole

The effects of initial solution pH on the aqueous phase adsorptive removal of ciprofloxacin and tinidazole in single and binary solutions by spent silica gel at pH 3, CIP and TIN in single and binary solutions uptake was 7.61 and 7.77 mg/g for single solutions, respectively, and 4.84 and 5.75 mg/g, respectively, for binary solutions. As the pH increased to 5 and then 7, maximum uptake of 16.91 and 16.54 mg/g for single solutions, respectively, and 9.17 and 8.27 mg/g, respectively, for binary solutions were achieved for SSG. An observation which may be attributed to hydrogen bonding between adsorbates and adsorbent [5]. A similar result was obtained by [27], who showed that the optimum pH for adsorption of ciprofloxacin onto functionalized silicates is 5.

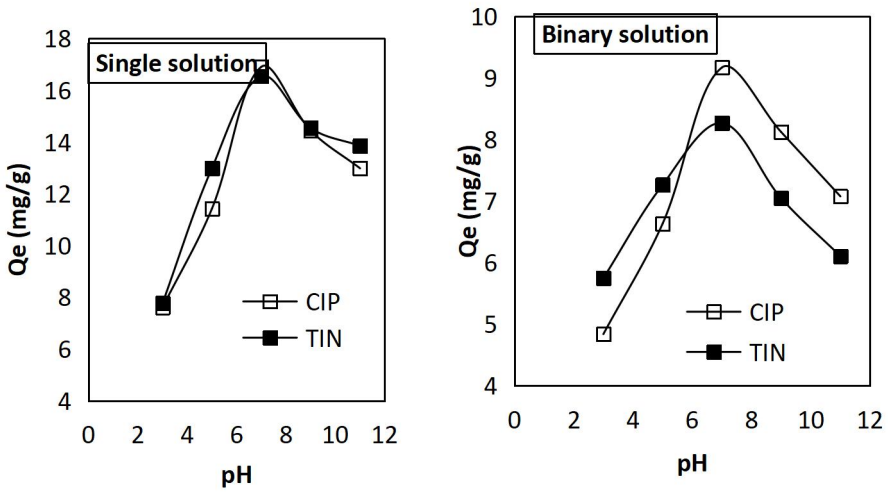

Figure 5: Effect of initial drug solution pH on adsorption of ciprofloxacin and tinidazole from single and binary solution onto Spent silica gel

Effect of adsorbent dosage on aqueous phase removal of ciprofloxacin and tinidazole

The effects of adsorbent SSG dosage on the adsorption of ciprofloxacin and tinidazole from their single and binary solutions per unit mass of adsorbent decreased with increasing adsorbent dosage (0.25–1.5 g). This trend may be explained based on the mass-balance relationship in Equation 5. At increasingly higher adsorbent dosages, fixed initial solution concentration (240 mg/L), and fixed volume (50 mL), the available ciprofloxacin and tinidazole molecules are not able to cover all the exchangeable sites on the adsorbents, resulting in low ciprofloxacin and tinidazole uptake [5].

The percentage quantity adsorbed (%q) increased linearly with increasing adsorbent dosage, this is because the quantity of available adsorption sites increases with increasing adsorbent dosage. A similar trend was observed for the adsorption of ciprofloxacin onto commercially activated carbon [28].

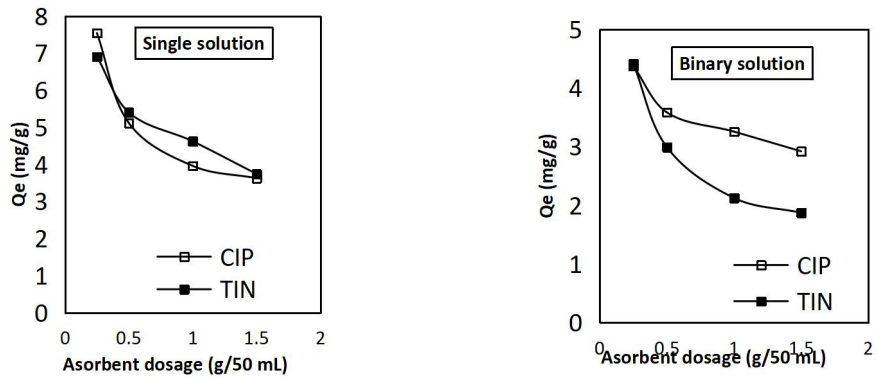

Figure 6: Effect of adsorbent dosage on adsorption of ciprofloxacin and tinidazole from single and binary solutions onto Spent silica gel

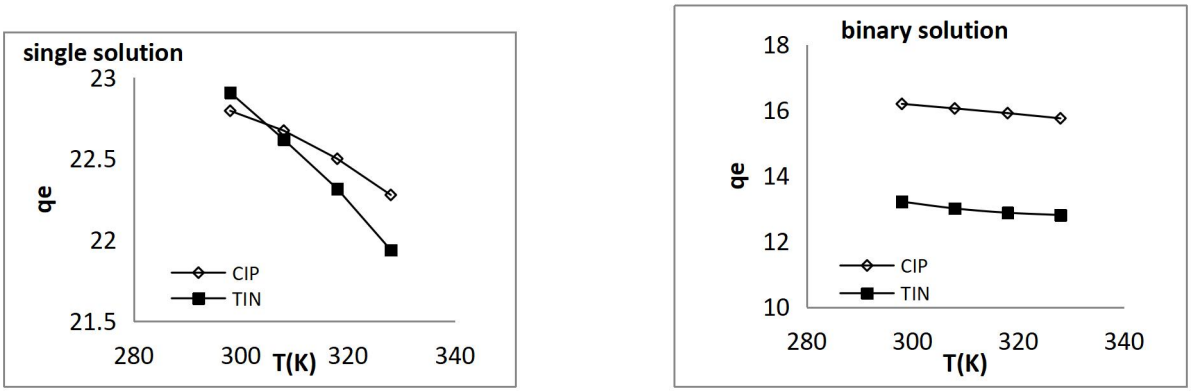

Figure 7: Isotherm profiles for aqueous phase removal of ciprofloxacin and tinidazole by spent silica gel in single solutions and binary solutions at different temperatures

Equilibrium adsorption capacities and isotherm profiles

Equilibrium data from adsorption experiments are usually presented in the form of an isotherm, which graphically displays the ratio of adsorbed to non-sorbed solute per unit mass of the adsorbent at constant temperature. The isotherm profiles provide information regarding the nature and mechanism of sorption for a particular adsorbate–adsorbent system. The isotherm profiles for the aqueous phase adsorption of ciprofloxacin and tinidazole on spent silica gel at different temperatures are illustrated in Figure 7.

At the operating initial concentrations [40 ≤ Co (mg/L) ≤ 240], it was observed that the adsorption is highly dependent on initial drug concentration. The amount of CIP and TIN in single and binary solutions adsorbed per unit weight of SSG increased with increasing initial concentration of CIP and TIN solutions. A similar trend was observed by [13] and was attributed to the increase in the driving force for adsorption with increasing initial concentrations.

Equilibrium data from adsorption experiments are presented in the form of an isotherm, which shows the ratio of adsorbed to non-sorbed solute per unit mass of the adsorbent at constant temperature. The isotherm profiles provide information regarding the nature and mechanism of sorption for a particular adsorbate–adsorbent system. The isotherm data obtained for the adsorption processes were analyzed using the Freundlich, Temkin, and Dubinin isotherms.

A comparison of the isotherms based on their linear regression coefficient (R^2) values shows that the Freundlich isotherm provided the best fit for the adsorption process, with R^2 values of 0.9611 and 0.9925 for single-dose CIP and TIN, and 0.935 and 0.9223 for binary-dose CIP and TIN. Hence, the adsorption of CIP and TIN onto silica gel can be attributed to multilayer coverage of both single and binary doses of CIP and TIN on the adsorbent surfaces [4].

Adsorption isotherm models

Equilibrium data for the aqueous phase removal of ciprofloxacin and tinidazole on spent silica gel were fitted into the linearized forms of the Freundlich and Dubinin-Radushkevich models given by Equations 6 and 7 respectively:

$$lnQe = \frac{1}{n_F} lnCe + lnK_F \quad (6)$$

$$lnqe = lnQ_D - B_D E^2 \quad (7)$$

where Q_e is the equilibrium amount of ciprofloxacin and tinidazole adsorbed per unit mass of the adsorbent (mg/g), and C_e is the equilibrium (residual) concentration (mg/L). K_F is Freundlich constant ($mg^{1-1/n}L^{1/n}/g$), related to the adsorption capacity and n_F is a dimensionless empirical parameter related to the adsorption intensity which varies with the heterogeneity of the material [9]. Q_D is the maximum sorption capacity (mol/g), and B_D is the Dubinin-Radushkevich constant (mol^2/kJ^2).

A linear plot of C_e/Q_e versus C_e gives the inverse of the slope as Q_o and K_L is derived from the intercept, while a linear plot of ln Q_e versus lnC_e gives the inverse of the slope as n_F and intercept as K_F. The Freundlich and Dubinin-Radushkevich isotherm plots are presented in Figs. 7 and 8. The parameters thereof are recorded in Table 2.

Freundlich isotherm parameters

The Freundlich adsorption isotherm posits that adsorption occurs on a heterogeneous surface with sites of varying energies, accommodating multilayer adsorption. This model is particularly applicable to surfaces where adsorption sites differ in affinity for the adsorbate.
Mathematically, the Freundlich equation is expressed as:

$$Q_e = K_f C_e^{\,1/n} \quad (8)$$

where:

1/n is a heterogeneity factor, which is a measure of intensity of sorption or affinity of the adsorbate for the adsorbent; k_f is the Freundlich constant

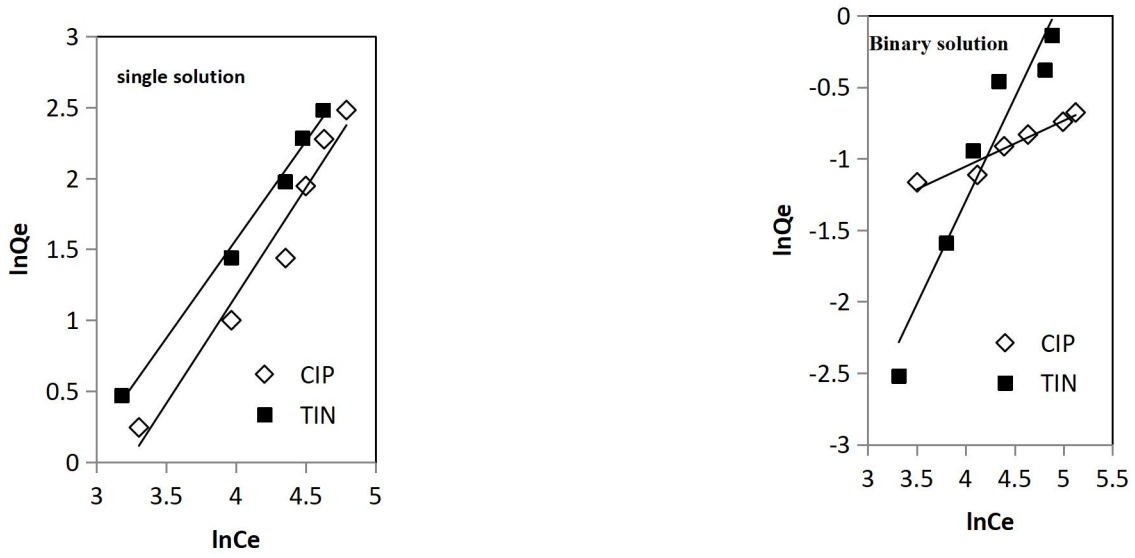

Figure 7: Linearized Freundlich isotherms for aqueous phase removal of ciprofloxacin and tinidazole by spent silica gel: (a) single solution; and (b) binary solutions

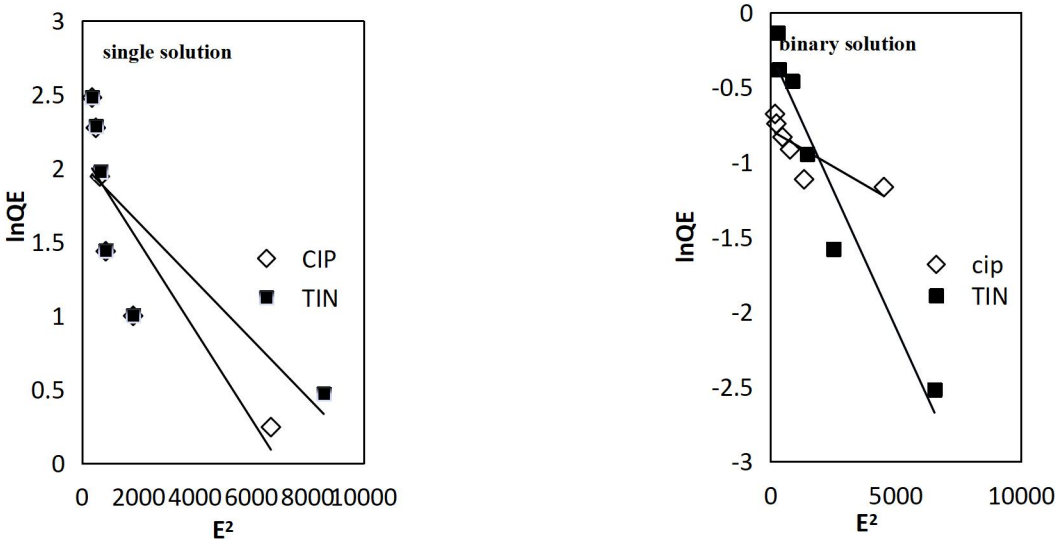

Figure 8: Linearized Dubinin-Radushkevich isotherms for aqueous phase removal of ciprofloxacin and tinidazole by spent silica gel: (a) in single solutions and (b) binary solutions

Table 2: Isotherm parameters for aqueous phase removal of ciprofloxacin and tinidazole by silica gel at 298 K

Adsorbent	Isotherm parameters	Single solution CIP	Single solution TIN	Binary solution CIP	Binary solution TIN
SSG	DUBININ				
	B_D (mol^2/kJ^2)	3×10^{-4}	2×10^{-4}	1×10^{-4}	4×10^{-4}
	Q_D (mol/g)	8.2128	7.60724	4.559×10^{-1}	7.661×10^{-1}
	R^2	0.7636	0.6585	0.6634	0.9343
	FREUNDLICH				
SSG	K_F($mg^{1-1/n}L^{1/n}/g$)	7.4496×10^{-3}	1.87×10^{-2}	9.7×10^{-2}	8.6084×10^{-4}
	n_F	0.6588	0.7886	3.12989	0.69425
	R^2	0.9611	0.9925	0.935	0.9223

Dubinin-Radushkevich adsorption isotherm

The Dubinin-Radushkevich isotherm postulates heterogeneous energetic distribution of active sites, accompanied by interaction between adsorbed molecules. Table 2 shows that at 298 K, as considered in this study, the Dubinin-Radushkevich parameters and R^2 values for CIP and TIN in single and binary matrices were within the following ranges: B_D (mol^2/kJ^2): 3×10^{-4} and 1×10^{-4} and 2×10^{-4} and 4×10^{-4}, R^2: 0.7636 7 and 0.66344 and 0.6585 and 0.9343, Q_D (mol/g): 8.2128 and 0.4559, 7.60724 and 0.7661 respectively. In magnitude, the Dubinin-Radushkevich (D-R) adsorption isotherm parameters were correspondingly higher for adsorption of ciprofloxacin (CIP) and tinidazole (TIN) in binary matrices than in single-solution matrices. This suggests that spent silica gel (SSG) is more potent for the removal of CIP and TIN in a binary matrix [9].

A similar trend was reported that the D-R isotherm model effectively describes the adsorption of fluoroquinolones onto modified silica materials, demonstrating enhanced adsorption performance in multi-component systems [4].

Thermodynamics of aqueous phase removal of ciprofloxacin and tinidazole

Thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°), entropy (ΔS°) for adsorption of ciprofloxacin and tinidazole onto spent silica gel were determined by Van't Hoff equation as seen in equation (9) at 298 K temperature.

$$lnK_D = \frac{\Delta S^\theta}{R} - \frac{\Delta H^\theta}{RT} \quad (9)$$

where:

R is the ideal gas constant = 8.314 J/molK, T is temperature in kelvin, ΔS^θ is standard entropy change of the system, ΔH^θ is standard enthalpy change of the system.

The Gibbs free energy change from definition can be determined by equation 10:

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta \quad (10)$$

The thermodynamic parameters: ΔG°; ΔH°, and ΔS° for aqueous phase adsorption of CIP and TIN in single and binary solutions are summarized in Table 3.

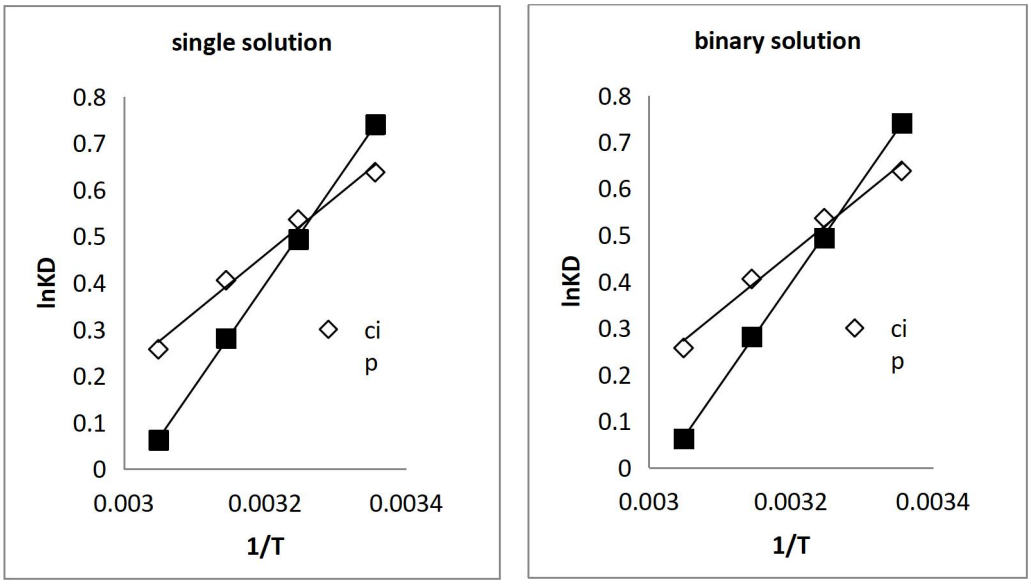

Figure 9: Linearized Van't Hoff plots for adsorption of ciprofloxacin and tinidazole from single and binary solutions onto Spent silica gel

Table 4: Thermodynamic parameters for aqueous phase removal of ciprofloxacin and tinidazole in single and binary solutions by spent silica gel at 298 K

Thermodynamic parameters	Single solution CIP	Single solution TIN	Binary solution CIP	Binary solution TIN
ΔG^0 (J/mol)	-1619.331	-1830.452	-999.547	-972.608
ΔH^0 (J/mol)	-10305.203	-18263,364	-9961.003	-11331.982
ΔS^0 (J/molK)	-29.147	-55.144	-30.072	-34.763

The negative values of Gibbs free energy (ΔG°) (kJ/mol) for the adsorption of ciprofloxacin (CIP) and tinidazole (TIN) on spent silica gel (SSG), with ΔG° values of -16.19 and -18.30 for single solutions of CIP and TIN, and -0.999 and -0.972 for binary solutions, respectively, indicate the feasibility of the adsorption process. From the literature, ΔG° values in the range [-20.00 ≤ ΔG° (kJ/mol) ≤ 0.00] represent physisorption, while those in the range [-400.00 ≤ ΔG° (kJ/mol) ≤ -80.00] indicate chemisorption [29]. The ΔG° values obtained in this study suggest that the removal of CIP and TIN occurred predominantly via a physisorptive mechanism.

Adsorption kinetics

Beyond adsorption capacity, which is determined through equilibrium analysis, adsorption time—defined as the duration required to eliminate half of the initial adsorbate concentration—is a crucial factor in evaluating an adsorbent's efficiency and optimizing operating conditions for wastewater treatment system design [30]. The rate curves depicting the aqueous-phase removal of ciprofloxacin and tinidazole in single and binary solutions by spent silica gel (SSG) are presented in Figure 10.

The experimental data for the aqueous phase removal of ciprofloxacin and tinidazole by spent silica gel as a function of contact time were fitted into the Lagergren pseudo-first-order (LFOR); Blanchard pseudo-second-order (BSOR) and the Weber-Morris intraparticle diffusion (WMID) kinetic models.

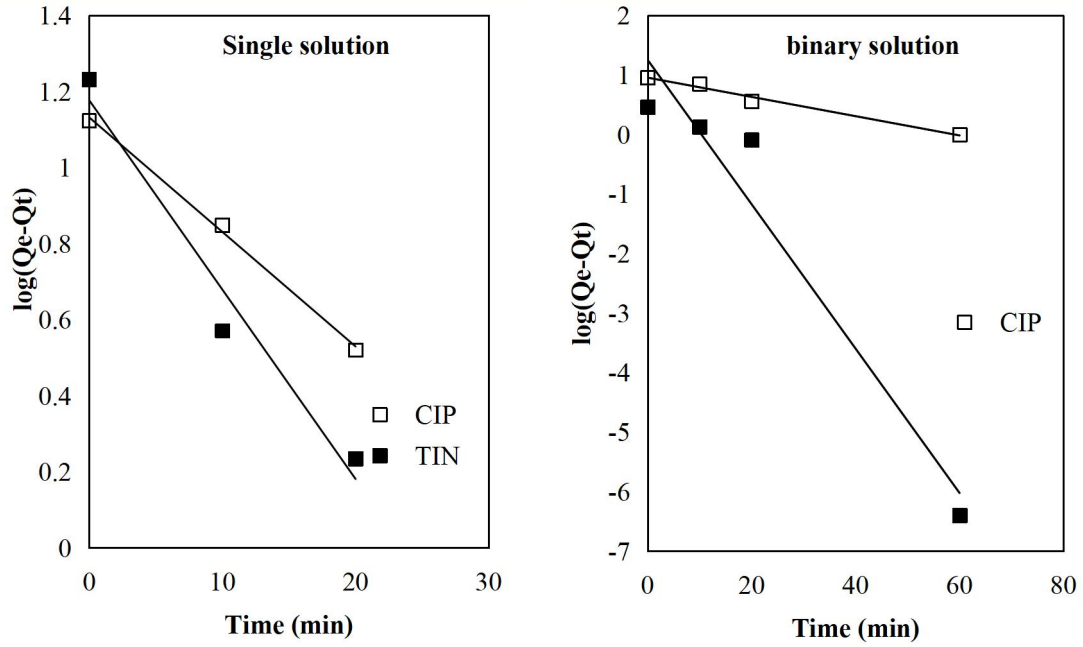

Figure 10: Linearized Pseudo-first-order model for adsorption of ciprofloxacin and tinidazole from single and binary solutions onto Spent silica gel

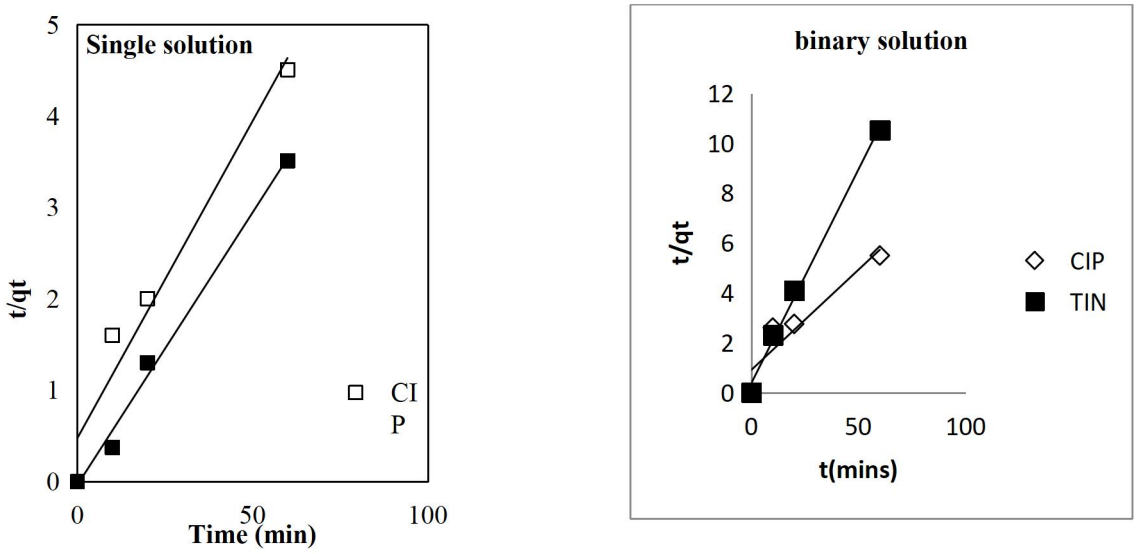

Figure 11: Pseudo-second order-model for adsorption of ciprofloxacin and tinidazole from single and binary solutions onto Spent silica gel

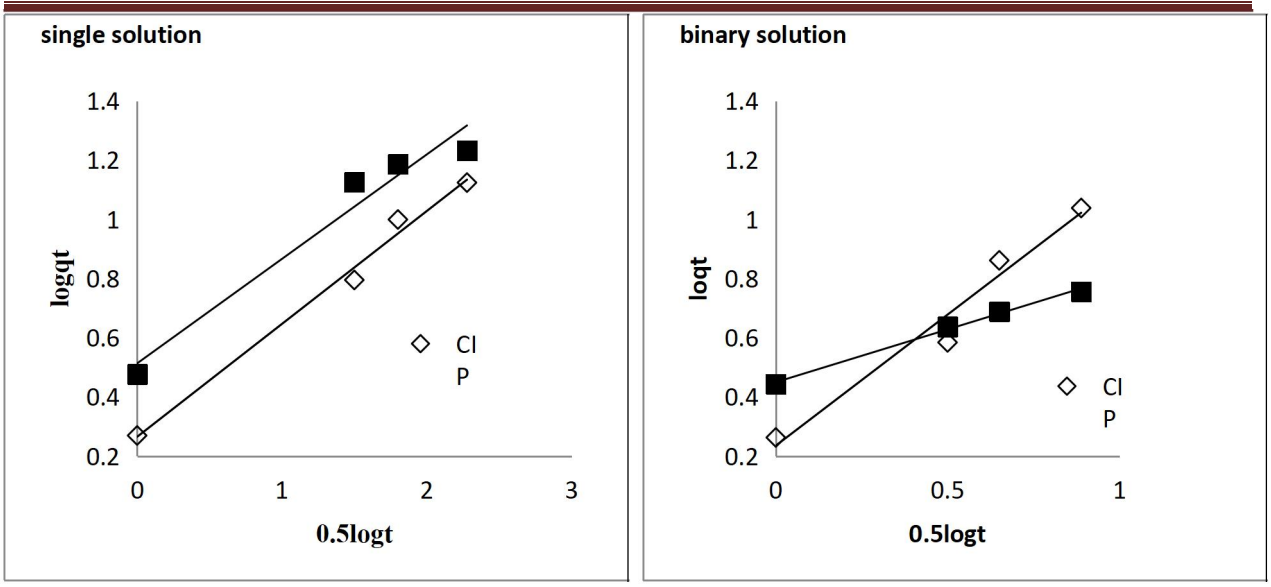

Figure 12: Linearized Weber-Morris Intra-Particle diffusion model for adsorption of ciprofloxacin and tinidazole from single and binary solutions onto Spent silica gel

Table 5: Kinetic parameters for aqueous phase removal of ciprofloxacin and tinidazole in single and binary solutions by SSG at 298 K

Kinetic model	Kinetic parameters	Single solution CIP	Single solution TIN	Binary solution CIP	Binary solution TIN
Lagergren	K_1(/min)	0.06955	0.1149	0.03731	0.2796
	R^2	0.9974	0.9659	0.9851	0.9403
Blanchard	K_2(g/mg.min)	1.03×10^{-2}	3.31×10^{-2}	7.12×10^{-3}	7.84×10^{-2}
	R^2	0.957	0.997	0.886	0.9953
Weber Morris	K_{id}(mg/g.$min^{1/2}$)	1.844	3.263	1.722	2.819
	R^2	0.990	0.956	0.964	0.995

A comparison of the various kinetic plots based on their linear regression coefficient (R^2) values showed that pseudo-first order model best described the adsorption of ciprofloxacin and tinidazole in single and binary solutions. Therefore, the adsorption of ciprofloxacin and tinidazole can best be described using the pseudo-first order model, the pseudo-first order rate constants (K_2) decreased while the equilibrium capacity values (qe) increased with increase in concentration of the adsorbates.

CONCLUSIONS

This study demonstrated the effectiveness of spent silica gel (SSG), a non-hazardous pharmaceutical waste material, as a low-cost adsorbent for the removal of ciprofloxacin (CIP) and tinidazole (TIN) from contaminated water. SSG exhibited favorable physicochemical properties, including a surface area of 198.42 m^2/g, bulk density of 0.99 g/cm^3, pH, attrition resistance, titratable surface charge, and an iodine adsorption number of 1.03×10^{-3} mol/g, as confirmed by FT-IR and other characterization techniques.

Chemical stability tests showed that CIP and TIN solutions remained stable without SSG for up to four days at 298 K. Batch adsorption experiments conducted under varying pH (3–11), adsorbent dosage (0.25–1.5 g), initial concentration (40–240 mg/L), contact time (0–60 minutes), and temperature (298–328 K) indicated optimal removal at pH 5–7 and a dose of 0.25 g. Maximum adsorption capacities of 16.91 mg/g for CIP and 16.54 mg/g for TIN were achieved in single-solute systems. Equilibrium data fitted the Freundlich isotherm model well (R^2 = 0.9611 for CIP, 0.9925 for TIN), suggesting multilayer adsorption on a heterogeneous surface. Kinetic studies showed that uptake was rapid within the first 10 minutes and reached equilibrium by 60 minutes, following the pseudo-first-order model. Thermodynamic analysis revealed that the adsorption process was feasible, spontaneous, exothermic, and dominated by physisorption, with $\Delta G°$ values ranging from -16.19 to -18.30 kJ/mol. Additionally, adsorption efficiency decreased with increasing temperature, indicating reduced performance at elevated temperatures.

Overall, this research highlighted the potential of reusing spent silica gel as a sustainable adsorbent for water purification and contributes to both environmental remediation and circular waste management strategies.

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