

HIGHLY EFFICIENT REMOVAL OF PHARMACEUTICALS FROM AQUEOUS WASTES: EVALUATION OF OPTIMAL PROCESS PARAMETERS

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Abstract

This study investigates the competitive adsorption potential of activated carbon prepared from cherry kernels (CScPA) to remove sulfamethoxazole, carbamazepine, ketoprofen, naproxen, diclofenac and ibuprofen from aqueous solution. The effect of operational parameters including initial pH, adsorbent dose, contact time and initial pharmaceutical concentration were studied in batch adsorption experiments. The results indicate that CScPA can be used as an alternative, effective and low-cost adsorbent that presents basis of sustainable technology for efficient pharmaceuticals wastewater remediation and decontamination.

Introduction

In recent years, the presence of pharmaceuticals and personal care products (PPCPs) discharged into the water environment has been recognized as one of the common emerging issues worldwide because their residues may damage or have other adverse effects on the environmental ecology [1]. Pharmaceutical antibiotic sulfamethoxazole (SMX) is produced in large quantities and extensively used in the farming industry as veterinary therapeutics and growth promoters [2]. Diclofenac (DCF) and carbamazepine (CBZ) are two of the most frequently detected pharmaceutical residues in aquatic environments. DCF is a non-steroidal anti-inflammatory drug (NSAIDs) commonly used for the treatment of arthritis, whilst CBZ is an antiepileptic drug used for the treatment of psychomotor and temporal lobe epilepsy and also for the treatment of trigeminal neuralgia [3]. Ketoprofen (KP) is a non-steroidal anti-inflammatory drug, widely used for the treatment of rheumatoid arthritis, osteoarthritis, ankylosing spondylitis, and also for non-rheumatoid diseases or postoperative pain [4]. Naproxen (NPX) is a member of the arylacetic acid group that exhibits anti-inflammatory and analgesic effects in medical treatments [5]. Ibuprofen (IBP) is one of the most highly utilized NSAIDs worldwide and therefore it has been one of the most commonly detected pharmaceuticals in the environment, with concentrations up to micrograms per liter [6].

Recently there has been a growing concern about the elimination of pharmaceutical compounds from wastewater, and technologies studied include photo-catalytic degradation [7], biodegradation [8], biofiltration [9] and membrane filtration [10]. Advanced oxidation processes and other chemical treatments, can break down organic molecules into simple compounds, but they have many disadvantages; for instance, the high capital and operational cost and possible generation of secondary pollutions resulting in high disposal costs [11]. In contrast, adsorption technique is one of the preferred methods due to its simplicity as well as the availability of wide range of adsorbents. The cost of adsorption technology application can be reduced, if the adsorbent is cheap. Previous studies have revealed adsorption of PPCPs onto various adsorbents, such as activated carbon [12–14], carbon nanotubes [15], mesoporous nanocomposite [16] and agricultural waste[17,18].

So far, activated carbon is the widely used adsorbent for the removal of PPCPs. In recent years growing research interest in the production of low-cost and highly efficient activated carbons. The suitable application of activated carbon depends on its properties which vary with used raw precursor and preparation technique [19]. Recently, activated carbons are derived from relatively cheap and effective raw materials with a high carbon and low inorganic content, such as agro-industrial wastes, fruit industry waste and various solid organic substances for a lower adsorption system cost.

In the current study, the green activated carbon from fruit processing industry waste (cherry/sweet cherry kernels) was investigated for PPCPs removal capacity from aqueous solutions following batch experiments. The effects of pH (2-9), adsorbent dosage (0.04-4 g/L), initial concentration of PPCPs in the solution (1-50 mg/L) and contact time (5-300 min) were evaluated. The goal of this work is to evaluate the performance of the CScPA for the competitive removal of PPCPs from aqueous wastes and to simulate complex pollutant conditions encountered in wastewater treatment plant influent.

Experimental

About 140,000 tons of sweet and sour cherry are produced in Serbia every year. Because of that prepared activated carbon was made from sour cherry/sweet cherry kernels which were washed with distilled water, crushed and dried. Phosphoric acid (50 wt.%) was used for thermochemical impregnation. Further procedure is shown in previously work [20].

Five PPCPs (CBZ, DCF, NPX, KP and IBP) were purchased from Sigma–Aldrich (Germany) while SMX was purchased from Fluka (Buchs, Switzerland). Water used for all standards were milli-Q prepared with Easypure II, Thermo Scientific. The stock solutions containing of SMX, CBZ, DCF, NPX, KP and IBP were prepared dissolving standards with 10 mL of water (milli-Q) and then 10 mL acetonitrile (HPLC grade, Sigma-Aldrich, Germany). After that 10 mL of 0.05% CH₃COOH, 250 mL of glacial CH₃COOH (Zorka Pharma, Serbia), diluted in volumetric flask of 500 mL filled with milli-Q water, and another 10 mL of acetonitrile were added. Standard solution concentration of pharmaceuticals was determined by HPLC (High Performance Liquid Chromatography, Agilent 1200 series).

Pharmaceuticals in filtered solution were detected by previously described chromatographic technique. The principle is states the separation and quantification of pharmaceuticals using XDB-C18 column and mobile phase, acidic solution with acetonitrile, with detection at various wave length. Separation was achieved with a type-C18 chromatography column (Zorbax Eclipse XDB-C18, 4.6 mm x 150 mm, particle size 5 μm); flow rate: 1 mL/min; column temperature: 30°C; injection volume: 15 μL; mobile phase: 0,05% CH₃COOH: acetonitrile (HPLC grade, Sigma-Aldrich, Germany) = 55:45; run time = 18 min; detection: 280, 220, 230 and 254 nm [21].

Adsorption tests were performed by shaking the flasks at 140 rpm for fixed time using mechanical stirrer Heidolph Unimax 1010 (Germany) in order to achieve equilibrium. The mixtures were then filtered through FIORONI qualitative filter paper (Grade 115) and residual concentrations of pharmaceuticals were measured using HPLC. Two important equations are used to calculate amount of adsorbed pharmaceuticals on activated carbon q_e (mg/g) and to determine percent of removal of pharmaceuticals from solution R_e (%):

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

$$R_e (\%) = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad (2)$$

Where C_0 is the initial pharmaceutical concentration (mg/L) and C_e is the pharmaceutical concentration at equilibrium (mg/L), V is the volume of solution (L) and m is the mass of activated carbon (g).

The effect of pH on pharmaceutical adsorption onto CScPA was investigated as following procedure: 0.1 g (2.0 g/L) of CScPA were added to 50 mL solution using initial concentration of 10 mg/L of each pharmaceutical for 60 min at room temperature (22 ± 1 °C). In order to study the effect of pH on pharmaceutical adsorption, the initial pH of the solutions varied from 2 to 9, by adding appropriate amounts of diluted NH_4OH and HCl solutions.

Influence of activated carbon dosage was studied by using CScPA concentration ranging from 2, 10, 20, 50, 80, 100, 150, 200 mg, (0.04-4 g/L) in 50 mL solution of 10 mg/l each pharmaceutical at optimal pH 6, for contact time of 60 min. Whole experiment was done at room temperature (22 ± 1 °C).

The effect of contact time was studied at various time intervals (5, 15, 30, 60, 120, 180, 240, 300 min) with initial concentration of 10 ml/L of each pharmaceutical at pH 6.0 and room temperature (22 ± 1 °C). In 50 ml solution CScPA dose was 0.1 g (2.0 g/L).

In order to assess the effect of pharmaceutical concentration on adsorption efficiency, initial adsorbate concentrations were varied at 1, 2, 5, 10, 20, 30, 40, 50 mg/L of each pharmaceutical with optimal pH (6.0), CScPA dose of 0.1 g (2.0 g/L), contact time 60 min at temperature (22 ± 1 °C).

Results and discussion

Fig. 1a shows the effect of pH on the removal of pharmaceutical into CScPA for different pH values. Generally, the adsorption of pharmaceuticals depends strongly on the pH of the solution [22]. From the Fig. 1a, it may be concluded that the retention of pharmaceuticals after adsorption onto CScPA is remarkably influenced by the pH. This parameter has very important role in adsorption process and in particular on the adsorption capacity [23]. In fact, the adsorption efficiency of SMX, CBZ, DCF, NPX, KP and IBP decreases when pH was increased from 6 to 9. The pK_a of KP, NPX, DCF and IBP are 4.45, 4.2, 4.15, 4.91, respectively, when pH is above pK_a , acidic pharmaceuticals have negative charge while surface of adsorbent becomes more negatively charged, leading to an electrostatic repulsion between them. The pK_{a1} and pK_{a2} of SMX are 1.6 and 5.7 which indicates that this molecule has zero charge which indicates that there is no electrostatic bonding. CBZ has pK_a 13.9 showing that it has a positive charge leading to potential electrostatic interaction between pharmaceuticals and surface groups of the CScPA.

Adsorption of acidic PPCPs decrease gradually for basic pH values. Dissociation degree of the surface functional groups and PPCPs is high, so the adsorbent and the solutes KP, NPX, DCF and IBP are in their negatively charged forms. In case of CBZ, it's neutral compound in the pH tested range; its binding onto CScPA is solely attributable to a non-electrostatic interaction involving hydrogen bonding probably through a nitrogen groups, oxygen groups of esters, carbonyl groups from aldehyde and ketones, methyl groups for hydrophobic bonding and Van der Waals interactions [24].

Adsorption efficiency is strongly affected by the adsorbent dosage, due to availability of the surface area and exchangeable sites. Fig. 1b presents results of the experiments with varying activated carbon concentrations. With the increase of activated carbon mass, from 2 mg to 200 mg, (0.04 - 4 g/L), the amount of adsorbed SMX, CBZ, DCF, NPX, KP and IBP decreases from 17.87 to 2.72 mg/g, 84.40 to 2.49 mg/g, 39.70 to 2.59 mg/g, 21.33 to 2.73 mg/g, 21.11 to 3.35 mg/g, 38.99 to 2.44 mg/g, respectively. After dosage of 2.0 g/L, the removal efficiency

was not increased rapidly. This dosage was adopted because the aim was to find optimal removal efficiency, while retaining minimal operating costs, for economic application for wastewater treatment plant.

The effect of contact time on the adsorption of SMX, CBZ, DCF, NPX, KP and IBP on the CScPA is presented in Fig. 1c. It is revealed, as expected, that increasing in contact time increased removal of PPCPs. In the first step of adsorption over 85% of pharmaceuticals are bounded in first 15 min and in the second phase equilibrium is attained within 60 min. It is easy to spot fast adsorption of every pharmaceutical on CScPA. CBZ showed in Fig. 1c represents that contact time is not strictly correlated with the adsorbate removal, because of its molecule nature. The amount of adsorbed pharmaceutical increased with time at initial stage of adsorption and after some point in time almost remained constant. Dynamic equilibrium was reached by the amount of adsorption from adsorbent, at this point. The time required to attain the state of equilibrium is termed the equilibrium time, and the amount of pharmaceutical adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under a given operation condition [25].

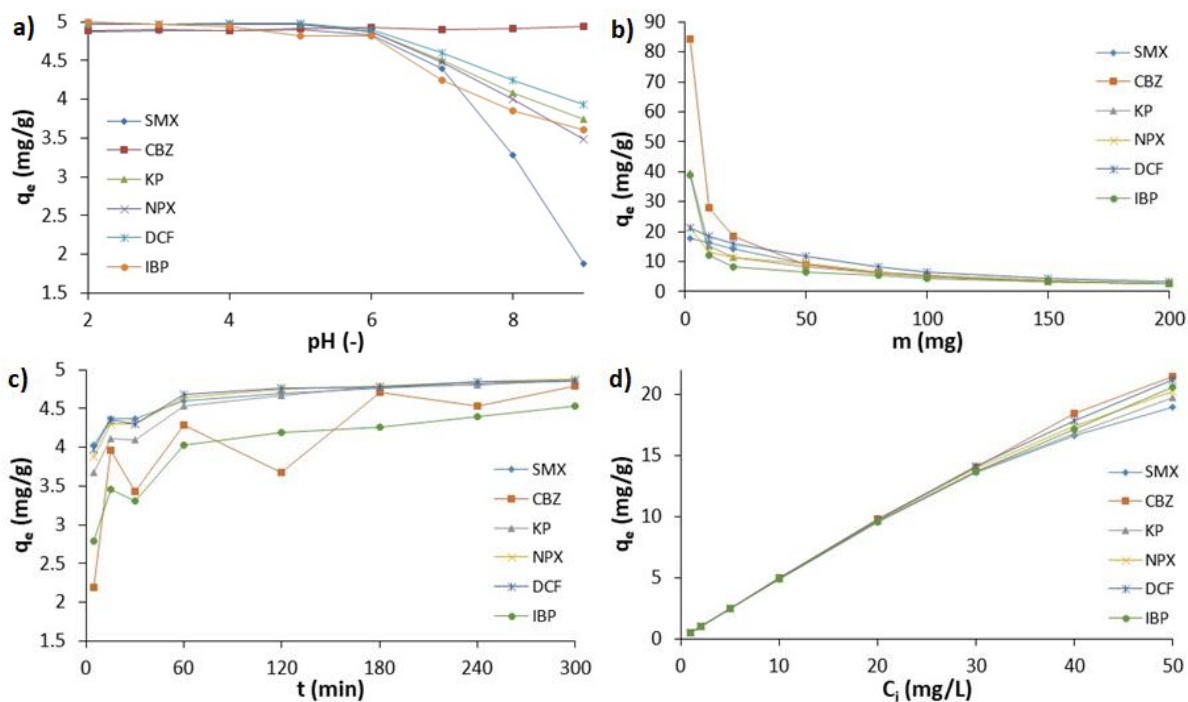


Figure 1. Effect of pH (a), adsorbent concentration (b), contact time (c) and initial concentrations (d) of SMX, CBZ, KP, NPX, DCF and IBP onto adsorption process

Varying pharmaceutical concentrations of 1-50 mg/L on optimal conditions showed decreasing in removal efficiency, for every pharmaceutical it was almost the same, up to 10 mg/L. After that, the removal efficiency was slightly decreasing up to 30mg/L, after which it decreased significantly. In whole process (Fig. 1d) of adsorption SMX, CBZ, DCF, NPX, KP and IBP removal efficiency dropped from 98.35 to 75.92%, 98.88 to 85.99%, 98.70 to 78.91%, 98.38 to 81.02%, 98.98 to 84.93%, 97.90 to 82.25%, respectively. Decrease in predicted process efficiency may be attributed to the lack of sufficient adsorption sites on surface area to accommodate more pharmaceutical available in the solution. Initial concentration of pharmaceuticals effected adsorption rate and capacity. Necessary driving

force was supplied by minimized mass transfer of initial concentration. In general, initial concentration boosts the adsorption of pharmaceuticals irrespective of the nature of adsorbent surface such as microporous, mesoporous, negatively or positively charge surface. The concentration increases the accessibility of pores for adsorbate molecules, as well as interactions at solid–liquid interface [26].

Conclusion

This paper describes the adsorption of six pharmaceuticals (SMX, CBZ, KP, NPX, DCF and IBP) onto green activated carbon CScPA in multi-solute solutions. The batch adsorption experiments showed that the optimal operation conditions at 140 rpm, pH 6.0, CScPA dosage 2 mg/L and contact time 60 min have removal efficiency over 95 % for SMX, CBZ, KP, NPX, DCF and IBP. According to obtained results, the CScPA was found to be a promising low-cost solution for PPCPs contaminated water remediation and decontamination.

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