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Original Research

What is the Effect of Changing pH on Pharmaceuticals' Sorption?

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Abstract

The present article aims to determine how the change in pH affects the adsorption efficiency of pharmaceuticals on adsorbents. Natural zeolites of various fractions and activated carbon (granular, powdered) were used as suitable and available adsorbents. A total of 102 drugs were detected at the outflow from the Devínska Nová Ves wastewater treatment plant (WWTP), and their total concentration was 12.2 μg/l. The results of the first test (pH = 7.0) show that the highest removal of the total drug concentration was observed in powdered activated carbon (PAC > 99%). On the other hand, zeolites achieved the highest removal efficiency of only 52%. Subsequently, the pH of the treated water was adjusted to 2.0, and an increase in the amount of drug removed in each of the sorbents used was observed. In granular activated carbon (GAC), a 35% increase in total drug removal was observed. An increase in elimination was also observed for all zeolite fractions. Subsequently, the sample was adjusted to pH = 12.0, where we can observe the opposite effect. Except for PAC, all substances were removed with minimal efficiency. The elimination decreased by almost 50% for all types of zeolite fraction and GAC.

Keywords: pharmaceuticals, sorption, GAC, PAC, zeolites

Introduction

The presence of pharmaceuticals in the environment, especially in water sources, is currently the subject of a few studies. Pharmaceuticals and their metabolites enter the water environment from various sources with the discharge of municipal wastewater effluents, industrial production, agricultural run-off, etc. Their occurrence poses a high risk to aquatic ecosystems, but their effects on human health are considered to be rare but statistically significant [1]. This fact forced the European Union to create a watch list of the emerging compounds that include the pharmaceutical's active substance, namely, 17a-ethinylestradiol, 17β-estradiol, estrone, erythromycin, clarithromycin, azithromycin, amoxicillin, and ciprofloxacin. The purpose of this list is to collect monitoring data and confirm the risk properties of these substances [2].

Monitoring of drugs in wastewater is relatively well mapped in many countries [3], such as Slovakia [4, 5]. The above studies show that drug concentrations in wastewater vary from unmeasurable values up to tens of μg/l. They also fluctuate significantly within

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individual places, during the seasons, etc. From our long-term monitoring measurements of pharmaceuticals in wastewater, we estimate that about 25-30 tons of pharmaceuticals (active pharmaceutical ingredients) enter the Slovak wastewater annually and, subsequently, a portion of them into the aquatic environment. The presence of these substances in the effluent from the wastewater treatment plant is undesirable, so it is necessary to start addressing this issue. One way to prevent the massive entry of pharmaceuticals into surface waters is to include a fourth stage of wastewater treatment.

Removal of pharmaceuticals by adsorption is one of the most promising techniques applied to current water treatment processes. Despite frequent detection and a relatively higher concentration of pharmaceuticals in sewage, their removal at full scale is quite limited [6, 7]. Ozonation followed by the activated carbon process is increasingly used at full scale, especially in Switzerland and Germany [8]. However, intensive research is underway to find new sorption materials and optimal conditions for adsorption of pharmaceuticals from sewage [9, 10].

Sorption processes are among the potentially real processes that could significantly reduce the entry of drugs into the biosphere. The sorbent capacity is also a crucial factor in sorption. Adsorbents may also include sewage sludges whose surface charge is negative. In the process of wastewater treatment, various chemicals and drugs are adsorbed on the sludge, but sorption on sludge represents a low portion of total removal. The most widely used adsorbents include activated carbon and zeolites, which usually have a negative charge on the surface [11, 12], which supports their sorption properties.

The size of the specific adsorbent surface also plays an important role. The larger the specific surface area, the more efficient the sorption. It is also necessary to know the pH value for the adsorption conditions. In general, with decreasing pH, the conditions for adsorption improve, with the $pH<pK_a$ relationship when the substance is in neutral (hydrophobic) form, and with increasing pH, the sorption conditions deteriorate as the opposite $pH>pK_a$ relationship applies as the substance is in the form of an anion [11-13]. However, the effect of pH on adsorption has not yet been fully investigated. Therefore, it is not possible to say unequivocally why and how individual drugs behave. It is relatively complicated to determine the behaviour of drugs in changing pH in the case of zwitterions.

The aim of the present work is to determine the sorption behaviour of pharmaceuticals in the effluent of wastewater treatment plant when changing the pH of the effluent of wastewater. Three fractions of natural zeolites and two types of activated carbon were used and compared as sorption materials.

Materials and Methods

Work Methodology

The sorption processes were carried out with real wastewater, which was taken at the effluent from the wastewater treatment plant in Devínska Nová Ves (35 000 p.e. with negligible portion of industrial wastewater, activated sludge system with pre-denitrification, anaerobic sludge stabilisation).

For each sorption test (realised as triple tests), 200 ml of treated wastewater was used, while its pH was adjusted to pH = 2.0, 7.0 and 12.0, respectively, using 0.05 M sulfuric acid solution or 0.05 M sodium hydroxide solution. Laboratory tests were performed with the following types of adsorbents: granular activated carbon (GAC), powdered activated carbon (PAC) and zeolites (three different fractions). The sorption tests were performed by weighing the required amount of activated carbon (1 g) or zeolites of each fraction (5 g), and wastewater was added to the adsorbents. The sorption test was performed on an RSLAB-7 shaker (290 rpm) for 2 h, and then the wastewater was filtered. Thus, the samples prepared were frozen at -20°C and transported to an analytical laboratory at Faculty a Fisheries and Water Protection of the University of South Bohemia (Czech Republic).

Zeolites

Zeolites are defined as crystalline alkaline earth metal or alkali metal aluminosilicates which are highly hydrated [14]. They are characterised by their three-dimensional tetrahedral structure SiO_4^{4-} and AlO_4^{5}. The individual parts of the three-dimensional chain of zeolites are formed by various geometric shapes (quadrilateral, octagon, cubes, etc.), the vertices of which consist of aluminium or silicon atoms [15]. Their lattice structure allows the zeolites to act as ion exchangers and/or as selective adsorbents. When the size of the ion coincides with the size of the inlet pores into the zeolite lattice, it is easier to trap and retain the sorbed substance therein [16].

The zeolites tested were from the company Zeocem (Slovakia), and three different zeolite fractions were used:

- Coarse fraction (1.5-2.5 mm) designation of zeolite A.
- Middle fraction (0.5-1 mm) designation of zeolite B.
- Powder fraction (200 µm) labelled as zeolite.

Activated Carbon

Activated carbon as a porous carbonaceous adsorbent consists of microcrystals, which are generally composed of the following elements approximately: C - 88%, H - 0.5%, N - 0.5%, S - 1%, O - 7% and inorganic ingredients - 3%. It has a large internal area, which is about 500–1,500 m^2/g, while the pore volume

Table 1. Specific surfaces of individual fractions of used zeolites [13], and used types of activated carbon.

Zeolite fraction	Specific surface
zeolites A	40-42 m^2/g
zeolites B	44-46 m^2/g
zeolites C	53-55 m^2/g
GAC Filtrasorb 300	950 m^2/g
PAC NORIT SUPER SAE	1 050 m^2/g

is 0.7-1.8 cm^3/g. Granular activated carbon (GAC) and powdered activated carbon (PAC) [17] are commonly used worldwide to remove micropollutants.

Two different forms of activated carbon were used in this work:

– Filtrasorb 300 granular activated carbon from the company Eurowater (Slovakia).
– Powdered activated carbon NORIT SAE SUPER from the company CABOT - activated carbon created specifically for the sorption of pollutants from wastewater.

Analysis of Samples by Liquid Chromatography

Prior to HPLC/MS/MS analysis, the samples were thawed and re-filtered through 0.20 µm cellulose membrane filters to prevent column damage. Water samples were isotopically labelled with internal standards. The extraction and analysis were performed in a single step using in-line solid-phase extraction (SPE) liquid chromatography coupled with a triple quadrupole mass spectrometer (TSQ Quantiva, Thermo Fisher Scientific, USA). The analytical method and its performance have benn previously described in detail [18].

Results and Discussion

At the beginning of the experiment, drug monitoring was carried out in the outflow from the Devínska Nová Ves WWTP. From the results, we can state that 102 drugs of different therapeutic groups were detected in the effluent, of which 40 drugs were below the limit of detection. The total concentration of drugs in the monitored sample was 12,200 ng/l. With a concentration above 100 ng/l, 14 drugs were detected with a summary concentration of 11,105 ng/l. These drugs included, for example: carbamazepine, tramadol, venlafaxine, azithromycin, clarithromycin, diclofenac, cetirizine, fexofenadine, metoprolol, telmisartan, valsartan, etc. At concentrations up to 100 ng/l, 43 drugs were detected, including oxazepam, citalopram, atenolol, clindamycin, sulfamethoxazole, etc.

The first set of sorption tests was performed with real wastewater from the outflow from the Devínska Nová Ves WWTP, which had a pH value of 7.0. Zeolites of three fractions and granular and powdered activated carbon were used as sorption materials (see Table 1). Fig. 1 shows the efficiencies of removing the total drug concentration on the tested sorbents at pH = 7.0.

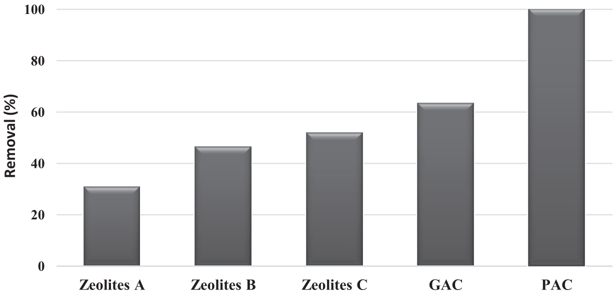

Fig. 1. Drug removal efficiencies with individual adsorbents at pH = 7.0.

The efficiency of drug removal from wastewater at pH = 7.0 was quite significantly different when using zeolites and activated carbon. When zeolites were used, the drugs were removed with an efficiency of 31% to 52%, and as the specific surface area of the zeolites increased, so did the sorption efficiency. Using activated carbon, we achieved 64% removal of the total drug concentration by GAC, and with powdered activated carbon, the value of the total concentration decreased to 26.6 ng/l, which represents > 99% efficiency.

Adsorption Trials at pH = 7.0

Individual drugs were also detected in the wastewater and were removed with different efficiency at pH = 7.0. An example is the antibiotic azithromycin (effluent concentration 340 ng/l), which was removed with an efficiency of over 97% after adsorption on all types of zeolites. With the GAC type adsorbent, azithromycin was removed ‘only’ to 90%, which is about 10% less compared with PAC. The drug verapamil had a similar course with an initial concentration of 60 ng/l, which was removed after adsorption to zeolites C by >99% efficiency. For zeolites B, the removal efficiency was 98% and, for zeolites A, only 93%. For PAC and GAC, the verapamil removal efficiency is >99%.

The opposite effect of removal can be observed. For example, for the contrast agent iopromide (effluent concentration 740 ng/l), its elimination efficiency for zeolites C was only 7% (690 ng/l). With the use of zeolites B, the elimination was at 18% (610 ng/l), and with zeolites A, they were able to remove the contrast medium only to 3%. Low iopromide removal efficiencies were also observed in GAC (65 %). The highest elimination of 99.7% was achieved by PAC, but it should be noted that the PAC used was a type of pulverised coal developed for the removal of drugs from WWTPs.

Relatively low elimination efficacy was also observed with diclofenac. The originally measured concentration at the effluent was 1,500 ng/l, and its elimination at neutral pH for zeolites C showed zero removal. For zeolites A, diclofenac removal was detected at 7 % and, with zeolites B, 'only' 13%. After completion of the sorption test with GAC and PAC adsorbents, the removal efficiency of diclofenac was relatively high: 87% for GAC and >99% for PAC. Drugs such as sulfamethoxazole, atenolol, tramadol, and many others have similarly shown extremely low efficacy. All of these removal effectivenesss are comparable to several works by other authors [6, 7].

Adsorption Trials at pH = 2.0 and 12.0

Based on the findings that the adsorbents, with the exception of powdered activated carbon, do not achieve high efficiency at pH = 7.0, the pH was adjusted to 2.0 and 12.0 (Fig. 2) to define the effect of an acidic and basic environment on the adsorption efficiency. The deep acidic or high alkaline environment in practice at the WWTP is rare to apply from an economic point of view, so the experiment could be used only in a specific industrial wastewater (pharmaceuticals production, hospital water, etc.) before entering the sewer network.

From the data of Fig. 2, we can state that by adjusting the wastewater to pH = 2.0, the efficiency of removing the total concentration of drugs in all monitored adsorbents significantly increased. This is due to the change in the solubility of the micropollutants in wastewater [19] and the effect of the pK_a value on drug behaviour. Compared with the sorption at pH = 7.0, zeolites C showed up to 22% increase in sorption efficiency, a 32% increase was observed in zeolites B, and up to 44% more adsorbed drugs were seen in zeolites A. GAC at pH = 2.0 eliminated up to 99% of the total drug concentration, representing almost a 35% improvement in sorption efficiency. In PAC, efficacy was still >99% drug elimination.

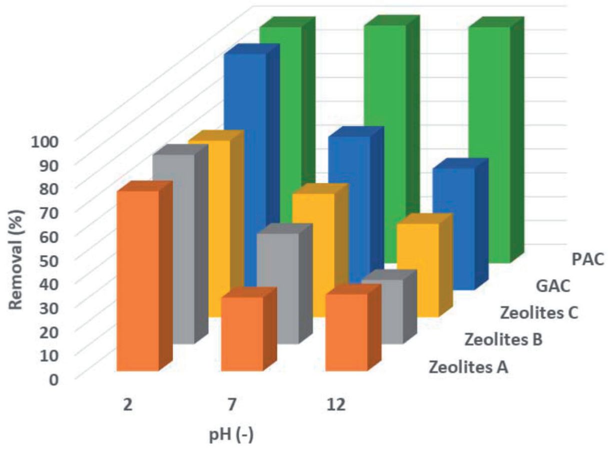

Fig. 2. Drug removal efficiencies for individual adsorbents at the monitored pH.

When comparing the sorption efficiencies at pH = 12.0 with pH = 2.0, we can observe the opposite effect when all substances were removed with lower efficiency, while this decrease ranged from 35% (for zeolites C) to 53% (zeolites B). Using PAC, the sorption efficiency did not show significant differences and was above 99% in all experiments.

It is clear from the results obtained that the adsorption efficiency is significantly dependent on the nature of the adsorbent, the chemical structure of the drug, and the pH used in the adsorption. The drugs studied contain different functional groups, which will also behave differently depending on the pH used. This results in the resulting charge of the whole molecule and thus the ability or inability to adsorb to different adsorbents. We can illustrate this with some examples.

Removal of Individual Pharmaceutics under Different pH Conditions

If we looked at the sorption of individual drugs in the monitored pH range in a little more detail, we could observe some relationships between the structure of the drug, pH, pKa, and binding changes in the molecule. Based on these relationships, we can generally divide all drugs into three basic groups – bases, acids, and so-called zwitterions.

Among the detected drugs, there is a group of drugs that can be classified as bases. These substances have an extremely high pKa value, which explains their easy (strong) ionization in aqueous solutions [20]. This group includes, for example, atenolol, caffeine, azithromycin, and many others.

A typical substance from the group of bases is atenolol. From the point of view of the structural formula of atenolol and its value pK = 9.6, it can be stated that at pH = 2.0, its protonated form -NH, i.e. NH^{2+}, dominates, whose sorption affinity for ionic structures of zeolites or the surface area of activated carbon is relatively high. By changing the pH to 7.0, the protonated form of atenolol no longer dominates, and at pH = 12.0, the molecule completely changes its character and shows rather basic properties, respectively. Thus, protonation of the molecule (at pH = 2.0) increased the removal efficiency of atenolol by 9%-41% using zeolites compared with pH = 7.0. When using zeolites, it can be stated with a certain probability that a significant part of the binding of atenolol was realised at pH = 2.0, in addition to sorption processes, also in the form of ion exchange. By increasing the pH, the sorption efficiencies decreased significantly in all zeolite fractions. However, when using GAC and PAC, no significant difference in atenolol removal was observed with changes in pH, which, in turn, can be explained by the predominance of rather adsorption forces between protonated atenolol and activated carbon forms. Similar changes in efficacy have been observed e.g. in ibuprofen sorption by Oh at al. [13].

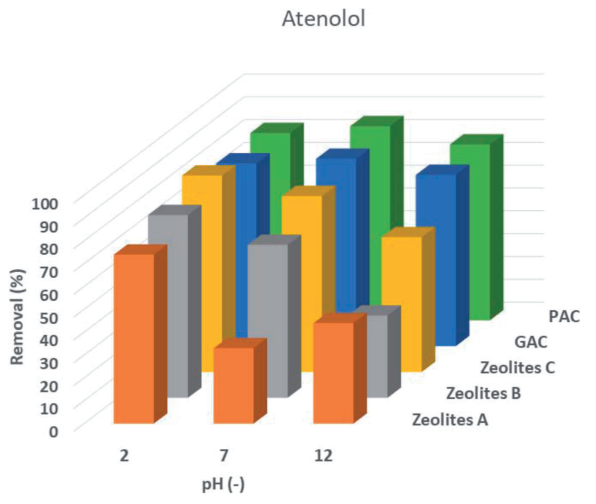

Fig. 3. Efficacy of atenolol removal on individual adsorbents at monitored pH values.

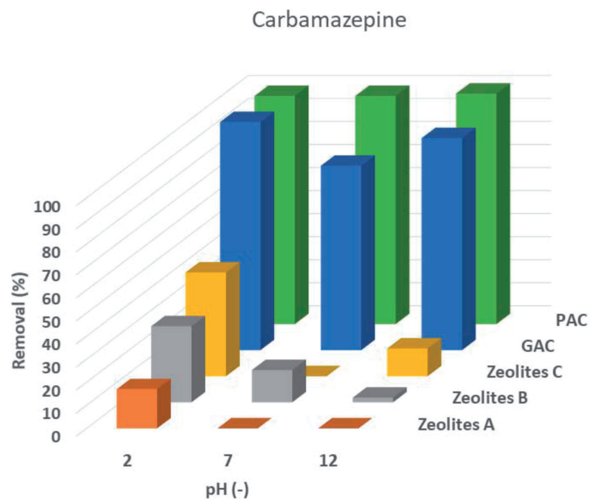

Fig. 4. Carbamazepine removal efficiencies for individual adsorbents at monitored pH values.

Another substance of interest in this group is caffeine. Caffeine is reported to have a high dipole moment, which increases with the polarity of the solution [1, 21, 22]. The neutral charge on the nitrogen atom interacts electrostatically with any negatively polarised functional group, and like that observed with atenolol, strongly positively charged caffeine ions are probably also capable of ion exchange in zeolites.

The results of our sorption test also showed a high elimination of caffeine on both types of activated carbon, which causes interactions of dipoles of caffeine molecules with n-electrons present on the adsorption surface [23]. Removal of this substance at pH = 2.0 ranged from 83% to more than 99% on all types of sorbents. In the medium pH range, the removal efficiency was from 25% to more than 99% at PAC. At pH = 12.0, caffeine removal was observed only at 25%-76%. However, even at pH = 12.0, the specially treated PAC eliminated the substance by more than 99%. Similarly high caffeine removal efficacies on clinoptilolitic sorbents were also achieved by Lelal et al. [24] and Martinez-Hernández et al. [25].

A third example of a base is carbamazepine. This drug cannot ionise at all, so at pH = 7.0, it behaves as a neutral compound, which has a significant effect on the sorption efficiency. In this case, it is necessary to be aware of the different adsorption properties of GAC and zeolites. This is because the adsorption force depends not only on the type of adsorbent but also, above all, on the mechanism by which the adsorption takes place. In the case of zeolites, where the sorption capacity is manifested mainly on ionic (dissociated) compounds, minimal efficiencies (in the range of 0%-14%) of carbamazepine removal were observed at both pH = 7.0 and pH = 12.0 (in the range of 0%-12%). By changing the pH to a strongly acidic range (pH = 2.0), the carbamazepine molecule was also slightly polarised, and removal efficiencies in the range of 17%-45% were observed. However, in the case of the use of activated carbon-based sorbents, removal efficiencies were significantly higher in the range of 80%-99% (GAC), resp. 99%-100% (PAC). This fact, as with other drugs investigated in the work, also confirms that the mechanisms of adsorption on zeolites and GAC (PAC) are significantly different.

Another group we can detect are substances that behave like acids. A good example is diclofenac. It is a polar molecule that additionally contains two bulky chlorine atoms. For adsorption, it is also necessary to consider the volume of the molecule, whether it can fit into the cavities of the adsorbent. Because of the value of pKa = 4.15 at pH = 7.0 and at pH = 12.0, deprotonation of the -COOH group to -COO- occurs, which makes the molecule negatively charged and thus tends to repel the surface charge of the adsorbent [11,13]. Therefore, the ion exchange reactions for zeolites were practically inefficient for all three fractions (0 %-27 %). However,

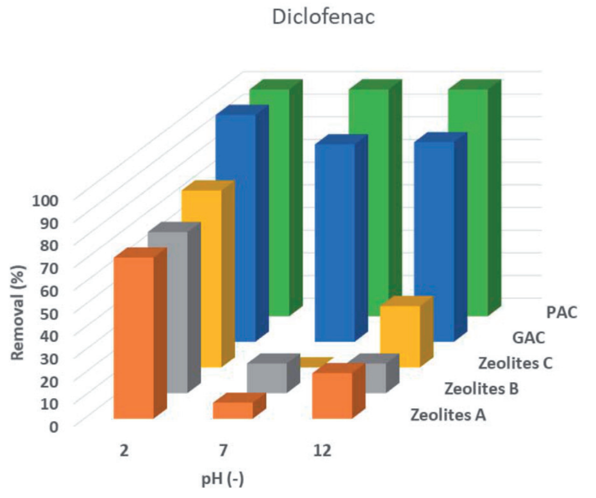

Fig. 5. Diclofenac drug removal efficiencies for individual adsorbents at monitored pH values.

at pH = 2.0, when deprotonation did not take place, the sorption efficiency on zeolites was relatively high (71%-78%). However, deprotonation of diclofenac did not adversely affect sorption on both forms of activated carbon, where sorption efficiencies were above 90% at all pH values.

The last group of detected drugs in the outflow from the Devínska Nová Ves WWTP included substances called zwitterions. Such substances consist, for example, the antibiotic sulfamethoxazole (SMX). Its initial concentration was 43 ng/l. The highest SMX removal efficiency was achieved at pH = 2.0, with PAC sorption medium. From the results, we can also state that the elimination of SMX at pH = 2.0 was extremely high for each sorption material. This fact is due to the influence of pKa value and pH. According to a study by Kah et al. [11], SMX has two pKa values. The first value is when the drug behaves as a base pKa1 = 1.7, and the second value is for the acid pKa2 = 5.7. At pH = 2.0, SMX behaves as a base and thus accepts a proton on the amino group and forms a cation. It is also true that the solubility of the neutral SMX molecule is much lower than that of the drug cation or anion. Sulfamethoxazole is a potent acceptor of π-electrons, which are provided by their amino functional groups (when protonated) and the N-heteroaromatic ring. The non-protonated sulfonamide group also has a high electron withdrawal capacity [11].

At medium pH (i.e. pKa (base) <pH <pKa (acid)), SMX contains a small proportion of zwitterions in the aqueous phase. The relative stability of zwitterion is thought to be higher in the sorbed state than in the solution [26]. However, because of the very low proportion of zwitterions at medium pH, charge interactions are expected to play only a minimal role in sorption.

The opposite phenomenon, i.e. a decrease in the sorption effect, was observed for SMX for pH = 12.0 when SMX behaves as an acid and thus a proton is cleaved from the sulfonamide group and a free electron pair remains on the nitrogen. The surface charge of the sorbent is a key property of the sorbent that needs to be considered when investigating drug interactions. The presence of ionizable functional groups on the surface of many carbonaceous sorbents forces them to develop a surface charge that varies depending on the pH of the medium. The surface is positively charged at low pH and gradually becomes negatively charged with increasing pH (and acidic functional groups dissociate). If both the sorbate and the sorbent carry the same charge (usually at pH = 12), electrostatic repulsion is expected, but partial sorption can take place through ion bridging [11].

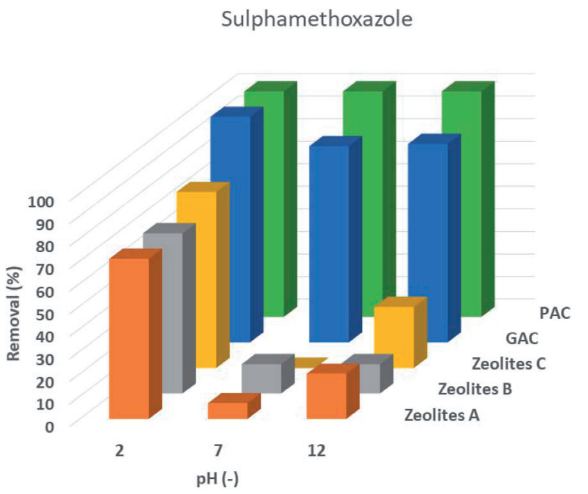

Fig. 6. Efficacy of sulfamethoxazole drug removal on individual adsorbents at monitored pH values.

Elimination of sulfamethoxazole was up to 12% for zeolites A, B, and C. For PAC sorption material, sorption was still >99%. With GAC sorbent, elimination was zero. In this case, the pH–pKa2 relationship applies, which indicates low drug sorption. In addition to the mechanisms proposed for acids, the decrease in sorption with increasing pH can be explained either by a decrease in electron-donor-acceptor (EDA) interactions (which decrease in the order cation >neutral molecule >>anion) or by cation exchange (this only applies if zero charge (PZC) is less than the pKa for the base) [11].

Like SMX, sulfapyridine (SUL) belongs to substances called zwitterions. The originally measured concentration of SUL in treated wastewater from the Devínska Nová Ves WWTP was 240 ng/l. As the pH decreased, the elimination efficiency increased with the use of all sorbents. Therefore, we can generally state that in zwitterions, substances behave as bases with decreasing pH. They are strong acceptors of π-electrons. The solophobic effect decreases with the formation of cations [11].

Since these interactions are often donor-acceptor in nature, it is necessary to define these interactions in addition to Brønsted's theory of acids and bases, which rather describes the formation of charges in the drug molecule after proton transfer, as well as the Lewis theory of acids and bases. According to this theory, a base is any compound that is capable of being an electron pair donor, and an acid is any compound that is capable of being an electron pair acceptor. The Lewis theory better reflects some types of drug-adsorbent interactions.

Conclusions

The work deals with sorption tests with five types of sorbents, namely, three fractions of natural zeolites and granular and pulverised coal.

The treated wastewater from the Devínska Nová Ves WWTP was used as a sample, in which 102 drugs were detected, with a total concentration of 12,198.5 ng/l. The first experiment was performed at pH = 7.0. The results of this test show that the highest removal of the total drug concentration was observed in PAC, which is specially formulated to eliminate micropollutants from wastewater. Using zeolites, the highest removal efficiency of only 52% was achieved for zeolites C. From these results, we concluded that drug elimination was not sufficient at pH = 7.0; therefore, subsequent experiments were performed at pH = 2.0 and pH = 12.0, respectively.

After adjusting to pH = 2.0, the amount of drug removed in each of the sorbents used increased. Again, the highest efficacy was detected in PAC. In GAC, a 35 % increase in total drug removal was observed. An increase in elimination was also observed for all zeolite fractions. From these data, we can state that adsorption at pH = 2.0 is more efficient than at pH = 7.0, which also follows from the literature data.

When comparing pH = 12.0 with pH = 2.0, we observed the opposite effect, and except for PAC, all substances were removed with minimal efficiency. The elimination decreased by almost 50% for all types of zeolite fraction and for GAC. At pH = 12.0, almost all drugs were above their pKa value. Therefore, our results confirm that if pH>pKa, sorption is less effective than in the case of pH<pKa.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.

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