Computational screening of zeolites for the adsorption of selected pharmaceutical pollutants

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Abstract

Molecular simulations have been used as a screening tool to identify promising zeolites for the removal of selected pharmaceutical pollutants. 40 zeolites with different structural and chemical configurations were studied. Galophosphate cloverite (CLO) of the chemical formula, $F_{24}Ga_{96}P_{96}O_{372}(OH)_{24}$, with pores of 20 rings and the lowest observed bulk density, showed exceptionally preferred adsorption of diclofenac [2-(2,6-dichlorophenyl)amino benzeneacetic acid], ciprofloxacin [1,3,7-Trimethylpurine- 2,6-dione] and chloramphenicol [2,2-dichloro-N-[(1R,2IR)-1, 3-dihydroxy-1-(4-nitrophenyl)propan-2-yl acetamide]. This selectivity was attributed to the geometry and structural composition of the cavities. We also investigated the most stable adsorbed compositions of the pollutants in the CLO zeolite. Our calculations show that diclofenac, ciprofloxacin and chloramphenicol molecules are adsorbed into the pores with adsorption energies of -78.23 , -173.68 and -84.46 kcal/mol respectively. Additional calculations were also made to obtain detailed information on desorbed products. It is seen that dechlorination is the most energetically preferred process compared to dehydrogenation and dehydroxylation.

Keywords Monte Carlo simulation · Adsorption isotherms · Pharmaceutical pollutants · Zeolites

1 Introduction

Pharmaceutical drugs are widely used in health care, injecting a large number into the environment in unused or metabolized form [1]. Their presence in the aquatic environment is considered a potential toxicological hazard because they pose long-term risk to aquatic organisms and their dependents through endocrine destruction and the development of drug-resistant bacterial strains [2]. Traditional sewage treatment plants are not designed to remove these contaminants effectively [3], so alternative water treatment methods are still needed. Adsorption

removal is one of the most promising techniques due to its efficiency [4]. Zeolites are interesting candidates because of their unique adsorption properties. They exhibit interesting properties such as adsorption, cation exchange, molecular sieving, and catalysis [5–7]. Zeolites have the basic structure which consists of tetrahedron having four oxygen atoms surrounding aluminum and silicon atoms. The framework is usually negatively charged, balanced by exchangeable cations such as K^+ , Na^+ , Mg^{2+} and Ca^{2+} [8]. Modification of zeolites can be done in different ways, whereby silicon can be replaced with other metal atoms, like germanium, aluminum, iron, boron etc. These changes

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can have a significant effect on the properties of the zeolite involved in adsorption and catalysis processes.

To date, most of the zeolite materials that have been investigated for the separation of organic compound mixtures belong to the MFI-type, [9–15] although others like Mordenite (MOR), [16] Linde Type A (LTA), [17, 18] Faujasite (FAU), [19–21] Deca-dodecasil 3R (DD3R), [22] chabazite (CHA) [23, 24] and Silicoaluminophosphate (SAPO), [23, 25] have also been studied. For example, Rossner et al. [26] investigated the removal of 25 organic pollutants from spiked lake water by mordenite (MOR topology) and zeolite Y (FAU topology), whereby mordenite showed promising results for quantitative removal of various compounds, whereas zeolite Y removed only one pharmaceutical (fluoxetine). Some experimental studies followed Rosner et al.'s work in assessing the performance of high silica zeolite in the removal of drugs and related contaminants [27–29]. For example, 15 pharmaceuticals were investigated on high-silica mordenite by De Ridder et al. [29] A few other studies for pharmaceutical adsorption employing high-silica zeolites have been done by Braschi, Martucci et al. [28]. Currently, molecular simulations play an essential role in enhancing our understanding of the properties of closed molecular fluids in zeolites [30–32]. It is difficult to do experiments that give us molecular level insights as most of the activity occurs inside the zeolite material. To get information of the processes inside the cavities, it is important to comprehend adsorption of the reactants, diffusion and then chemical transformation at the active sites. The reaction rate and the products formed can be affected by each step. Thus, the experimental efforts can be nicely complemented by the molecular simulations [33, 34]. Although computational chemistry methods are widely used in zeolite science, computational investigations of drug adsorption in zeolite are rare [35]. Force-field based Monte Carlo (MC) simulations have been used to study the adsorption of organic molecules in all-silica zeolites for various species, like aromatics [36], organic structure-directing agents (OSDAs) [37], and glucose [38]. In contrast to this, force field methods have rarely been used to study the interaction of pharmaceuticals with zeolites and the molecular dynamics (MD) investigation of salbutamol and theophylline diffusion in zeolite BETA by Fatouros et al. [39] is a rare example. While a similar MD-based approach was later used by Spanakis et al. [40] and Fischer [26], on two all-silica zeolites, it is noteworthy that modelling techniques have not been employed to investigate the adsorption of pharmaceuticals in a large variety of zeolites, aiming at applications in either drug delivery or wastewater treatment. This work aims at establishing whether molecular simulation approach can be used for an approximate prediction of pharmaceutical pollutant removal efficiency on a large variety of zeolites i.e; CLO,

SBT, MFI, SBE, FAU, TSC, PAR, ITE, CGF, RTH, RUT, DOH, MTF, THO, CZP, AHT, MON, EUO, SAO, SFE, OSI, LTN, MTN, STO, AEL, FRE, MOR, DDR, WEI, SBS, MSO, HEU, KFI, LTA, NAT, RHO, ESV, SAT, BOG and NON [41]. This study focuses on diclofenac, ciprofloxacin and chloramphenicol pharmaceuticals. Diclofenac is the mostly used non-steroidal anti-inflammatory drug used to reduce inflammation and also as a painkiller for the relief of mild to moderate pain associated with head ache, backache and postoperative pain, [33, 42] while ciprofloxacin and chloramphenicol are broad-spectrum antibiotics. The focus on the three pharmaceutical drugs is motivated by the fact that they are largely consumed [43] resulting in their detection in surface water and sewage treatment plants effluents [43].

2 Computational models and methods

The molecular mechanical methods are based on classical mechanics. These methods allow the study of materials at atomic level and determine the bulk properties through force fields, which are a set of potential functions and parameters. The potential functions define the interactions in a molecular system. These functions can be parameterised in a variety of analytical forms to give the correct energies and forces. The parameters encompass optimal values of balance, such as distances, bond angles and force constants. In the force field based approach, the molecules are represented as a set of spheres of different sizes and masses, connected by springs of different lengths and spring continuously. The atoms interact through a series of forces like bond stretching, bond bend and dihedral torsion, and through interactions between non-bonded atoms such as van der Waals and electrostatic interactions. Those forces can be written in term of potential energy functions. To define the zeolite structure by molecular mechanics, most simulation studies are performed using the method proposed by Kiselev et al. [44]. According to the model by Kiselev et al. [44], the zeolite framework is kept rigid and the non-framework molecules are allowed to move freely in the zeolite.

The Monte Carlo (MC) method was used in this study. To generate a set of configurations according to a Markovian stochastic process, the algorithm by Teller et al. [45] is used. The strength of the MC method lies in its capability to calculate statistical averages without explicitly sampling the entire partition function. The capability to deal with complex variation in spatial and energetic variables is what makes MC such an attractive method. To study the adsorption properties, the grand-canonical ensemble is a natural choice. For each zeolite, we conducted a single GCMC simulation for the pharmaceuticals at 298 K in order to screen the structures exhibiting

the most interesting adsorption properties. For the selected structures whole adsorption isotherms were calculated. The adsorption isotherm measures the number of adsorbed molecules as a function of the chemical potential (pressure) of the fluid that is in contact with the porous material at a given temperature, T . An adsorption isotherm is conveniently computed in the grand canonical ensemble in which the temperature, volume (V), and chemical potential of the adsorbed component (μ) are imposed. For the grand-canonical ensemble the partition function reads [35] (Eq. 1);

$$Q_{\mu,V,T} = \sum_{N=0}^{\infty} \frac{\exp(\beta\mu N)V^N}{\Lambda^{3N}N!} \int ds^N \exp[-\beta U(r^N)] \quad (1)$$

The connection with the thermodynamics is made via the grand-potential Ω , which is related to the partition function via (Eq. 2);

$$\beta\Omega = -\ln Q_{\mu,V,T} \quad (2)$$

In this ensemble, the number of adsorbed molecules (N/V) is an ensemble average (Eq. 3);

$$\frac{N}{V} = \frac{1}{Q_{\mu,V,T}} \sum_{N=0}^{\infty} \frac{N \exp(\beta\mu N)V^N}{\Lambda^{3N}N!} \int ds^N \exp[-\beta U(r^N)] \quad (3)$$

We also explored the most stable adsorbed configurations of the pharmaceuticals on the zeolites using the simulated annealing approach [46], as embedded in the material studio adsorption locator module. The zeolite structures were extracted from the IZA structure database [41], and then optimized using material studio Forcite module [47]. The DREIDING force field (Material Studio Forcite module) [47], has been previously used with success in the theoretical investigation of organic structure directing agents interacting with zeolites [37]. Thus, it can be expected that this force field can represent the interaction between organic molecules and zeolites. In the simulations, rigid zeolite models were used and guest–guest interactions were ignored. Openly available data repository, PubChem [48] was the source for the molecular structures of the pharmaceutical contaminants. They were then imported into the Biovia Materials Studio 2017 software [49]. Geometry optimization and frontier molecular orbital analysis of the pharmaceuticals was done using DMol³ method [50, 51], prior to Monte Carlo simulations. For the following discussion, we report on the results obtained using the generalized gradient approximation (LDA) with the PDW exchange–correlation functional [52] and the double-numerical basis set [50] while the energies calculated at GGA/PW91, B3LYP, GGA/BLYP, m-GGA/MO6-L, m-GGA/M11-L, LDA/PWC and GGA/HCTH levels of theory are also listed in S2 (supporting information).

3 Results and discussion

We first plotted the frontier orbitals and the optimized structures of diclofenac, ciprofloxacin and chloramphenicol as seen in Fig. 1. The HOMO orbital energy (E_{HOMO}) is normally related to the electron-donating ability of a molecule whereas LUMO orbital energy (E_{LUMO}) is associated with the electron-accepting ability of a molecule from which the global hardness (η) can be calculated. The energy gap between HOMO and LUMO also helps to describe the chemical behavior and electrical properties of molecules, with lower energies indicating higher reactivity and lower stability. It can be observed that the HOMO of diclofenac is concentrated on benzene ring and around N– and OH– groups, similar to the LUMO but less pronounced. In ciprofloxacin the HOMO is localized on lower side on dinitro-phenyl ring, while the LUMO on the upper phenyl ring having nitrogen in the ring extending to OH group and O[−], which are attached to the phenyl ring. For chloramphenicol, the HOMO is also on lower part of the molecule and appears around the benzene ring, OH group and the acetamide group in which δ -interaction bonding system is on semicircle of the ring, while the LUMO is localized on nitro-phenyl ring.

The calculations of the energy levels of the electron orbitals allowed quantifying the value of the HOMO and LUMO energies, whereby diclofenac has the lowest HOMO energy (− 4.64 eV) while chloramphenicol has a relatively higher HOMO energy (− 1.92 eV). Previous studies have established that the larger the HOMO–LUMO energy gap, the harder and more stable/less reactive the molecule [53, 54]. It is seen that diclofenac has a relatively higher chemical hardness of 1.36 eV (Table 1), compared to that of chloramphenicol and ciprofloxacin, implying that diclofenac has a higher stability. On the contrary, chloramphenicol and ciprofloxacin molecules with a relatively smaller LUMO–HOMO gap, are termed as “soft”. In terms of chemical change, “softer” molecules are more reactive than “harder” ones. Based on this, we initially screened the adsorption of diclofenac on the forty zeolites. The adsorption isotherms are shown in Figures S1–S40 (supporting information). According to Giles and co-workers, [55] adsorption isotherms are classified into the four groups. The first group is the C-shaped adsorption isotherm which describes a linear increase of the pollutants adsorption loading with the equilibrium concentration of pollutant in solution. The second category is the L-shaped isotherm that occurs when the adsorbent has a limited number of adsorption sites, leading to the appearance of a plateau in the adsorption isotherm after a specific equilibrium concentration of pollutants, suggesting the saturation of the

Fig. 1 **a** Optimized structures of ciprofloxacin, diclofenac and chloramphenicol. **b** Frontier molecular orbitals of ciprofloxacin, diclofenac and chloramphenicol. Atoms in grey, red, white, green, blue color represent Carbon, Oxygen, Hydrogen, Chlorine and Nitrogen respectively. Yellow and blue regions correspond to positive and negative values of the orbital

Table 1 Key quantum chemical descriptors obtained for the three pharmaceutical products

Pharmaceuticals	Chemical potential (eV)	Chemical hardness (eV)	Chemical softness (eV)
Diclofenac	- 3.28	1.36	0.74
Ciprofloxacin	- 3.86	0.36	2.80
Chloramphenicol	- 1.62	1.15	0.87

adsorbent. Thirdly, the H-shaped isotherms that indicate that the adsorbent have a higher affinity for OMPs, and lastly, the S-shape that is attributed to a higher attraction between the pollutants at the surface of the adsorbent. Among the various zeolites tested, it was observed that only CLO exhibited the L-shape isotherm with an almost maximum loading and a pronounced inflection at a maximum loading of 60 mol per unit cell (Fig. 1 and S41). Conversely, all the other zeolites exhibited low loading. For example, the MFI zeolite (family of high silica zeolites, a medium pore zeolite, featuring a 10-ring pore opening with a diameter of approximately 5.5 Å and a chemical formulae $\text{Al}_{27}\text{Si}_{69}\text{O}_{165}$), showed no loading as seen in Fig. 1 (more details are shown in Fig. S42), due to its narrow channel openings [56] and as a result the cations tend to be located in the intersections, blocking the favorable adsorption sites. Also, the SBT (with a 12-ring pore, 7.2 × 7.4 nm in diameter), SBE (12-ring

pore), FAU (3-dimensional channel system with large pore openings formed by 12 rings, 7.4 × 7.4 nm in diameter) and TSC (8-ring pores, 4.2 × 4.2 nm in diameter) type of zeolites with chemical formulae $\text{Ga}_{36}\text{Zn}_{36}\text{P}_{72}\text{O}_{288}$, $\text{Al}_{32}\text{CO}_{32}\text{P}_{64}\text{O}_{256}$, $\text{Al}_{58}\text{Si}_{134}\text{O}_{384}$ and $\text{Al}_{192}\text{Si}_{192}\text{O}_{768}$ respectively, exhibited low loading of 3, 5, 8 and 12 mol (Fig. 1) of diclofenac per unit cell, respectively (more details are shown in Figs. S41–S46). The adsorption is minimal when the size of diclofenac is larger than the pore opening size of zeolite. Zeolites would then behave as molecular sieves [57]. Sorption fields of diclofenac on several representative zeolites are also shown in Fig. S56 (supporting information). It is seen that CLO has more sorption fields for diclofenac compared to other zeolites. It is clear from Fig. S56 that the diclofenac molecule prefers to locate at the intersections in CLO zeolite structure. Since these intersections have a maximum capacity of 60 mol per cell, an excess loading of four molecules per cell can only be achieved by “pushing” diclofenac into the straight and zigzag channels. The simulation results indicate that CLO is a promising adsorbent for the removal of diclofenac and it demonstrates that the very good packing of diclofenac is directly related to the probability of cross-ing and bending at the intersections of CLO (Fig. 2).

The most stable adsorbed configurations of the pharmaceuticals in the CLO zeolite alongside the corresponding adsorption energies was also probed as seen in Fig. 3A. Diclofenac molecule was observed to be located at the

Fig. 2 Adsorption isotherms of diclofenac on various zeolites at 298 K

centre of the 20 ring channel, facing the direction of the channel, while the phenyl group directly lie on the phenyl ring. This can be an indication that the reaction takes place inside the zeolite. Adsorption energy of -78.23 kcal/mol was observed for the most stable configuration. On the other hand, Fig. 3B shows the calculated Gibbs free energy of formation of various products relative to diclofenac in CLO. Differences in the Gibbs free energy of formation determine the equilibrium concentration of the various reaction intermediates [58]. If we use the free energies of formation [59], we can predict the various contributing routes and the possible products that can form. For example, the Gibbs free energy of formation for the removal of chlorine from diclofenac is smaller (16.38 kcal/mol compared to dehydrogenation (140.95 kcal/mol) and dehydroxylation (101.48 kcal/mol). Thus the formation of the later products is likely to be suppressed.

We also studied the adsorption behavior of ciprofloxacin on several representative zeolites. Figure 4, shows

Fig. 4 Adsorption isotherms of ciprofloxacin on various zeolites at 298 K

the adsorption isotherms for ciprofloxacin on CLO, SBT, MFI, SBE, FAU and TSC zeolites (more details are shown in Figs. S47–S50, supporting information). Among the various zeolites, only CLO exhibited the L-shape isotherm with maximum loading and a pronounced inflection at a maximum loading of 29 mol of ciprofloxacin per unit cell which is less compared to sorption of diclofenac. It is also seen that MFI showed zero loading. The SBT, SBE, FAU and TSC exhibited low loading of 1 , 3 , 4 and 8 mol of ciprofloxacin per unit cell. Additionally, CLO has more sorption fields compared to SBT, SBE, FAU and TSC (Fig. S57). Figure 5A, visualizes the lowest-energy configuration of ciprofloxacin in the CLO structure. The central part of the molecule occupies a 20-ring window connecting two super cages, while the phenyl moieties and the side chain are located to the side assemblies of the 20-rings bordering these cages of the 8 rings. This can be an indication that the reaction takes place inside the zeolite. The most

Fig. 3 **A** Structures of the most stable configuration of diclofenac adsorbed on the CLO. **B** The calculated Gibbs free energy of formation of various products relative to diclofenac in CLO. Energies are in kcal/mol

Fig. 5 **A** Structures of the most stable configuration of ciprofloxacin adsorbed on the CLO. **B** The calculated Gibbs free energy of formation of various products relative to ciprofloxacin in CLO. Energies are in kcal/mol

Fig. 6 Adsorption isotherms of chloramphenicol on various zeolites at 298 K

stable configuration energy of ciprofloxacin gave absorption energy of -84.46 kcal/mol which is lower than that of diclofenac. Figure 5B shows the calculated Gibbs free energy of formation of various products relative to ciprofloxacin in CLO. It is seen that the Gibbs free energy of formation for the removal of chlorine from ciprofloxacin is smaller (315.24 kcal/mol) compared to dehydrogenation (332.95 kcal/mol) and dehydroxylation (315.93 kcal/mol). Thus the formation of the later products is likely to be suppressed.

Figure 6 shows the adsorption isotherms of chloramphenicol on the CLO, SBT, MFI, SBE, FAU and TSC representative zeolites (more details are shown in Figs. S51–S55, supporting information). Just like for diclofenac and ciprofloxacin, it is only CLO that exhibited the L-shape isotherm with maximum loading and a pronounced inflection at a maximum loading of 48 mol of chloramphenicol per unit cell. It is interesting to note that diclofenac sorption on the CLO is higher compared to the ciprofloxacin and

Fig. 7 **A** Structures of the most stable configuration of chloramphenicol adsorbed on the CLO. **B** The calculated Gibbs free energy of formation of various products relative to chloramphenicol in CLO. Energies are in kcal/mol

chloramphenicol. It is also seen that just like sorption of diclofenac and ciprofloxacin, chloramphenicol showed zero loading on MFI. The SBT, SBE, FAU and TSC exhibited low loading of 4, 3, 6 and 10 mol of chloramphenicol per unit cell, respectively. It is also seen that CLO has more sorption fields for chloramphenicol compared to SBT, SBE, FAU and TSC (Fig. S58).

On the other hand, Fig. 7A, shows structures of the most stable configuration of chloramphenicol adsorbed on the CLO. The conformation of chloramphenicol adsorbed in CLO is very similar to that of the free molecule just like ciprofloxacin. The central part of the molecule occupies a 20-ring window connecting super cages, and both phenyl moieties with the side chain are located to the upper and down assemblies of 20-rings bordering these cages. The most stable configuration gave adsorption energy of -173.23 kcal/mol which is two folds lower than that of diclofenac and ciprofloxacin. Figure 3B shows the calculated Gibbs free energy of formation of various products relative to chloramphenicol in CLO. It is seen that the Gibbs free energy of formation for the removal of chlorine is smaller (-105.01 kcal/mol) compared to dehydrogenation (31.33 kcal/mol) and dehydroxylation (160.23 kcal/mol). Hence the formation of the later products is likely to be suppressed.

4 Conclusion

According to the molecular simulation results in this research, CLO zeolite has proved to be the satisfactory zeolite suited for adsorption of diclofenac, ciprofloxacin and chloramphenicol, since its structure has more adsorption sites. The simulations using a universal force field yielded rather unsatisfactory results for the adsorption isotherms of diclofenac, ciprofloxacin and chloramphenicol in other zeolites as it showed low loading. The most stable adsorbed configurations of the adsorbed pollutants on the CLO zeolite was also probed, whereby diclofenac, ciprofloxacin and chloramphenicol molecules get adsorbed at the pores with reasonably high adsorption energies (-78.23 , -173.68 and -84.46 kcal/mol for diclofenac, chloramphenicol and ciprofloxacin respectively). The larger adsorption energy at the pores appears due to the strong electrostatic interactions between the symmetric, electron-rich pore. Thus these simulations have proven to be very useful for the initial screening of adsorbents, prior to experimental work. This screening has considerable potential that can lead to the development of new remediation techniques for wastewater treatment.

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Compliance with ethical standards

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.

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