Chemical Papers (2022) 76:3413–3423
https://doi.org/10.1007/s11696-022-02085-4

ORIGINAL PAPER

Mathematical modeling studies for the adsorptive removal of ciprofloxacin drug from water samples using functionalized silica resin

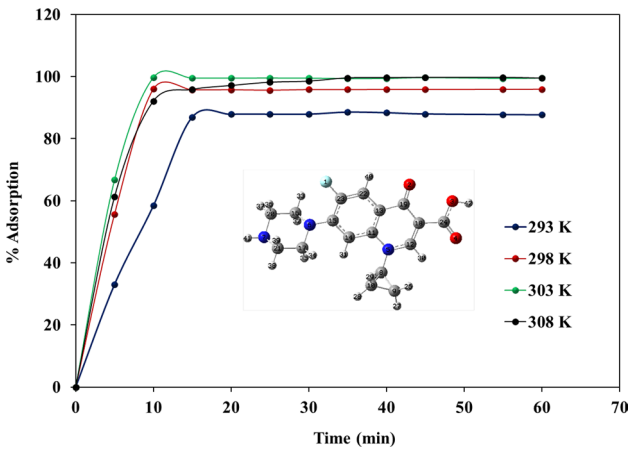
Ranjhan Junejo[1] · Nida Shams Jalbani[1] · Savas Kaya[2] · Goncagül Serdaroglu[3] · Mustafa Elik[4]

Received: 9 June 2021 / Accepted: 16 January 2022 / Published online: 7 February 2022

Abstract

The current research demonstrates the adsorptive removal of ciprofloxacin antibiotic drug from pharmaceutical wastewater samples using functionalized silica (FS) resin through batch adsorption experiments. The adsorption experiments were performed under the optimized parameters such as pH effect, FS-resin amount, ciprofloxacin concentration, equilibrium time and temperature. Results demonstrate that the maximum adsorption of ciprofloxacin was achieved at pH (6.5), while the effective resin dose was 20 mg L^{-1}. The Langmuir and Freundlich models were applied on equilibrium data, and it has been observed that the adsorption was best fit to the Freundlich model with a good correlation coefficient ($R^2 = 0.999$). Moreover, the thermodynamic and kinetic parameters show that the adsorption of ciprofloxacin is endothermic and spontaneous in nature followed by pseudo-second-order kinetic model. To explore the efficiency of resin, the real wastewater samples were collected and it has been observed that resin has better potential to treat pharmaceutical effluents. Furthermore, the FS-resin and ciprofloxacin interaction were analyzed at a molecular level through quantum chemical calculation.

Graphical abstract



Keywords Adsorption · Antibiotic ciprofloxacin · Equilibrium modeling · Silica-based adsorbent · DFT calculations · Thermodynamic and kinetic studies

Introduction

The antibiotics in pharmaceutical effluents, discharged into fresh water, cause adverse effects on human as well as aquatic life (Rik et al. 2019). However, the sewage water

✉ Ranjhan Junejo
ranjhanjunejo@yahoo.com

Extended author information available on the last page of the article

treatment plants are not more efficient in removing these micro-contaminants that are the major environmental pollutant. The high solubility of pharmaceuticals in wastewater causes various diseases, and their misuse creates serious health problems (Limbu et al. 2018; Zhou et al. 2021). Among all the antibiotics, ciprofloxacin is the most regularly used drugs for infectious disease therapy (Wu et al. 2013). The ciprofloxacin is a fluoroquinolone-based synthetic antibiotic drug that is used in all over the world to treat different types of bacterial and viral infections by blocking the DNA replications. Ciprofloxacin drug molecule binds itself through their reactive sites with DNA gyrase enzyme as to prevent their ability to untwist the DNA double helix used for DNA replication purpose (Khokhar et al. 2019). Moreover, this drug is useful for the cure of gastrointestinal anthrax and Crohn's disease (El-Shafey et al. 2012). Besides the application and high usage of this drug, it becomes necessary to treat pharmaceutical effluents containing ciprofloxacin contaminant.

In the literature, different methods were used for the removal of ciprofloxacin from water such as membrane techniques (nanofiltration), oxidation, photocatalytic degradation and adsorption. Among these all methods, adsorption is very simple, cheaper and effective method to remove the ciprofloxacin. In adsorption technique, the different adsorbent materials were applied including activated carbon fly ash, chitosan, carbon nanotubes nano-fibers, peanut shells, wood peat, etc. (Balarak et al. 2020; Xu et al. 2021).

Scientific research is under process to develop some innovation to have stability and highly efficient materials with enhanced removal capacity for the treatment of pharmaceutical effluents. In this regard, the calixarenes, third-generation compounds of supramolecular chemistry, prepared from condensation of phenol formaldehyde, which are widely used in host–guest chemistry as building blocks for various receptors for anionic, cationic and neutral species (Gutsche 2008). Calixarenes can be functionalized on upper and lower rims by different organic moieties (Deligz et al. 2008). The chemical attachment or immobilization of functionalized calixarenes on a polymeric matrices produces a very stable and insoluble adsorbents which are chemically, physically and thermally stable and possess good ability as well as selectivity for different toxicants form wastewater (Kamboh et al. 2011). However, the silica polymeric material is the most stable and cheaper material which have silanol groups that can be modified with organic moieties to design new excellent are chelating resins. In the literature, different calix[n]arene immobilized silica resin adsorbents were used for the removal of drugs, dyes and toxic metals from water (Memon et al. 2018; Bhatti et al. 2017, 2020).

In the current research, the *p*-piperdinomethylcalix[4]arene attached silica resin or simply functionalized silica (FS-resin) is applied with novel application of ciprofloxacin removal from water along with effective parameters of concentration, time, temperature, dosage pH and quantum chemical studies.

Experimental work

Materials and methods

The ciprofloxacin drug (Fig. 1) was obtained from Merck Company and prepared 1.0 M standard solution in water for further studies. The concentration of ciprofloxacin has been examined through UV–Vis spectrophotometer (Agilent Cary-100) at the wavelength of 277.6 nm. NaOH and HCl solutions have been used to adjust the pH of solutions using Inolab pH meter 720 (Germany). The batch adsorption was carried out using a Gallenkamp thermostat. The adsorbent used for the adsorption of ciprofloxacin was synthesized (Fig. 2) and characterized by our published work (Junejo et al. 2019, 2020). The details of each chemical used in the experiment are given in Table 1.

Synthesis

The compounds 1–3 have been synthesized by already reported method, while the compound 4 was prepared and characterized by our already published paper (Junejo et al. 2019, 2020).

Adsorption experiments

The batch adsorption study was performed for the adsorption of ciprofloxacin drug from water. First of all, a certain dose of FS-resin was added into 25 mL of ciprofloxacin solutions (3.1×10^{-4} M) and equilibrated on shaken for 50 min. The FS-resin was filtered off from ciprofloxacin solution, and remaining concentration was determined by UV–Vis spectrophotometer at λmax 277 nm. During adsorption experiments, different parameters were optimized such as contact time (5, 10, 15, 20, 25, 30,

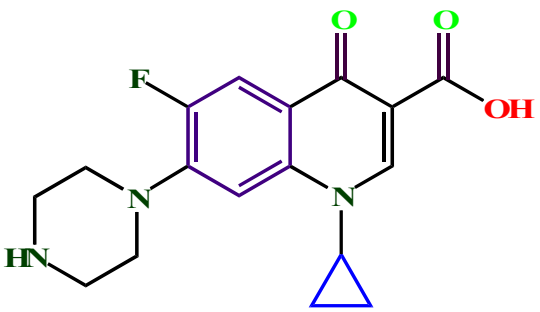


Fig. 1 Molecular structure of ciprofloxacin drug

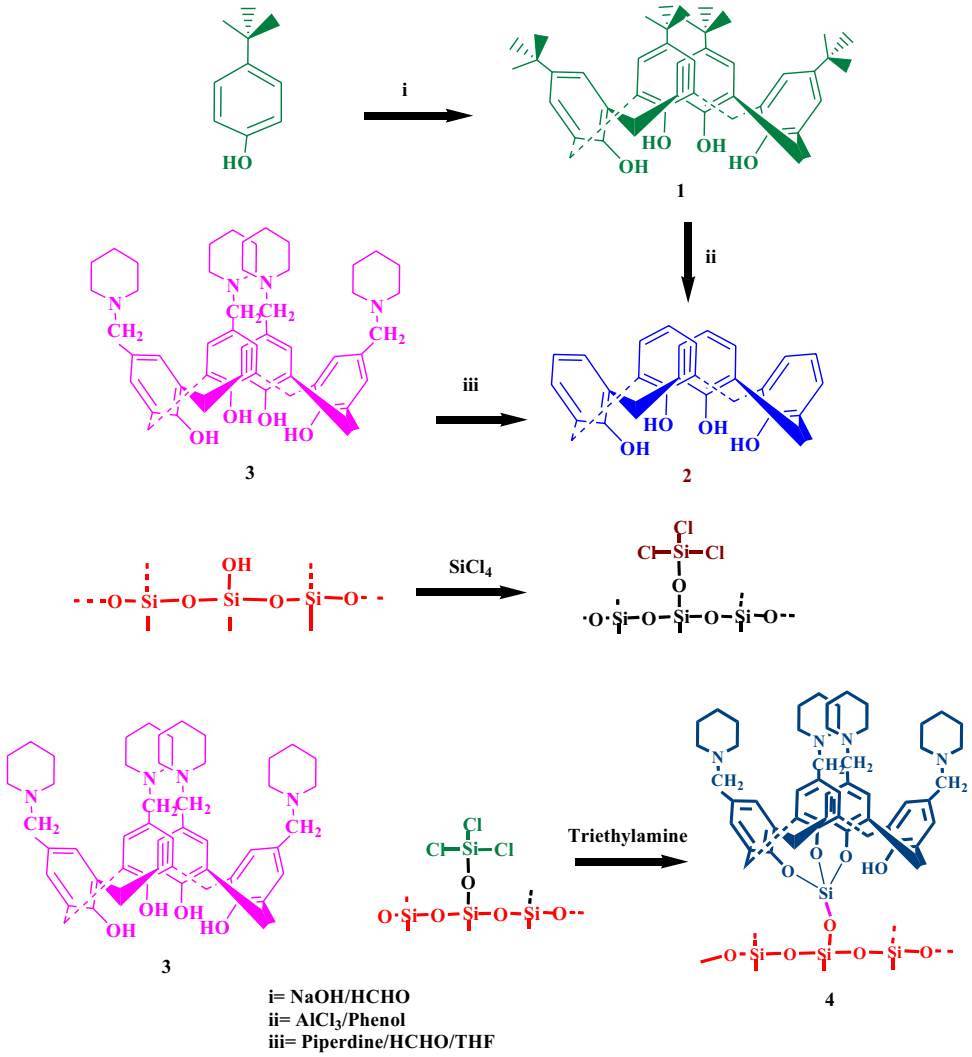


Fig. 2 Schematic route for the synthesis of functionalized silica resin

Table 1 List of chemicals

Name of chemical/reagent	Supplier	%Purity
p-piperdinomethylcalix[4]arene based silica resin (Adsorbent)	Prepared in our labs at (National Centre of Excellence in Analytical Chemistry University of Sindh Jamshoro, Pakistan	
Ciprofloxacin Drug (Adsorbate)	Sigma: CAS No: 85721-33-1	98.0%,
HCl	Scharlau CAS No: 7647-01-0	37%
Sodium hydroxide	Sigma: CAS No: 0001310732	99%

35, 40, 45, 50, 55, 60 min.), ciprofloxacin concentration (3.10×10^{-4} to 1.89×10^{-8} M), FS-resin dose 5–50 mg. L^{-1}, pH of the solution (1.5–9.5), temperature (293, 298, 303 and 308 K). The temperature effect has been optimized from 293–308 K. The % adsorption of ciprofloxacin was calculated by the following Eq. (1), while the standard deviation and relative standard deviations are calculated using Eqs. 2 and 3.

$$\%\ Adsorption = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f (mol.L^{-1}) show initial and final concentrations of ciprofloxacin drug.

$$s = \sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2/(n-1)} \quad (2)$$

$$\%\mathrm{RSD} = \frac{100}{\bar{x}} \left(\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N-1} \right)^{1/2} \quad (3)$$

Results and discussion

Effect of pH

In the adsorption process, pH of the solution has a significant role because of its influence on functional moieties of resin and adsorbate. Thus, the adsorption of ciprofloxacin on FS-resin was performed at various pH ranges from 1.5–9.5 as shown in Fig. 3. It is observed in Fig. 3 that the adsorption percentage of ciprofloxacin on FS-resin increases with increasing pH from 1.5 to 6.5. At this pH (6.5), the maximum force of attraction is observed in between FS-resin surface and ciprofloxacin while above pH 6.5 the adsorption percentage decrease due to increase the repulsive forces. Therefore, all the experiments were performed at this optimized pH. The surface of FS-resin is electron rich due to electron donating nature of amine moieties at low pH protonation takes place at amine group which creates an electronic hindering between drug and resin. As pH increases slightly acidic to neutral the force attraction between drug and resin dominates and maximum adsorption achieved. At higher pH, the electronic repulsion takes place between resin and drug molecule thus adsorption percentages decreases.

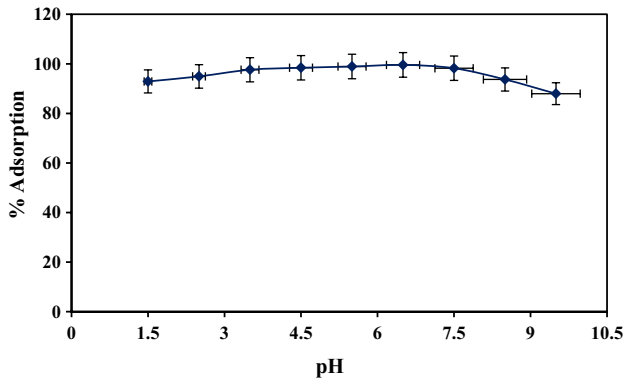


Fig. 3 Effect of pH on the adsorption of ciprofloxacin

Resin dose

The FS-resin dosages were optimized (5–50 mg.L^{-1} solution of ciprofloxacin) keeping the other parameters constant. Figure 4 shows that the percentage adsorption is increasing with increasing the resin amount up to 20 mg.L^{-1}; further higher doses have no effect on % adsorption of ciprofloxacin due to saturation of all binding sites with ciprofloxacin molecules; therefore, adsorption percentages remain constant at further higher doses.

Optimization of equilibrium time and temperature

The effect of equilibrium time and temperature on adsorption of ciprofloxacin has been optimized (Fig. 5). Initially, the adsorption of drug was increased and then becomes constant after 10 min, at that time the maximum concentration of ciprofloxacin being adsorbed onto the FS-resin. Moreover, the temperature plays an important role for the adsorption of ciprofloxacin; thus, the study was conducted using four temperatures (293, 298, 303, 308 K). Result describes that

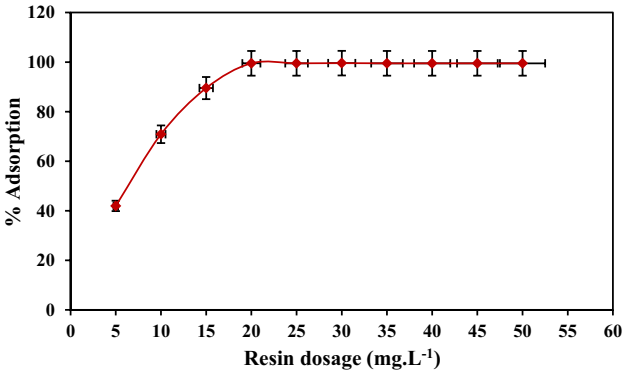


Fig. 4 Effect of FS-resin dose on adsorption of ciprofloxacin drug from water

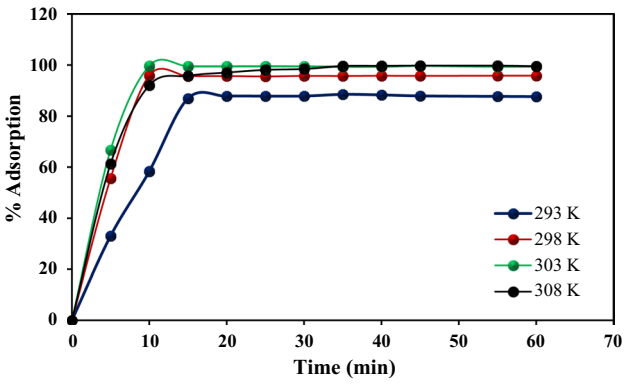


Fig. 5 Effect of contact time and temperature for the adsorption of ciprofloxacin by FS-resin

the adsorption rate increases with increase in the temperature from 293 to 303 and then became constant. The maximum adsorption at higher temperature is due to the nature of functional moieties present on FS-resin surface and ciprofloxacin. Thus, all the experiments were performed at 10 min of equilibrium time at 303 K as an optimized temperature.

Adsorption isotherms

Adsorption isotherms were measured for adsorption of ciprofloxacin to explain the equilibrium phenomenon between ciprofloxacin drug molecules and FS-resin. The experimental data were subjected toward the Langmuir and Freundlich models.

The Langmuir isotherm model describes monolayer surface formation onto FS-resin. The linear form of Langmuir model is given below in Eq. (4):

$$\frac{Ce}{qe} = \frac{Ce}{q} + \frac{1}{qKL} \tag{4}$$

where Ce (mol L^{-1}) is the equilibrium concentration of ciprofloxacin, q shows the maximum capacity (mol g^{-1}), K_L is the affinity of the binding sites and energy of adsorption (L mol^{-1}) also known as Langmuir constant. The Langmuir model can be expressed by essential characteristics and dimensionless constant known as separation factor denoted by (R_L), calculated by Eq. 5.

$$R_L = \frac{1}{\left(1 + bC_i\right)} \tag{5}$$

The Freundlich adsorption model describes the multilayer formation on FS-resin by using the Eq. 6.

$$\ln qe = \ln KF + \left(\frac{1}{n}\right) \ln q_e \tag{6}$$

where K_F shows the Freundlich constant related to adsorption capacity (L mol^{-1}), $1/n$ is the adsorption intensity.

The adsorption equilibrium data were analyzed using linear equations of the Langmuir (Fig. 6) and Freundlich (Fig. 7) models. The values of the Langmuir and Freundlich constants for the adsorption of ciprofloxacin onto FS-resin are listed in Table 2. It has observed that the equilibrium adsorption data were best fit by the Freundlich model with the higher values of the R^2 (0.999) and the good values of K_F (80.24, 143.74 and 107.76 L mol^{-1}), which shows that the FS-resin have the higher adsorption capacity and affinity for ciprofloxacin antibiotic drug, while the n values are less than 1, indicates the adsorption is favorable. However, the maximum adsorption capacity calculated from the Langmuir model is 8271.299 mmol g^{-1}. The adsorption capacity of other reported adsorbents-material was compared with

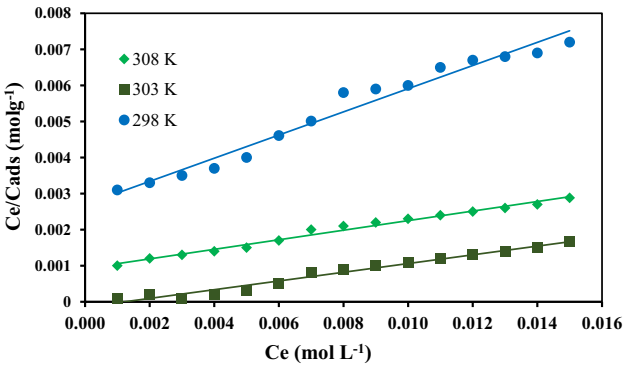


Fig. 6 Langmuir adsorption isotherm of the ciprofloxacin onto FS-resin

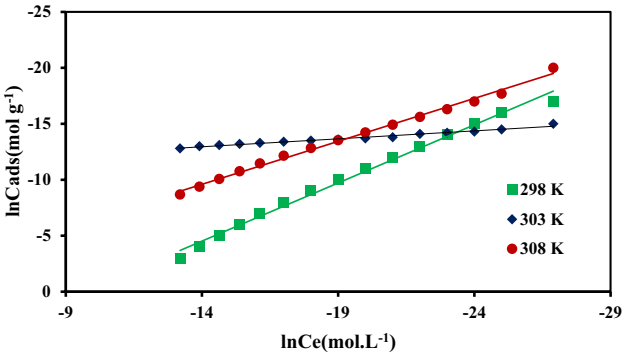


Fig. 7 Freundlich adsorption isotherm of the ciprofloxacin onto FS-resin

FS-resin shown in Table 3, and FS-resin has comparable capacity with others.

Kinetic study

The kinetic study for the adsorption of ciprofloxacin antibiotic drug onto FS-resin was performed at constant concentration and temperatures (298, 303 and 308 K). During kinetic experiments, adsorption rate of ciprofloxacin onto FS-resin has been determined using pseudo-first-order kinetic and pseudo-second-order kinetic models. The linear form of both models is given in Eqs. (7) and (8), respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

$$\frac{t}{q_t} = \left(\frac{t}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) \tag{8}$$

In Eq. (7), q_t (mol g^{-1}) is the ciprofloxacin quantity adsorbed at time t, while in Eq. (8), q_e (mol g^{-1}) is adsorbed quantity at equilibrium and k_1 (min^{-1}) and k_2 ($g.mol^{-1}.min^{-1}$) are the rate constants for pseudo-first- and

Table 2 Langmuir and Freundlich isotherm parameters for adsorption of ciprofloxacin

Temperature	Q (mmol/g)	K_L(L mol^{-1})	R_L	R^2
298	3112.356	11.90	0.77–0.991	0.986
303	8271.299	12.09	0.99–0.998	0.970
308	7535.795	14.74	0.97–0.999	0.972
Freundlich model				
Temperature	K_F (L mol^{-1})		in	R^2
298	80.24		0.962	0.9926
303	143.74		0.764	0.9919
308	107.76		0.768	0.9949

Table 3 Comparison of adsorption capacity of ciprofloxacin onto various adsorbents

Adsorbent	Adsorbate	Adsorption capacity/ % Adsorption	References
Oat Hulls	Ciprofloxacin	83 mg.g^{-1}	Movasaghi et al. (2019)
Wheat bran	Ciprofloxacin	145 mg.g^{-1}	Khokhar et al. (2019)
Carbon nanofibers	Ciprofloxacin	10 mg.g^{-1}	Li et al. (2016)
Walnut shell activated carbon	Cephalexin	233.1 mg.g^{-1}	Nazari et al. (2016)
FS-resin	Ciprofloxacin	(8272 mmol) 99.98%	This study

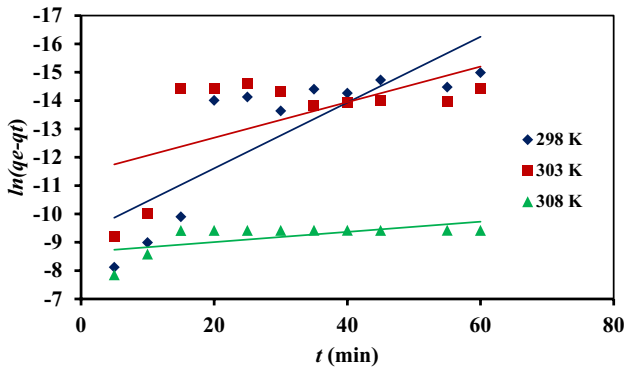


Fig. 8 Pseudo-first-order kinetic graph for the adsorption ciprofloxacin

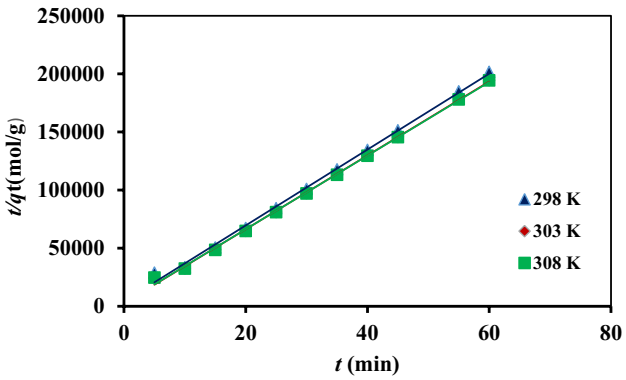


Fig. 9 Pseudo-second-order kinetic graph for the adsorption ciprofloxacin

second-order reactions, respectively. The constant values of q_e, K_1, and k_2 have been calculated from the slope and intercept of plots of (q_e-q_t) versus t and t/q_t versus t, respectively, as shown in Figs. 8 and 9, while the constant values are given in Table 4. The constant values show that the R^2 values of pseudo-first-order kinetic model is less as compared to pseudo-second-order kinetic model; thus, the adsorption of ciprofloxacin is well defined by pseudo-second-order model.

Thermodynamic study

Thermodynamic constant parameters ($\Delta H°$, $\Delta S°$, and $\Delta G°$) have been calculated to demonstrate the feasibility of adsorption process. Thermodynamic parameters are calculated by using Eqs. (9) and (10):

$$\ln k_c = \frac{-\Delta H}{\mathrm{RT}} + \frac{\Delta S}{R} \tag{9}$$

$$\Delta G = -RT \ln k_c \tag{10}$$

where k_c, R and T show the equilibrium constant, ideal gas constant and temperature, respectively. The thermodynamic study was performed at different temperatures (298, 303 308 ± 1 K), and it has noticed that adsorption percentage increases with rise of temperature. By plotting the graph

Table 4 Comparisons of pseudo-first-order and pseudo-second-order kinetic models

Temperature	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	K_1 min^{-1}	q_e $molg^{-1}$	R^2	K_2 g mol^{-1} min^{-1}	q_e mol g^{-1}	R^2
298	0.1069	29.74	0.325	5.304	88.104	0.9923
303	0.0958	43.882	0.492	5.308	97.784	0.9988
308	0.0180	176.14	0.592	4.936	98.312	0.9987

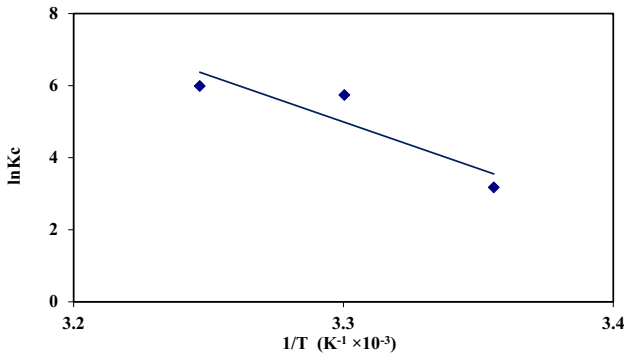


Fig. 10 The plot of lnkc versus 1/*T* for the adsorption of ciprofloxacin

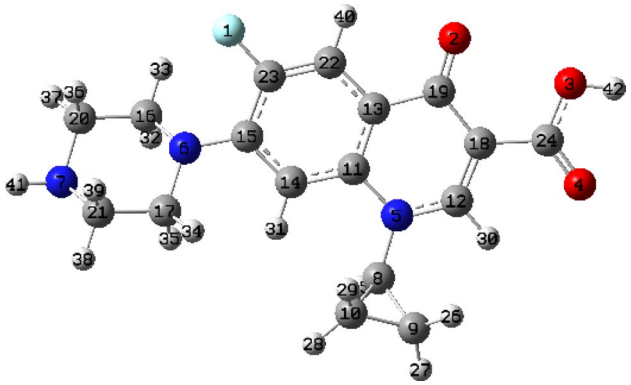


Fig. 11 The optimized structures of the ciprofloxacin agent at B3LYP/6-311G** level

Table 5 Thermodynamic parameters for adsorption of ciprofloxacin

Δ*H*(kJ/mol)	Δ*S* (kJ/mol/K)	Δ*G* (kJ/mol)		
		298 K	303 K	308 K
0.2154	0.752	− 7.87	− 14.45	− 15.33
		lnkc = 3.2	lnkc = 5.7	lnkc = 6.0

between *ln Kc* versus *1/T* (Fig. 10), thermodynamic parameters were calculated from the slope and intercept and given in Table 5. The negative values Δ*G*° in Table 5 demonstrate the spontaneity, and the value of Δ*H*° indicates that the adsorption process is endothermic in nature, while the value of Δ*S*° suggests randomness increases during the adsorption.

Quantum chemical studies

The optimized structure and thermochemical quantities of the ciprofloxacin agents are presented in Fig. 11 and Table 6, respectively.

From Table 6, the dipole moment and polarizability values of the ciprofloxacin agent were calculated in the vacuum as 7.978 D and 229.327 au, respectively. As expected, the solvent environment has great effect on the polarizability and related parameters. Namely, DM (D) and α (au) values of ciprofloxacin were calculated very close to each other in polar aprotic (DMSO) and diprotic (water) environments and quite different from that of the gas phase. The DM (D) and α (au) values of ciprofloxacin agent were calculated as 11.377 D and 309.721 au in the DMSO, and as 11.422 D and 310.725 au in the water, respectively. Also, the dielectric media provided the ciprofloxacin more stable in comparison with the vacuum. The electronic solvation energies ($\Delta E_{sol.}$) for DMSO and water phase were calculated as 59.097 kJ/mol and 59.741 kJ/ mol, whereas the solvation free energy for the same solvents of ciprofloxacin agent was predicted as 58.454 and 59.092 kJ/ mol. Thus, the absolute entropy (*S*) of the agent was calculated as 152.132 (vacuum), 149.529 (DMSO) and 149.523 cal/mol K (water) as expected.

The important interactions determined in the DMSO and water and their energies were quite similar to each other but were calculated differently from the gas phase in terms of energy. Namely, the $E^{(2)}$ for Π N5-C11 → Π* C12–C18 interaction was determined as 29.85 kcal/mol

Table 6 The calculated physiochemical quantities of the ciprofloxacin agent at B3LYP/6-311G** level

	Gas	DMSO	Water
DM (debye)	7.978	11.377	11.422
α (au)	229.327	309.721	310.725
Δ*E* (au)	− 1148.351719	− 1148.374228	− 1148.374473
Δ*H* (au)	− 1148.330361	− 1148.352912	− 1148.353157
Δ*G* (au)	− 1148.401694	− 1148.423958	− 1148.424201
$\Delta E_{thermal}$ (kcal/mol)	223.913	223.663	223.661
Cv (cal/molK)	80.209	80.290	80.291
S (cal/molK)	150.132	149.529	149.523

Table 7 NBO Results for of the ciprofloxacin at B3LYP/6-311G** level

Donor (*i*)	ED$_i$/*e*	Acceptor (*j*)	ED$_j$/*e*	$E^{(2)}$/kcal/mol	*E*(*j*)–*E*(*i*)/ a.u	*F*(*i*,*j*)/ a.u
Gas						
Π N5-C11	1.77567	Π* C12-C18	0.26713	29.85	0.37	0.094
Π C12-C18	1.77080	Π* O2-C19	0.27381	23.71	0.32	0.078
		Π* O4-C24	0.28630	23.15	0.30	0.075
Π C14-C15	1.69812	Π* N5-C11	0.82252	34.22	0.22	0.090
		Π* C22-C23	0.30304	15.63	0.30	0.061
Π C22-C23	1.71394	Π* C14-C15	0.39407	20.50	0.29	0.071
LP (3) F1	1.92796	Π* C22-C23	0.30304	17.13	0.44	0.083
LP (2) O2	1.87961	σ C13-C19	0.07128	19.75	0.68	0.105
		σ C18-C19	0.06726	20.31	0.70	0.108
LP (2) O3	1.80823	Π* O4-C24	0.28630	47.77	0.33	0.116
LP (2) O4	1.85091	σ C18-C24	0.06552	18.05	0.69	0.102
DMSO						
Π N5-C11	1.75481	Π* C12-C18	0.29510	32.36	0.36	0.097
Π C12-C18	1.74087	Π* O2-C19	0.32035	27.37	0.30	0.082
		Π* O4-C24	0.29765	26.44	0.28	0.078
Π C14-C15	1.68163	Π* N5-C11	0.80383	35.20	0.22	0.090
		Π* C22-C23	0.30383	16.22	0.29	0.062
Π C22-C23	1.72964	Π* C14-C15	0.38462	19.12	0.30	0.069
LP (3) F1	1.92974	Π* C22-C23	0.30383	16.98	0.44	0.082
LP (2) O2	1.89045	σ C13-C19	0.06623	18.06	0.70	0.102
		σ C18-C19	0.06325	18.94	0.72	0.106
LP (2) O3	1.81199	Π* O4-C24	0.29765	47.23	0.33	0.115
LP (2) O4	1.85591	σ C18-C24	0.06302	17.36	0.70	0.100
Water						
Π N5-C11	1.75455	Π* C12-C18	0.29545	32.39	0.36	0.097
Π C12-C18	1.74051	Π* O2-C19	0.32096	27.42	0.30	0.082
		Π* O4-C24	0.29776	26.48	0.28	0.078
Π C14-C15	1.68139	Π* N5-C11	0.80360	35.21	0.22	0.090
		Π* C22-C23	0.30386	16.23	0.29	0.062
Π C22-C23	1.72984	Π* C14-C15	0.38450	19.10	0.30	0.069
LP (3) F1	1.92976	Π* C22-C23	0.30386	16.98	0.44	0.082
LP (2) O2	1.89058	σ C13-C19	0.06617	18.04	0.70	0.102
		σ C18-C19	0.06320	18.93	0.72	0.106
LP (2) O3	1.81207	Π* O4-C24	0.29776	47.21	0.33	0.115
LP (2) O4	1.85595	σ C18-C24	0.06300	17.36	0.70	0.100

(ED$_i$ = 1.77567e) in gas, 32.36 kcal/mol (ED$_i$ = 1.75481e) in DMSO, and 32.39 kcal/mol (ED$_i$ = 1.75455e) in water. Electron delocalization occurred over the carboxyl group made a great contribution to the reduction in stabilization energy: the $E^{(2)}$ for the resonance interaction "LP (2) O3 → Π* O4–C24" were calculated in 47.77 kcal/mol (ED$_i$ = 1.80823e) in gas, 47.23 kcal/mol (ED$_i$ = 1.81199e) in DMSO, and 47.21 kcal/mol (ED$_i$ = 1.81207e) in water. The Π C14-C15 → Π* N5-C11 interaction contribution to $E^{(2)}$ was calculated as 34.22 kcal/mol (ED$_i$ = 1.69812e) in gas, 35.20 kcal/mol (ED$_i$ = 1.68163e) in DMSO, and 35.21 kcal/mol (ED$_i$ = 1.68139e) in water, remarkable. In the gas phase, the other resonance interactions over the carboxyl group were determined as Π C12–C18 → Π* O2-C19 ($E^{(2)}$ = 23.71 kcal/mol) and Π C12–C18 → Π* O2–C19 ($E^{(2)}$ = 23.15 kcal/mol) interactions. In addition, the remaining resonance interactions in the gas were predicted as Π C14–C15 → Π* C22–C23 ($E^{(2)}$ = 15.63 kcal/mol) and LP (3) F1 → Π* C22-C23 ($E^{(2)}$ = 17.13 kcal/mol). The movement of lone pair electrons of the oxygens belonging to both the carbonyl groups on the ring and in the aliphatic chain toward to antibonding sigma bonds contributed to the reduction in energy. In the gas phase, these interactions were predicted as the LP (2) O2 → σ C13-C19 ($E^{(2)}$ = 19.75 kcal/mol), LP (2) O2 → σ C18-C19 ($E^{(2)}$ = 20.31 kcal/mol), and LP (2) O4 → σ C18-C24 ($E^{(2)}$ = 18.05 kcal/mol), remarkable (Table 7).

Nowadays, the chemical reactivity parameters obtained from quantum chemical computations have been used to elucidate the underlying reason in many kinds of the chemical processes (Serdaroğlu and Mustafa 2018; Düşünceli et al.

2020; Serdaroğlu et al. 2020; Guo et al. 2017). In this work, the calculated reactivity parameters of ciprofloxacin are presented in Table 8. Accordingly, the energy of both HOMO and LUMO was decreased as the solvent dielectric constant increased from the gas to water, but that of LUMO more lowered than the HOMO, which this situation caused to narrow of the energy gap. Namely, ΔE (L–H) value (in eV) was calculated as Gas (4.4945) > DMSO (4.4077) > water (4.4061). The solvent environment makes the ciprofloxacin prefer the intramolecular interactions would rather than the intermolecular interactions. In addition, the ciprofloxacin was more stable electronically in the water phase in comparison with the other media. Based on the ω values, the ciprofloxacin had the highest electrophilicity index in the water. Also, it is worth to mention that the electrodonating tendency of ciprofloxacin is more than the electroaccepting power because of the heteroatoms, mostly oxygen. Besides, the water dielectric constant makes the ciprofloxacin more have electrodonating power. Namely, ω^- (eV) power was calculated in the order of Gas (0.1904) < DMSO (0.2010) < water (0.2011). Also, the $\Delta\varepsilon_{\text{back-donat}}$ tendency and ΔNmax index of ciprofloxacin in the water were calculated higher than the other media. The solvent effect on the chemical reactivity tensors can be clearly shown as below.

μ (eV): Gas (-3.7014) > DMSO (-3.8080) > water (-3.8091).
η (eV): Gas (2.2473) > DMSO (2.2039) > water (2.2030).
ω (eV): Gas (3.0483) < DMSO (3.2898) < water (3.2929).
ω^+ (eV): Gas (0.0543) < DMSO (0.0611) ≤ water (0.0611).
ω^- (eV): Gas (0.1904) < DMSO (0.2010) < water (0.2011).
$\Delta\varepsilon_{\text{back-donat.}}$ (eV): Gas (− 0.5618) < DMSO (− 0.5510) < water (− 0.5508).
ΔNmax (eV): Gas (1.6471) < DMSO (1.7279) < water (1.7290).

Table 8 The quantum chemical quantities of the ciprofloxacin agent at B3LYP/6-311G** level

	Gas	DMSO	Water
H (−I)	− 0.2186	− 0.2209	− 0.2209
L (−A)	− 0.0534	− 0.0590	− 0.0590
ΔE (L–H)	4.4945	4.4077	4.4061
μ	− 3.7014	− 3.8080	− 3.8091
η	2.2473	2.2039	2.2030
ω	3.0483	3.2898	3.2929
$\omega+$	0.0543	0.0611	0.0611
ω-	0.1904	0.2010	0.2011
$\Delta\varepsilon_{\text{back-donat}}$	− 0.5618	− 0.5510	− 0.5508
ΔN_{max}	1.6471	1.7279	1.7290

From Fig. 12, HOMO density as an indicator of the nucleophilic attack site was focused over the six-membered rings, whereas the LUMO as the sign of the electrophilic attack region was expanded mainly over the two six-membered rings and partially on the third ring, in all environments. In addition, the MEP plots also give very helpful information related to electron density localization on the molecular systems. Accordingly, the oxygen atom of the carbonyl group seemed by the red color that indicated the negative electrostatic potential showed the best region for the electrophilic attacks. The remaining part of the ciprofloxacin seemed light blue color indicated the moderate-size electrostatic potential.

Interference study

The check the effect of other micro-chemicals in wastewater samples interference study has been evaluated using glucose, uric acid, methylene blue dye and Na^+, K^+ ions as interfering species. During the adsorption process, the presence of metal ions decreased adsorption percentage of ciprofloxacin, while the presence of glucose, uric acid, and methylene blue dye has no significant effect on adsorption of drug (Fig. 13).

Real wastewater samples

The FS-resin has been applied onto drug contaminated wastewater samples. The water samples were collected from local pharmaceutical effluents of Karachi–Sindh Pakistan. Preliminarily, batch adsorption has been performed under the already optimized parameters and it was observed that FS-resin is an efficient adsorbent for the treatment of drug contaminated wastewater (Table 9).

Conclusions

This study demonstrates the adsorptive removal of ciprofloxacin antibiotic from water using FS-resin. During adsorption, the maximum adsorption (99.9%) was obtained at (6.5) pH using 20 mg L^{-1} of FS-resin at the optimized contact time of 10 min. The equilibrium data were best fit with Freundlich model, i.e., ($R^2$0.99). Moreover, thermodynamic and kinetic data reveal that the adsorption is spontaneous and endothermic followed by pseudo-second-order kinetic model. To check the potential of FS-resin, real wastewater sample has been analyzed which shows that the resin is effective adsorbent for the treatment of pharmaceutical effluents. The interaction between FS-resin and ciprofloxacin drug was investigated through quantum chemical calculations.

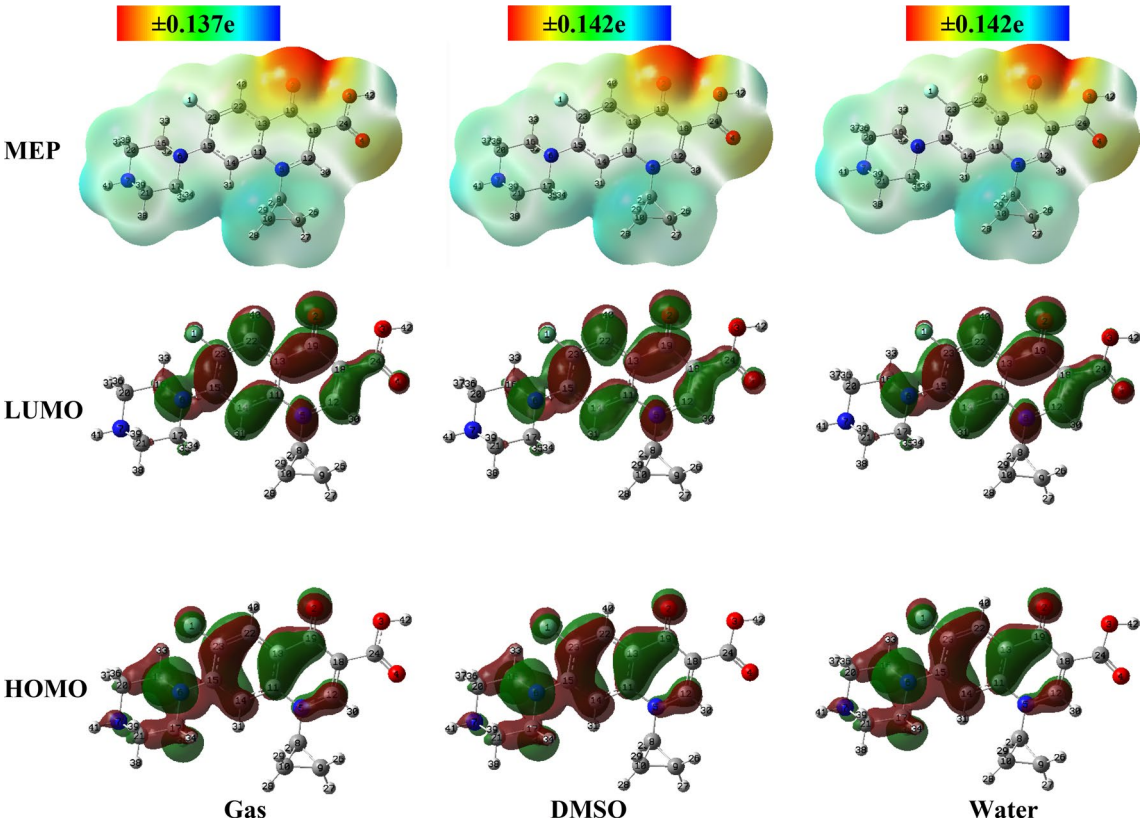


Fig. 12 HOMO and LUMO (isoval:0.02), and MEP (isoval:0.0004) pilots of the ciprofloxacin agent at B3LYP/6-311G** level

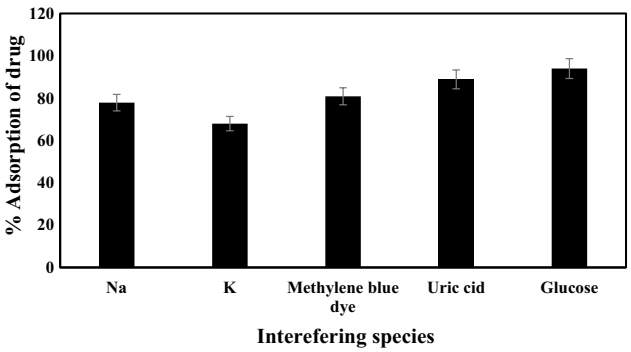


Fig. 13 Effect of co-existing species on the adsorption of ciprofloxacin drug

Table 9 Wastewater sample analysis

Sample No	Concentration (mol L^{-1}) before treatment with FS-resin	Concentration (mol L^{-1}) after treatment with FS-resin	% Adsorption
01	9.87×10^{-5}	1.10×10^{-5}	88.86
02	1.35×10^{-4}	1.90×10^{-5}	85.88
03	2.10×10^{-6}	1.00×10^{-6}	52.38

Acknowledgements Authors thank National Centre of Excellence in Analytical Chemistry, University of Sindh, Jamshoro, Pakistan, for facilitating this work.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Balarak D, Baniasadi M, Bazzi M (2020) Adsorption equilibrium and thermodynamic studies of ciprofloxacin from aqueous solutions by magnetic bentonite nanocomposites. Int J Pharm Invest 10(3):339–343

Bhatti AA, Oguz M, Yilmaz M (2017) Magnetizing calixarene: Azo dye removal from aqueous media by Fe3O4 nanoparticles fabricated with carboxylic-substituted calix [4] arene. J Chem Eng Data 62(9):2819–2825

Bhatti AA, Oguz M, Yilmaz M (2020) New water soluble p-sulphonatocalix [4] arene chemosensor appended with rhodamine for selective detection of Hg2+ ion. J Molecular Struct 1203:127436

Deligz H, Ak MS, Memon S, Yilmaz M (2008) Azocalixarene. 5: p-substituted azocalix 4 arenes as extractants for dichromate anions. Pak J Anal Environ Chem 9(1):5

Düşünceli SD, Ayaz D, Üstün E, Günal S, Özdemir N, Dinçer M, Özdemir İ (2020) Synthesis, antimicrobial properties, and theoretical analysis of benzimidazole-2-ylidene silver (I) complexes. J Coord Chem 73(13):1967–1986

El-Shafey E-SI, Al-Lawati H, Al-Sumri AS (2012) Ciprofloxacin adsorption from aqueous solution onto chemically prepared carbon from date palm leaflets. J Environ Sci 24(9):1579–1586

Guo L, Ren X, Zhou Y, Xu S, Gong Y, Zhang S (2017) Theoretical evaluation of the corrosion inhibition performance of 1, 3-thiazole and its amino derivatives. Arab J Chem 10(1):121–130

Gutsche CD (2008) Calixarenes: an Introduction, vol 10. Royal Society of Chemistry, London

Junejo R, Memon S, Durmaz F, Ahmed AA, Memon FN, Jalbani NS, Memon SS, Bhatti AA (2020) Synthesis of piperdinomethylcalix [4] arene attached silica resin for the removal of metal ions from water: equilibrium, thermodynamic and kinetic modelling studies. Adv J Chem-Sect A 3:680–691

Junejo R, Memon S, Memon FN, Memon AA, Durmaz F, Bhatti AA, Bhatti AA (2019) Thermodynamic and kinetic studies for adsorption of reactive blue (RB-19) dye using calix [4] arene-based adsorbent. J Chem Eng Data 64(8):3407–3415

Kamboh MA, Solangi IB, Sherazi S, Memon S (2011) Synthesis and application of p-tert-butylcalix [8] arene immobilized material for the removal of azo dyes. J Hazard Mater 186(1):651–658

Khokhar TS, Memon FN, Memon AA, Durmaz F, Memon S, Panhwar QK, Muneer S (2019) Removal of ciprofloxacin from aqueous solution using wheat bran as adsorbent. Sep Sci Technol 54(8):1278–1288

Li X, Wang W, Dou J, Gao J, Chen S, Quan X, Zhao H (2016) Dynamic adsorption of ciprofloxacin on carbon nanofibers: quantitative measurement by in situ fluorescence. J Water Process Eng 9:e14–e20

Limbu SM, Zhou L, Sun S-X, Zhang M-L, Du Z-Y (2018) Chronic exposure to low environmental concentrations and legal aquaculture doses of antibiotics cause systemic adverse effects in Nile tilapia and provoke differential human health risk. Environ Int 115:205–219

Memon NA, Memon AA, Memon FN, Sherazi STH, Memon S, Leghari MK (2018) Method development for determination of antibiotic drugs using newly prepared p-morpholinomethylcalix [4] arene mesoporous silica-based HPLC column. Chromatographia 81(10):1373–1380

Movasaghi Z, Yan B, Niu C (2019) Adsorption of ciprofloxacin from water by pretreated oat hulls: equilibrium, kinetic, and thermodynamic studies. Ind Crops Prod 127:237–250

Nazari G, Abolghasemi H, Esmaieli M (2016) Batch adsorption of cephalexin antibiotic from aqueous solution by walnut shell-based activated carbon. J Taiwan Inst Chem Eng 58:357–365

Farhang Rik B, Ranjineh khojasteh R, Ahmadi R, Karegar Razi M, (2019) Evaluation of C60 nano-structure performance as nanocarriers of procarbazine anti-cancer drug using density functional theory methods. Eurasian Chemical Communications 1(4):359–368. https://doi.org/10.33945/sami/ecc.2019.4.5

Serdaroğlu G, Kaya S, Touir R (2020) Eco-friendly sodium gluconate and trisodium citrate inhibitors for low carbon steel in simulated cooling water system: Theoretical study and molecular dynamic simulations. J Mol Liq 319:114108

Serdaroğlu G, Mustafa E (2018) A Computational study predicting the chemical reactivity behavior of 1-substituted 9-ethyl-βCCM derivatives: DFT-based quantum chemical descriptors. Turk Comput Theor Chem 2(1):1–11

Wu S, Zhao X, Li Y, Zhao C, Du Q, Sun J, Wang Y, Peng X, Xia Y, Wang Z (2013) Adsorption of ciprofloxacin onto biocomposite fibers of graphene oxide/calcium alginate. Chem Eng J 230:389–395

Xu S, Zhu Q, Xu S, Yuan M, Lin X, Lin W, Qin Y, Li Y (2021) The phase behavior of n-ethylpyridinium tetrafluoroborate and sodium-based salts ATPS and its application in 2-chlorophenol extraction. Chin J Chem Eng 33:76–82

Zhou L, Dai S, Xu S, She Y, Li Y, Leveneur S, Qin Y (2021) Piezoelectric effect synergistically enhances the performance of Ti32-oxo-cluster/BaTiO3/CuS pn heterojunction photocatalytic degradation of pollutants. Appl Catal B Environ 291:120019

Authors and Affiliations

Ranjhan Junejo[1] · Nida Shams Jalbani[1] · Savas Kaya[2] · Goncagül Serdaroglu[3] · Mustafa Elik[4]

[1] National Centre of Excellence in Analytical Chemistry, University of Sindh, Jamshoro 76080, Pakistan

[2] Health Services Vocational School, Department of Pharmacy, Sivas Cumhuriyet University, 58140 Sivas, Turkey

[3] Department of Mathematics and Science Education, Sivas Cumhuriyet University, 58140 Sivas, Turkey

[4] Department of Mathematics and Science Education, Faculty of Education, Sivas Cumhuriyet University, Sivas, Turkey