



# Simultaneous removal of inorganic and organic pollutants from multicomponent solutions by the use of zeolitic materials obtained from fly ash waste

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## Abstract

Fly ash is an energy waste considered as a global environmental hazard. Annually, it is generated in the amount of over 50 million tons. One of the ways of fly ash management is its conversion into porous structures, which then can be applied to capture other pollutants from the aquatic environment. This paper presents the adsorption capabilities of four products of hydrothermal reaction of fly ash (HC FA), i.e., zeolites (Na-X, NA-P1) and their composites with carbon (Na-X(C), Na-P1(C)). All five materials were characterized in terms of their structure and used as adsorbents of heavy metals (Pb(II), Zn(II) ions) and organic compounds (diclofenac – popular anti-inflammatory drug, poly(acrylic acid) – polymer commonly used in industry) from their mixed solutions. Adsorption–desorption, electrokinetic and stability measurements were performed to determine the mechanisms driving the formation of the mixed adsorption layers. It was found that Na-X zeolite adsorbed 322.1 mg/g of Pb(II), 332.5 mg/g of Zn(II) and 6.68 mg/g of DCF, whereas Na-P1 bounded 332.9 mg/g of Pb(II), 103.6 mg/g of Zn(II) and 21.19 mg/g of DCF. In the mixed systems of adsorbates, these values were different, but also satisfactory. For example, in the Zn(II) presence, the adsorption of DCF on Na-X increased from 6.68 to 12.86 mg/g and that on Na-X(C), from 8.49 to 21.95 mg/g. The adsorbed pollutants changed the structure of electrical double layer of zeolitic materials. Moreover, they affected the stability of the examined suspensions. The presented results are promising for the further application of obtained zeolitic materials for environmental remediation.

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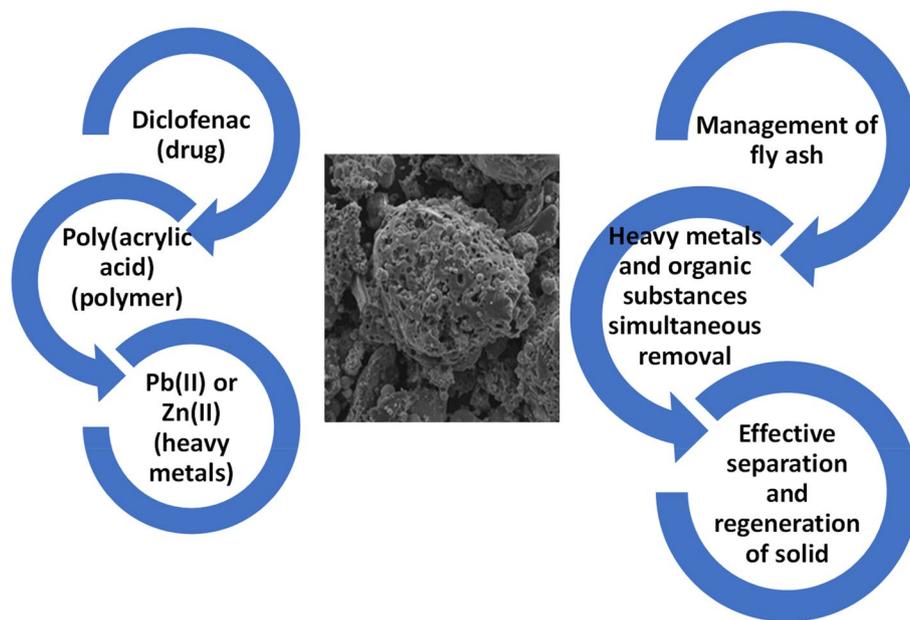
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## Graphical Abstract



**Keywords** Water purification · Heavy metal removal · Simultaneous separation · Organic pollutants · Zeolitic adsorbents · Fly ash management

## Introduction

Fly ash (FA) is a by-product of coal combustion. It has high heterogeneity and consists principally of silicon(IV) oxide, aluminum(III) oxide and iron(III) oxide. The annual production of fly ash reached 122 million tons in India (Dwivedi and Jain 2014) and over 500 million tons worldwide (2010–2011) (Ahmaruzzaman 2010). Such high production makes it a problematic waste in many economies around the world. The current use of FA is gradually increasing, but globally it is estimated at around 16%. This amount is too small to be considered satisfactory. FA is mainly deposited on agricultural land or in various landfills, which will probably cause even greater environmental problems in future. There are several ways of utilization of this compound, e.g., adding to various types of cement, fertilizers, or using for road construction and embankments (Alam and Akhtar 2011). Fly ash is also a treasury of metals and mineral substances, the availability of which in the natural environment is decreasing. Thus, the fly ash pollution can be reduced by using it as a reservoir for recovering industrially beneficial substances (Sahoo et al. 2016). Another opportunity to manage this waste is production of zeolitic structures, which can be used to remove hazardous pollutants from the environment (Merrikhpour and Jalali 2013; Khader et al., 2022).

In the presented research, the adsorption abilities of four materials created in this way were investigated.

The use of hazardous substances as materials to remove other residual substances in the environment is a double profit. For this reason, scientists around the world are looking for solutions to reuse or process FA. Zhou et al. (2015) obtained a mesoporous Al-MCM-41 material by exploiting fly ash with high silica content and used it to adsorb methylene blue. The adsorbed amount of this dye on Al-MCM-41 was equal to 277.78 mg/g. Sun et al. (2010) used FA to capture four different dyes. Its adsorption capacity toward these substances was as follows: Reactive Red 23–2.102 mg/g, Reactive Blue 171 – 1.860 mg/g, Acid Blue 193–10.937 mg/g and Acid Black 1–10.331 mg/g. Banerjee et al. (2005) compared adsorption capacities of fly ash, ash impregnated with aluminum (IFAAL) and ash impregnated by iron (IFAF<sub>e</sub>). Relative to Cr(VI), this parameter was 1.379, 1.820 and 1.667 mg/g, whereas relative to Hg(II), it was 11.00, 12.50 and 13.40 mg/g, respectively. The capabilities of fly ash were also studied by Akgerman and Zardkoohi (1996). They examined the adsorption of organic substances, such as phenol, 3-chlorophenol and 2,4-dichlorophenol, and the adsorption capacity of the examined material was 67, 20 and 22 mg/g, respectively. Fly ash was also used by Kusum et al. (2020) as an additive to cement. It reduced leaching of

calcium ions from concrete, which in turn limited formation of fat, oil and grease deposits in sewer lines.

This work describes the method of fly ash management, that is, the production of new materials as potential adsorbents of organic and inorganic pollutants. Four different materials were synthesized from FA, i.e., two zeolites (Na-X, Na-P1) and two zeolite-carbon composites (Na-X(C), Na-P1(C)). The properties of the obtained materials were examined in multicomponent solutions containing both heavy metal ions (zinc (Zn) or lead (Pb)) and organic pollutant molecules (diclofenac (DCF) or poly (acrylic acid) (PAA)). In this way, the effect of individual adsorbates on the binding of others with the examined solids was studied. What is more, the conditions encountered in the natural environment or in real wastewater were mapped. The amounts and parameters measured for zeolites and zeolite-carbon composites were compared with those obtained for the FA precursor.

Taking all these facts into account, the presented results can be considered as novel and environmentally important. The removal of divalent heavy metals or drugs is quite a popular topic, but in most cases it is limited to single systems or systems with two adsorbates of the same nature (Ternes, 1998; Bailey et al., 1999; Davis et al., 2003; Blanchard et al., 1984). The adsorption of two heavy metals, i.e., lead and zinc ions, on fly ash, Na-X, Na-X(C), Na-P1, and Na-P1(C) in single and mixed systems has already been determined in the previous studies (Panek et al., 2021a, 2021b), similarly for the adsorption of two organic substances – diclofenac and poly(acrylic acid), on the same solids. This paper continues that research proposing adsorption mechanisms occurring in the systems containing both inorganic and organic substances simultaneously. It proves that materials from the processing of coal combustion by-products can be successfully used not only to remove one type of pollutants, but also to remove dangerous compounds of different nature.

## Experimental

### Materials

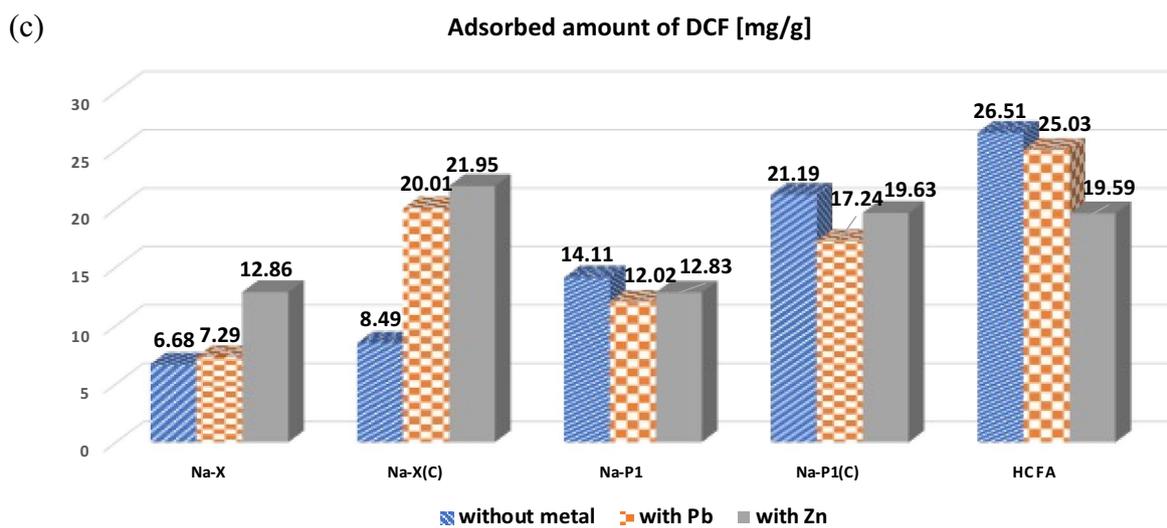
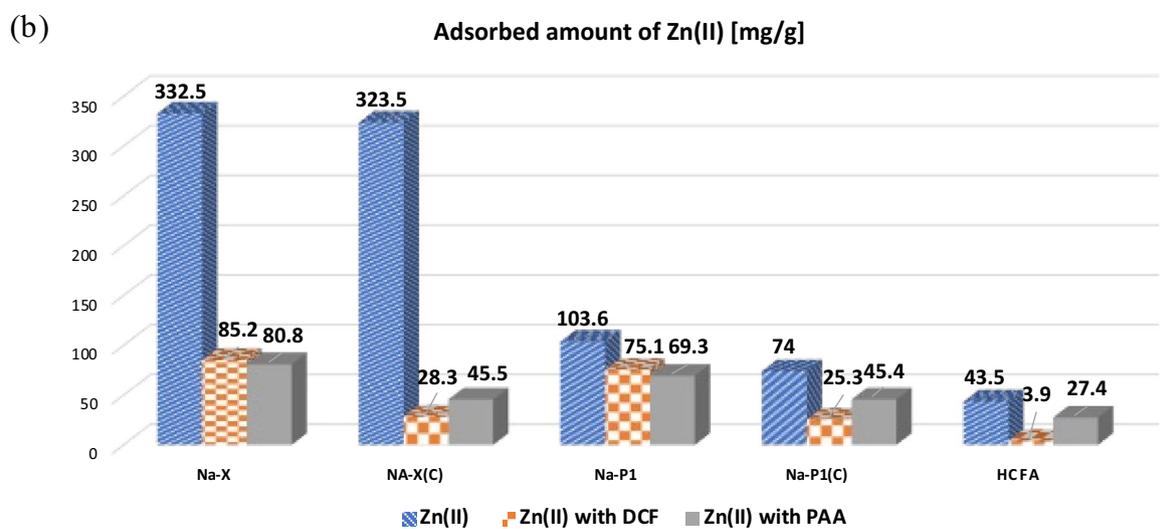
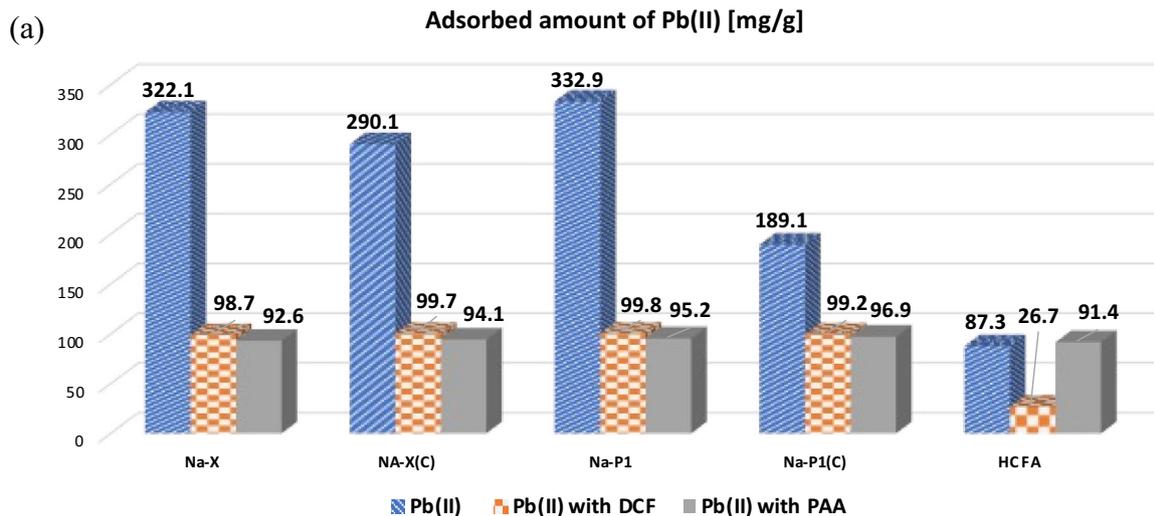
The used adsorbents: zeolite-carbon composites (Na-X(C), Na-P1(C)) were prepared by the hydrothermal reaction of aqueous sodium hydroxide solution (NaOH) and by-product of coal combustion generated in the Janikowo Thermal Power Plant—high-carbon fly ash (HC FA). Then, pure synthetic zeolites (Na-X, Na-P1) were obtained from the post-reaction waste rich in silicon and aluminum. The last adsorbent investigated in this paper was the precursor of the above-mentioned structures – HC FA (Panek et al., 2017; Wdowin et al., 2014; Franus et al., 2014; Bandura et al., 2021). The textural parameters of porous materials obtained with an ASAP 2020 apparatus (Micromeritics Instrument Corporation, Norcross, GA, USA) are shown in Table 1. The detailed characteristics of composition as well as structural, textural and surface properties of the examined materials were presented in our previous papers (Panek et al., 2021a, 2021b).

All measurements were performed in 0.001 mol/dm<sup>3</sup> NaCl solution, which was applied as the supporting electrolyte to ensure the same ionic strength in the investigated samples.

Poly(acrylic acid) (PAA) (*Aldrich*) with an average molecular weight of 240,000 and the non-steroidal anti-inflammatory drug diclofenac (DCF) (*Sigma-Aldrich*) were used as anionic adsorbates for the experiments conducted. Both substances have carboxyl groups of weak acidic properties which dissociate with the increasing pH. This is reflected in the pK<sub>a</sub> values – 4.15 for DCF and 4.5 for PAA (Jodeh et al., 2016). Lead nitrate(V) and zinc nitrate(V) (*Sigma-Aldrich*) were used as the source of lead(II) and zinc(II) ions, respectively. Their concentration was 100 ppm. In the desorption study, 0.1 M sodium hydroxide (NaOH) and 0.1 M hydrochloric acid (HCl) were used as desorbing agents.

**Table 1** Textural parameters of applied adsorbents

Adsorbent	BET surface area [m <sup>2</sup> /g]	Micropore area [m <sup>2</sup> /g]	Pore volume [cm <sup>3</sup> /g]	Micropore volume [cm <sup>3</sup> /g]	Mean pore diameter [nm]
HC FA	46.2	10.7	0.06	0.006	5.7
Na-X	727.9	694.1	0.31	0.27	1.7
Na-X(C)	271.9	188.8	0.17	0.07	2.6
Na-P1	26.7	4.3	0.05	0.002	6.9
Na-P1(C)	69.8	16.9	0.12	0.007	6.7



**Fig. 1** Adsorbed amounts of: (a) Pb(II) on the surfaces of fly ash precursor, zeolite-carbon composites and pure zeolites without and in the presence of DCF or PAA, (b) Zn(II) on the surfaces of fly ash precursor, zeolite-carbon composites and pure zeolites without and in the presence of DCF or PAA, (c) DCF on the surfaces of fly ash precursor, zeolite-carbon composites and pure zeolites without and in the presence of Pb(II) or Zn(II); pH 5,  $C_{\text{Pb(II)/Zn(II)}}$  100 ppm,  $C_{\text{PAA}}$  50 ppm,  $C_{\text{DCF}}$  50 ppm

## Methods

Adsorption and desorption were carried out in the following systems, analogous for each solid (here on the example of Na-X zeolite): (1) Na-X + DCF, (2) Na-X + DCF + Pb, (3) Na-X + DCF + Zn, (4) Na-X + PAA, (5) Na-X + PAA + Pb, (6) Na-X + PAA + Zn. The adsorbed amounts of Pb/Zn and DCF were studied at 25 °C using a static method, based on the change in specified adsorbate concentration before and after the adsorption process (Jutakrudsada et al., 2016). The samples were prepared by adding 0.01 g of the appropriate solid to 10 cm<sup>3</sup> solution containing 100 ppm Pb or Zn and 50 ppm PAA or DCF, as well as NaCl as the supporting electrolyte. The same method was used to prepare the samples with the Pb(II) and Zn(II) ions in single systems. In this case 0.003 g of the appropriate porous material was weighed and added to analogous amounts of solutions to obtain final suspensions. After the sample preparation, the pH was adjusted to the value of 5 using NaOH and HCl with concentration of 0.1 mol/dm<sup>3</sup>. This pH value was selected to avoid the formation of metal hydroxides. Usually, at pH close to 6, the Zn(OH)<sub>2</sub> and Pb(OH)<sub>2</sub> species begin to form. The adsorption process was carried out under constant shaking conditions (*Unimax 1010, Heidolph, Schwabach, Germany*) for 24 h. After the process completion, the solids were separated from the solutions. In the case of heavy metal ions, this was done by centrifugation (*310 b, Precision Mechanics, Poland*), while in the case of diclofenac, by paper and syringe filters. The concentration of heavy metals in the obtained supernatants was determined using inductively coupled plasma-optical emission spectrometry (*Thermo Scientific iCAPTM 7200 ICP-OES analyzer, Waltham, MA, USA*). In turn, the DCF concentration was determined using high-performance liquid chromatography (*Ultimate 3000, Dionex*) equipped with DAD detector.

In the desorption study, the solids with adsorbed substances were used. Desorption was carried out in the solution of 0.1 mol/dm<sup>3</sup> NaOH or 0.1 mol/dm<sup>3</sup> HCl for 1 h, under shaking conditions.

Electrokinetic measurements, potentiometric titrations and stability tests were performed in the following systems, analogous for each solid (here on the Na-X zeolite example): (1) Na-X, (2) Na-X + DCF, (3) Na-X + DCF + Pb, (4) Na-X + DCF + Zn, (5) Na-X + PAA, (6) Na-X + PAA + Pb, (7) Na-X + PAA + Zn. In order to determine the isoelectric

point (iep) and zeta potential ( $\zeta$ ) of the investigated suspensions, electrophoretic mobility ( $U_e$ ) measurements were conducted. Initially, a stock suspension was prepared by adding 0.005 g of the appropriate solid to 100 cm<sup>3</sup> of a solution containing NaCl and PAA/DCF with concentration 50 ppm/ and Pb<sup>2+</sup>/Zn<sup>2+</sup> ions with concentration of 10 ppm. Then, the obtained suspension was sonicated for 3 min and divided into 8 samples. After the pH adjustment to the selected value (changing in the range 3–10), the electrokinetic experiments were performed on the samples using Nano ZS zetameter (*Malvern Instruments, Cambridge, UK*) equipped with immersion dip cell (Oshima, 1994).

On the other hand, in order to determine the point of zero charge (pzc) and the surface charge density ( $\sigma_0$ ) of the investigated suspensions, potentiometric titrations were conducted. The automatically controlled kit containing thermostated Teflon vessel, glass and calomel electrodes (*Beckman Instruments*), PHM 240 pH meter (*Radiometer*), laboratory stirrer, RE 204 thermostat (*Lauda*), Dosimat 765 automatic microburette (*Metrohm*) and computer equipped with the special program "titr\_v3" were applied. The program enabled calculation of surface charge density as a function of solution pH, based on the difference in volume of the titrant added to the examined solution and the supporting electrolyte providing the specified pH value (Janusz, 1999). Potentiometric titration studies were conducted in the samples containing 0.03 g of Na-X, 0.075 g of Na-X(C), 0.4 g of Na-P1, 0.2 g of Na-P1(C) or 0.4 g of HC FA in 50 cm<sup>3</sup> of solution containing supporting electrolyte. The PAA/DCF concentration was 50 ppm, whereas that of heavy metal ions was 10 ppm.

A spectrophotometric method was applied to determine the stability of the investigated suspensions. Cary 100 UV–VIS spectrophotometer (*Varian*) was used for this purpose. The samples were obtained by adding 0.025 g of the selected solid to 10 cm<sup>3</sup> of solution containing supporting electrolyte, DCF/PAA with concentration 50 ppm and Pb/Zn with concentration 100 ppm. The samples were sonicated for 3 min before the addition of adsorbates. The absorbance was measured over time at wavelength 500 nm (Wiśniewska et al., 2021a, b). Each measurement was conducted for 1 h and the absorbance values were recorded every 2 min.

## Results and discussion

### Characterization of fly ash and prepared zeolitic materials

High-carbon fly ash (HC FA) generated in the combustion of hard coal was the starting material for the synthesis of zeolitic materials. It was composed of silicon (30%), carbon (30%), aluminum (13.5%), iron (8.6%) and small amounts

**Table 2** Comparison of adsorption capacity of fly ash, prepared zeolitic materials and other adsorbents relative to inorganic and organic pollutants in the single and multicomponent systems

Adsorbent	Adsorbates	Adsorption capacity	References
Na-X	Pb(II)	332.1 mg/g	this study
	Pb(II) with DCF	98.7 mg/g	
	Pb(II) with PAA	92.6 mg/g	
Na-X(C)	Pb(II)	290.1 mg/g	this study
	Pb(II) with DCF	99.7 mg/g	
	Pb(II) with PAA	94.1 mg/g	
Na-P1	Pb(II)	332.9 mg/g	this study
	Pb(II) with DCF	99.8 mg/g	
	Pb(II) with PAA	96.2 mg/g	
Na-P1(C)	Pb(II)	189.1 mg/g	this study
	Pb(II) with DCF	99.2 mg/g	
	Pb(II) with PAA	96.9 mg/g	
HC FA	Pb(II)	87.3 mg/g	this study
	Pb(II) with DCF	26.7 mg/g	
	Pb(II) with PAA	91.4 mg/g	
$\beta$ -Cyclodextrin/ZrO <sub>2</sub>	Pb(II) with Bisphenol A	274.4 mg/g	Usman et al. (2021)
Fe NPs	Pb(II) with rifampicin	100 mg/g	Lin et al. (2019)
Ru-NPs-AC	Pb(II) with methylene blue	19.29 mg/g	Mazaheri et al. (2015)
DK4	Pb(II) with 2, 4-dichlorophenol	33.78 mg/g	Huang et al. (2015)
Fe <sub>3</sub> O <sub>4</sub> -PEI/ $\beta$ -CD	Pb(II) with methyl orange	73.1 mg/g	Chen et al. (2018)
Na-X	Zn(II)	332.5 mg/g	this study
	Zn(II) with DCF	85.2 mg/g	
	Zn(II) with PAA	80.8 mg/g	
Na-X(C)	Zn(II)	323.5 mg/g	this study
	Zn(II) with DCF	28.3 mg/g	
	Zn(II) with PAA	45.5 mg/g	
Na-P1	Zn(II)	103.6 mg/g	this study
	Zn(II) with DCF	75.1 mg/g	
	Zn(II) with PAA	69.3 mg/g	
Na-P1(C)	Zn(II)	74 mg/g	this study
	Zn(II) with DCF	25.3 mg/g	
	Zn(II) with PAA	45.4 mg/g	
HC FA	Zn(II)	43.5 mg/g	this study
	Zn(II) with DCF	3.9 mg/g	
	Zn(II) with PAA	27.4 mg/g	
CSH-Mt	Zn(II) with p-nitrophenol	16.74 mg/g	Wang et al. (2021)
ECMBB	Zn(II) with methyl orange, Cd(II)	50.8 mg/g	Zhang et al. (2022)
nANB	Zn(II) with Cu(II), Cr(VI)	11.904 mg/g	Maheshwari et al. (2015)
Na-X	DCF	6.68 mg/g	this study
	DCF with Pb(II)	7.29 mg/g	
	DCF with Zn(II)	12.86 mg/g	
Na-X(C)	DCF	8.49 mg/g	this study
	DCF with Pb(II)	20.01 mg/g	
	DCF with Zn(II)	21.95 mg/g	
Na-P1	DCF	14.11 mg/g	this study
	DCF with Pb(II)	12.02 mg/g	
	DCF with Zn(II)	12.83 mg/g	

**Table 2** (continued)

Adsorbent	Adsorbates	Adsorption capacity	References
Na-P1(C)	DCF	21.19 mg/g	this study
	DCF with Pb(II)	17.24 mg/g	
	DCF with Zn(II)	19.63 mg/g	
HC FA	DCF	26.51 mg/g	this study
	DCF with Pb(II)	25.03 mg/g	
	DCF with Zn(II)	19.59 mg/g	
HSANGs	DCF with ibuprofen, ketoprofen, naproxen	19.3 mg/g	Al-Khateeb et al. (2017)
MWCNTs	DCF	19.9 mg/g	Hu et al. (2017)
ICAC	DCF	144 mg/g	Tomul et al. (2019)
OP	DCF	6.44 mg/g	
PCAC	DCF	5.51 mg/g	

of potassium (2.3%), calcium (3.7%), sulfur (1.2%), magnesium (1.5%), sodium (0.6%) and titanium (1%). The mineral composition of HC FA included quartz, mullite, hematite, unburned carbon and amorphous aluminosilicate glaze created during rapid cooling of ash performed after the coal combustion process. Complex mineral composition as well as the presence of unburned carbon contributed to developed specific surface area ( $S_{\text{BET}}$ ) of HC FA equal to 46 m<sup>2</sup>/g.

Zeolite-carbon composites, NaX(C) and NaP1(C), were created as a result of hydrothermal reaction of high-carbon fly ash with aqueous sodium hydroxide solution. For Na-P1(C), 20 kg of HC FA and 90 dm<sup>3</sup> of 3 M NaOH were used, the temperature was 90 °C, and the reaction was conducted for 24 h. For Na-P1(C), 25 kg of HC FA and 90 dm<sup>3</sup> of 3 M sodium hydroxide solution were applied, the temperature was 80 °C, and the reaction lasted 48 h. The separation of the solid phase after the zeolite-carbon composites synthesis led to the formation of silicon and aluminum-rich liquid waste, which derived from dissolved aluminosilicate glaze of HC FA. This solution was used to obtain pure NaX and NaP1 zeolites in another hydrothermal reaction. For Na-P1, 40 cm<sup>3</sup> of waste solution, 10 cm<sup>3</sup> of aqueous NaOH solution and 80 g of aluminum foil were used, the temperature was 100 °C, and the process lasted 48 h. For Na-X, 50 cm<sup>3</sup> of waste solution, 50 cm<sup>3</sup> of aqueous NaOH solution and 450 g of aluminum foil were used, the temperature was 70 °C, and the reaction was conducted for 24 h. The pure zeolite material had a monophasic structure with no ash residues.

The phase composition of zeolitic materials was checked using the XRD (X-ray diffraction) technique. The presence of zeolite NaX phase was confirmed by dhkl = 7.21; 5.05; 4.11; 3.20; 2.91; 2.69; 2.53; 2.38; 1.97 Å for NaX and NaX(C). In turn, the presence of zeolite Na-P1 phase was confirmed by dhkl = 14.44; 8.84; 5.74; 3.81; 3.34; 2.89 Å for Na-P1 and Na-P1(C). Apart from the zeolite phase, the diffraction patterns of Na-X(C) and Na-P1(C) also showed the components constituting the ash residue. They were

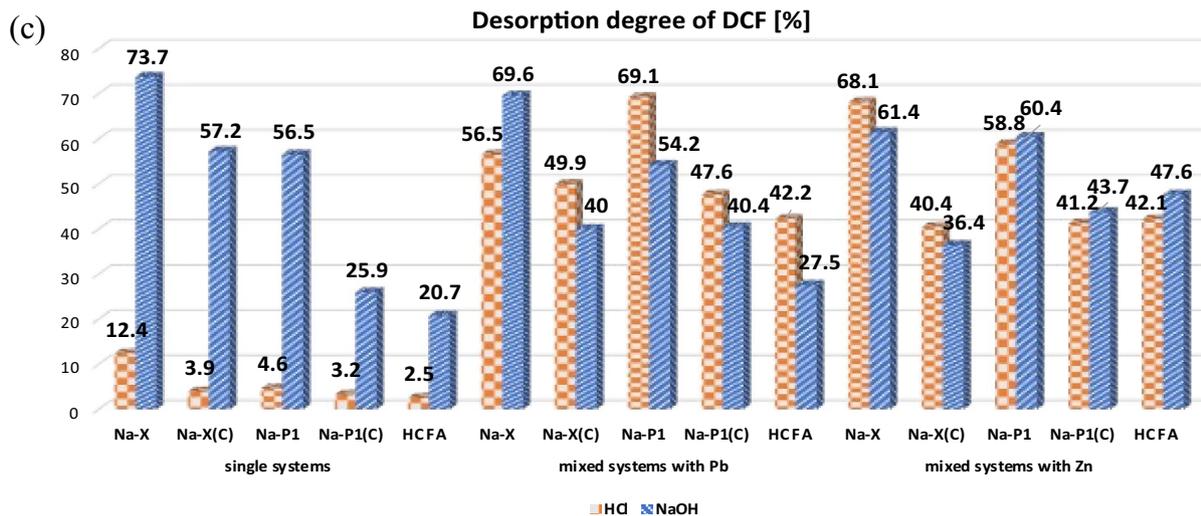
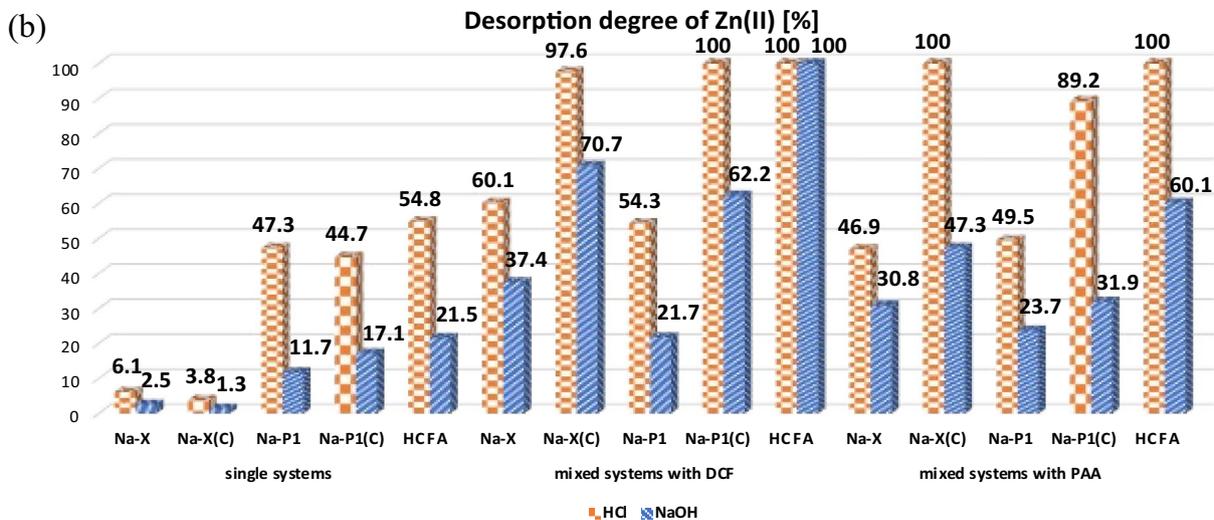
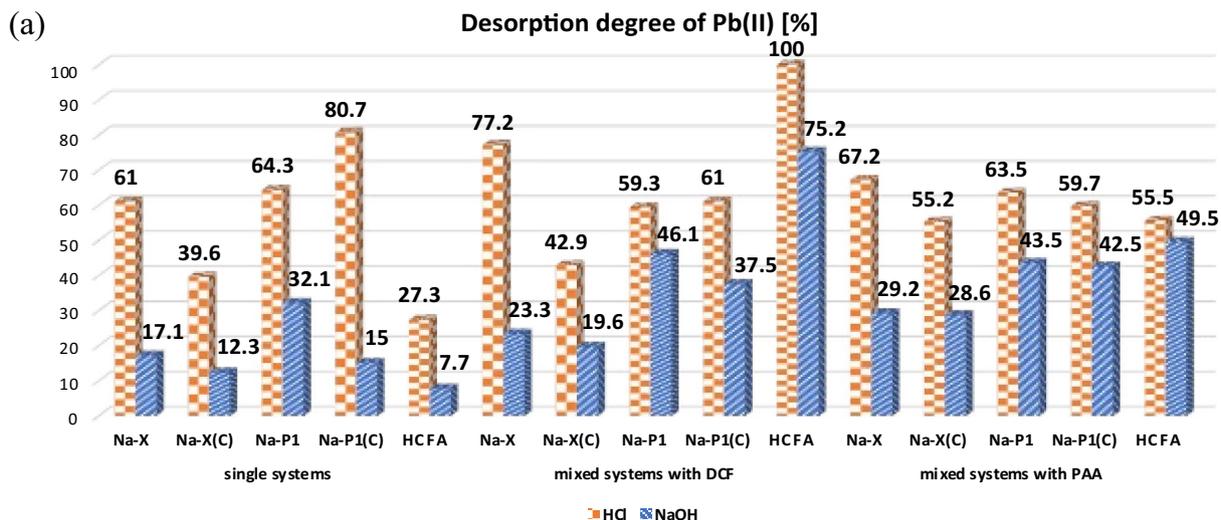
dominated by mullite (dhkl = 5.39; 3.41; 2.78; 2.58 Å), quartz (dhkl = 4.25; 3.34; 2, 45; 2.28; Å) and amorphous aluminosilicate glaze in the form of a raised background on the diffractogram in the angular range of 15–30° 2 $\theta$ .

The chemical composition of zeolitic materials was dominated by silicon (41%, 28%, 49%, 18% for Na-X, Na-X(C), Na-P1, Na-P1(C), respectively), aluminum (23%, 14%, 18%, 10% for Na-X, Na-X(C), Na-P1, Na-P1(C), respectively), sodium (3.5–8%), iron (0.5–9.3%) and small amounts of other ingredients such as magnesium, calcium, potassium, and titanium. In the case of the zeolite-carbon composite, the carbon content was also high (31.5% and 44.5% for Na-X(C) and Na-P1(C), respectively).

The porous nature of zeolitic materials translated into their developed specific surface area, which was equal to 728 m<sup>2</sup>/g, 272 m<sup>2</sup>/g, 27 m<sup>2</sup>/g and 70 m<sup>2</sup>/g for Na-X, Na-X(C), Na-P1 and Na-P1(C), respectively (Table 1).

### The influence of organic compounds on the adsorption–desorption of heavy metal ions in the aqueous suspensions of zeolitic materials

Figures 1 a, b present the adsorbed amounts of Pb(II) and Zn(II) ions with and without DCF and PAA. In the case of zeolites and their composites, the adsorption of Pb(II) ions is significantly reduced in the presence of organic compounds. It is slightly lower in the systems with PAA than in the systems with DCF. In turn, the adsorption of Pb(II) on the carbon precursor is reduced in the system containing DCF, whereas the presence of PAA results in a slight increase in the Pb(II) adsorbed amount. Similarly, the adsorption of zinc(II) ions on zeolites and their composites, but also on the carbon precursor, decreases with the addition of organic compounds to the system. In the case of Na-X and Na-P1, the decrease in the adsorbed amount of ions is slightly greater in the presence of PAA than in the presence of DCF. On the other hand, in the



**Fig. 2** Desorption degrees of: (a) Pb(II) from the surfaces of fly ash precursor, zeolite-carbon composites and pure zeolites without and in the presence of DCF or PAA, (b) Zn(II) from the surfaces of fly ash precursor, zeolite-carbon composites and pure zeolites without and in the presence of DCF or PAA, (c) DCF on the surfaces of fly ash precursor, zeolite-carbon composites and pure zeolites without and in the presence of Pb(II) or Zn(II); pH 5,  $C_{\text{Pb(II)/Zn(II)}}$  100 ppm,  $C_{\text{PAA}}$  50 ppm,  $C_{\text{DCF}}$  50 ppm

case of Na-X(C), Na-P1(C) and HC FA, the adsorption of Zn(II) ions in the presence of PAA is greater than after the addition of DCF. All above changes may result from different mechanisms of adsorption and accompanying phenomena. In such complex systems, both competition for adsorbent active sites and the formation of complexes between adsorbed molecules and ions occur certainly. As was mentioned above, DCF and PAA are characterized by anionic nature, whereas the other adsorbate in the mixed system are in the form of divalent metal cations. Under the conditions in which the adsorption study is carried out (pH 5), the solids assume positive charge, which favors DCF/PAA adsorption and limit Pb(II)/Zn(II) binding. In the examined mixed systems, the formation of complexes between two types of adsorbate with opposite ionic character can also be present. This phenomenon contributes to the reduction of the adsorption of heavy metal ions. Moreover, the adsorption of big organic molecules and small inorganic ions can lead to the blockade of solid active sites by the first ones. Then, the entrance to the pores is inaccessible to heavy metal ions. The radius of hydrated Pb ions is 0.401 nm, and the radius of hydrated Zn ions is 0.430 nm (Oter and Akcay, 2007). On the other hand, the hydrodynamic radius ( $r_h$ ) of PAA is about 2.7 nm (Wiśniewska et al., 2013a), and the  $r_h$  of most drugs is in the range of 0.5–5 nm (Axpe et al., 2019). The blockade of ions can occur during the adsorption of organic substance-metal complexes – both of intramolecular and intermolecular structure. The affinity of these complexes to the surface is not as high as that of organic molecules. Heavy metal ions neutralize negative charge of DCF or PAA and, as a consequence, the complexes formed are not attracted to the surface of zeolitic materials effectively.

The measured adsorbed amounts of both inorganic and organic pollutants on zeolitic materials can be considered satisfactory. In the single and multicomponent systems, they were higher than those determined for other adsorbents. The comparison of adsorption capacities of HC FA, prepared zeolitic materials and other adsorbents described in the literature was made in the form of (Table 2).

Percentage desorption of pollutants caused by HCl and NaOH in the examined systems containing lead(II) and zinc(II) ions with and without DCF or PAA is shown in Figs. 2a and 2b. Such desorbing agents are the most commonly used substances for adsorbent regeneration. The

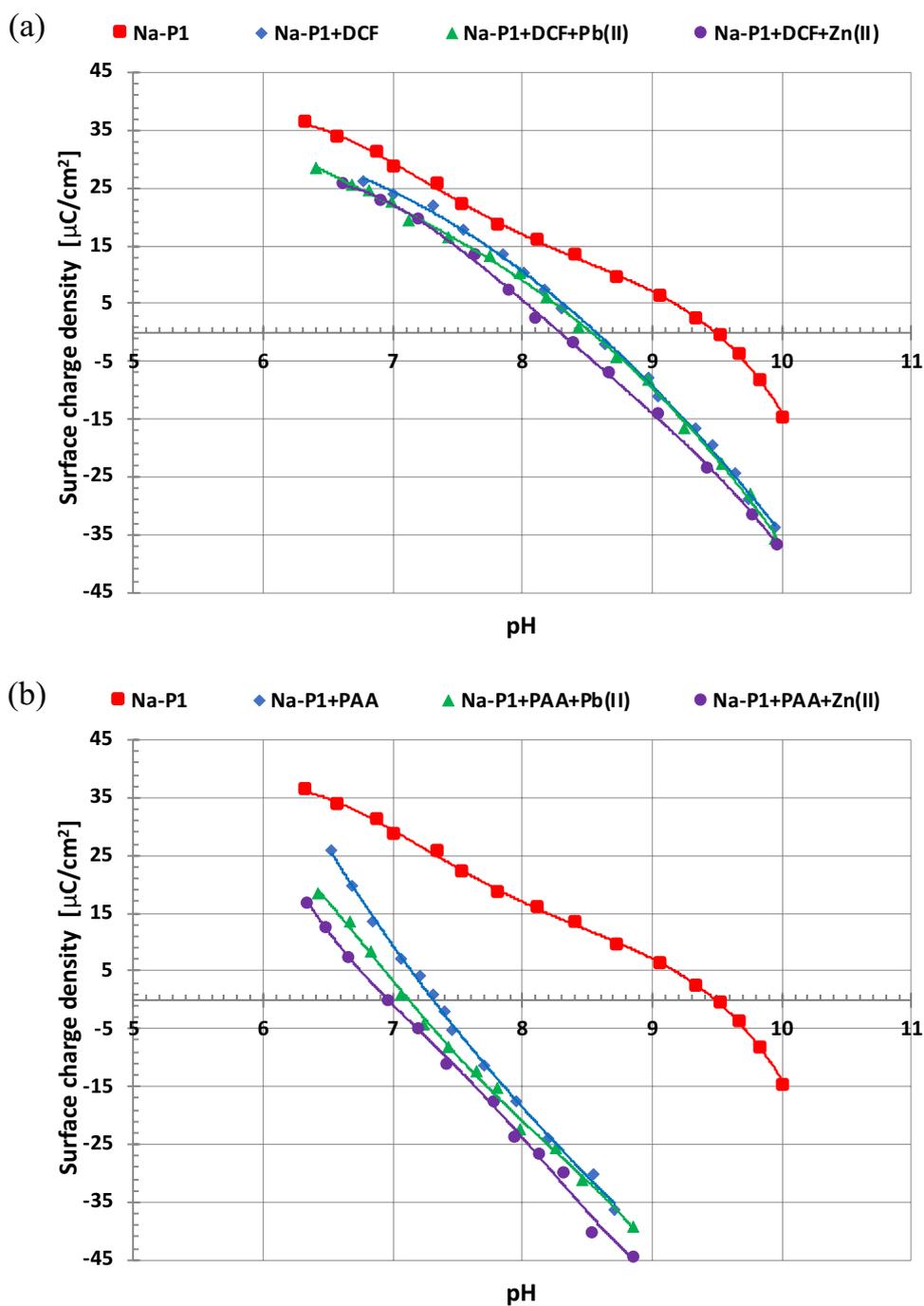
previous studies indicated that the desorption of inorganic and organic pollutants from different adsorbents using water was minimal (Szewczuk-Karpisz et al., 2022; Tomczyk and Szewczuk-Karpisz, 2022). In the examined systems, considerably higher desorption occurs when HCl is used as the desorbing agent. Such tendency is observed for both single and mixed solutions with organic compounds. In most systems, greater desorption occurs in the samples in which adsorption was rather small, that is, in those in which the binding of metal ions to the surface of porous materials is weak. The suspensions containing Zn(II) ions are characterized by higher desorption in comparison to that occurred in analogous systems with Pb(II) ions.

### The influence of divalent cations on the adsorption–desorption of diclofenac in the aqueous suspensions of zeolitic materials

The comparison of adsorbed amounts of diclofenac with and without Pb(II) and Zn(II) ions is presented in Fig. 1c. In the systems containing Na-X and Na-X(C), the addition of Pb(II) and Zn(II) ions noticeably increases the adsorption of the drug molecules. For both materials, the presence of zinc(II) increases the adsorption of zinc(II) to greater extent than lead(II). In contrast, in the systems containing HC FA, Na-P1 and Na-P1(C), the addition of heavy metals causes decrease in the DCF adsorption. In the case of Na-P1 and its composite, this decrease is more visible with Pb(II) ions than with Zn(II) ions, whereas in the case of HC FA, this trend is opposite. As it was mentioned in the previous section, the adsorption of pollutants in their mixed systems is driven by various factors. The favored binding of DCF in the systems containing heavy metal ions may be caused by electrostatic attraction between them and the solid surface as well as by the formation of DCF-Pb(II) or DCF-Zn(II) complexes. In the examined solutions, the creation of intermolecular complexes, in which one divalent cation interacts with two drug molecules, is more probable. The hydrophobic forces and hydrogen bonds can also be responsible for diclofenac adsorption on the surface of zeolitic materials (Li et al., 2021). The slight decrease in adsorption due to the addition of heavy metals to the systems containing Na-P1, Na-P1(C) and HC FA may also be related to the formation of complexes. The mean pore sizes of these solids are in the range of 5.7–6.9 nm (Table 1), which allows effective adsorption of DCFs with a size of  $0.97 \times 0.98$  nm and area of  $0.52 \text{ nm}^2$  (Sotelo et al., 2014). The intermolecular complexes of DCF with Pb(II) or Zn(II) ions can be too large to effectively penetrate the pores.

The comparison of percentage desorption of diclofenac caused by hydrochloric acid and sodium hydroxide from the surface of the examined materials with and without

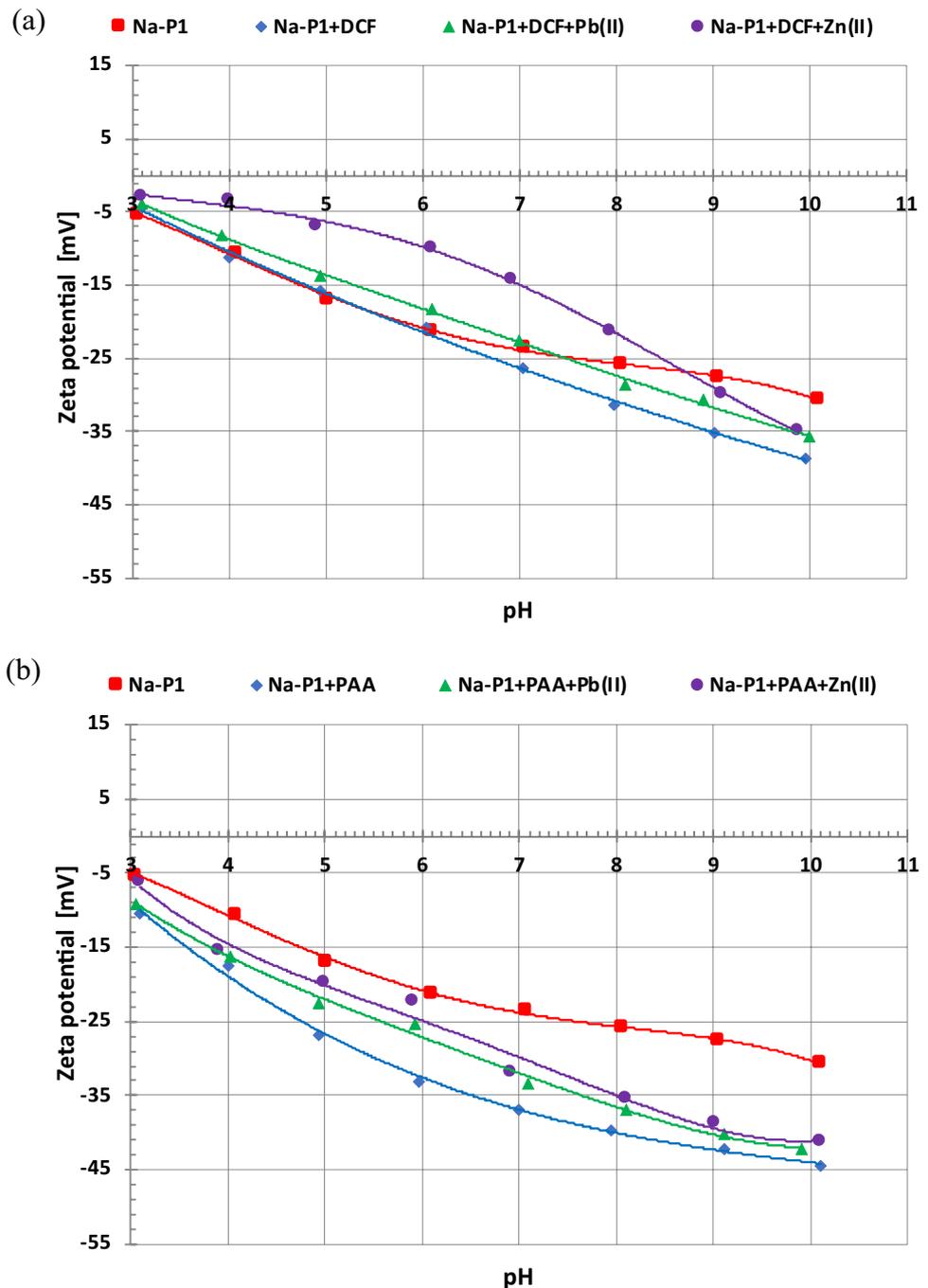
**Fig. 3** Surface charge density of Na-P1 particles as a function of pH without and in the presence of: (a) DCF, (b) PAA and Zn(II) or Pb(II) ions;  $C_{Pb(II)/Zn(II)}$  10 ppm,  $C_{PAA}$  50 ppm,  $C_{DCF}$  50 ppm



**Table 3** Points of zero charge (pzc) of fly ash, zeolites and its carbon composites with and without adsorbates

Adsorbent	pzc without adsorbates	pzc with DCF	pzc with DCF and Pb(II)	pzc with DCF and Zn(II)	pzc with PAA	pzc with PAA and Pb(II)	pzc with PAA and Zn(II)
HC FA	9.5	9.0	8.9	8.0	7.5	7.0	6.5
Na-X	9.0	8.5	8.4	8.2	8.0	7.8	7.6
Na-X(C)	8.5	7.8	7.5	7.5	7.3	6.8	6.3
Na-P1	9.5	8.6	8.5	8.3	7.3	7.1	6.9
Na-P1(C)	8.8	7.6	7.5	7.4	7.3	7.1	7.0

**Fig. 4** Zeta potential of Na-P1 particles as a function of pH without and in the presence of: (a) DCF, (b) PAA and Zn(II) or Pb(II) ions;  $C_{\text{Pb(II)/Zn(II)}}$  10 ppm,  $C_{\text{PAA}}$  50 ppm,  $C_{\text{DCF}}$  50 ppm

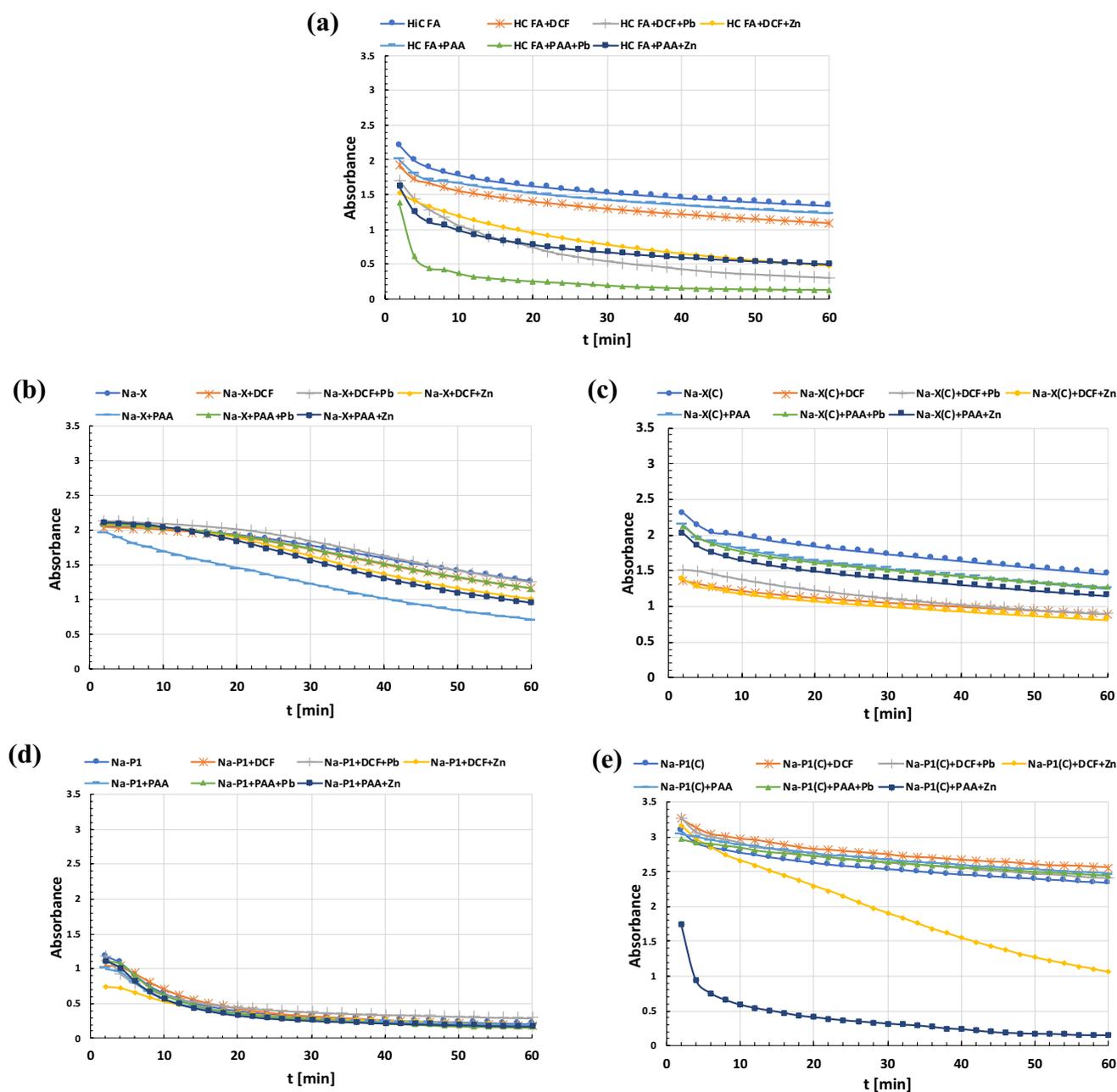


heavy metal ions is given in Fig. 2c. In the single systems of adsorbates, more efficient desorption occurs with NaOH, whereas in the mixed ones, HCl proves to be the preferable desorbing agent. This tendency is not observed in the systems containing Na-X and lead(II) ions as well as in the systems of Na-P1(C) or HC FA with zinc(II) ions. In these 3 cases, slightly more efficient desorption takes place in the NaOH presence. In the single systems, where diclofenac is the only adsorbate, NaOH is a better desorbent due to higher affinity of the acidic

carboxyl groups present in the drug molecule. In the mixed systems, this affinity is not so significant due to the neutralization of carboxyl groups by heavy metal ions.

#### Electrokinetic study of zeolitic materials modified by adsorption layers of small divalent cations and organic compounds

The effect of organic compounds and heavy metal cations on surface charge density ( $\sigma_0$ ) of Na-P1(C) is presented



**Fig. 5** Absorbance of the suspensions in the function of time of: (a) HC FA, (b) Na-X (c) Na-X(C), (d) Na-P1 and (e) Na-P1(C) without and in the presence of Zn(II) or Pb(II) and DCF or PAA; pH=5,  $C_{\text{Pb(II)/Zn(II)}}$  100 ppm,  $C_{\text{PAA}}$  50 ppm,  $C_{\text{DCF}}$  50 ppm

in Figs. 3a and 3b. Similar tendencies were obtained for all investigated solids. The results of the potentiometric titration are presented as a function of solution pH value. These curves allowed determination of the points of zero charge (pzc) of the examined solids. The pzc parameter indicates the pH value, at which the concentrations of positively and negatively charged surface groups are the same ( $\sigma_0=0$ ). At  $\text{pH} > \text{pzc}$ , the solid surface charge is negative, and at  $\text{pH} < \text{pzc}$ , it is positive. Under the conditions in which adsorption is conducted (pH 5), the investigated

solid assumes positive sign of charge. This means that the adsorption of both diclofenac and poly(acrylic acid) is favored electrostatically due to their anionic character. The opposite tendency occurs for the cations of lead(II) and zinc(II), which are repelled from positively charged surface of zeolitic materials.

The addition of DCF and PAA decreases surface charge density of the solids, which is also accompanied by lowering of the pzc value. The points of zero charge of the examined suspensions are summarized in Table 3. In the case of the

Na-P1 zeolite, there is a decrease from a value of 9.5 to 8.6 after the addition of DCF and to 7.3 after the addition of PAA. Furthermore, the addition of Pb(II) or Zn(II) ions to the Na-P1 suspension results in even greater decrease in this parameter. For the system of DCF and Pb(II), pzc is equal to 8.5, for the system of DCF and Zn(II), 8.3, for the system of PAA and Pb(II), 7.1, whereas for the system of PAA and Zn(II), 6.9. This is most likely caused by the combination of effects accompanying the adsorption of metal cations and anionic macromolecular compounds. The described above complexes' formation is very important here (Wiśniewska et al., 2021a, b). The addition of zinc(II) or lead(II) ions alone usually decreases surface charge density of the solids. This is due to the interaction of these cations with hydroxyl groups of zeolitic materials resulting in the formation of additional number of negatively charged surface groups (Fijałkowska et al., 2019, 2020a, 2020b; Skwarek et al., 2014). But, in the case of adsorption of large anionic molecules including long-chain polymers or drug molecules, the decrease in surface charge density is related to the existence of negatively charged groups belonging to PAA or DCF in the near-surface layer of the solution. They are not directly bound to the surface of porous materials and thus other interactions, besides electrostatic forces, can affect their adsorption (Nibou et al., 2010). In summary, the effect of adsorbate on surface charge density of the examined solids is strictly dependent on the adsorbate type, i.e., ionic character and molecular size, as well as it is closely associated with the formation of adsorbates complexes.

The changes in zeta potential ( $\zeta$ ) of the Na-P1 zeolite as a function of solution pH value in the single systems of DCF or PAA and the mixed ones containing also Pb(II) or Zn(II) ions are presented in Figs. 4a and 4b. All tendencies discussed in the systems of Na-P1 are similar to those occurring for other investigated adsorbents. For Na-P1, it is impossible to determine the isoelectric point (iep). This parameter indicates the pH value, at which the concentrations of positively and negatively charged ions in the area of slipping plane are the same ( $\zeta = 0$ ). The zeta potential of the Na-P1 particles assumes only negative values, that is, negatively charged groups prevail in the slipping plane area. An increase in zeta potential is observed after the DCF addition to the system (in the pH range of 3–7). The addition of Pb or Zn cations to the Na-P1 suspension induced smaller increase in zeta potential than DCF. In contrast, the addition of PAA as well as PAA together with Pb(II) or Zn(II) decreases the zeta potential values. This decrease is smaller in the mixed systems containing also metal cations. All noted changes in the  $\zeta$  parameter are associated with the adsorbates' complexation described in the previous subchapters. The passage of electrolyte counter ions ( $\text{Na}^+$ ) from the surface layer to the diffusion part of the electrical double layer (edl) is responsible for the increase of the zeta potential after the

DCF addition. In contrast, the decrease caused by the addition of PAA is related to the presence of negatively charged carboxyl groups of the polymer in the slipping plane area. The addition of PAA reduce the zeta potential also due to the shift of slipping plane area from the solid by adsorbed macromolecules (Wiśniewska et al., 2015; M'Pandou and Siffert, 1987).

Electrokinetic potential is also considered as parameter determining the stability of colloidal systems. A stable suspension has an absolute  $\zeta$  value in excess of 30 mV. Nevertheless, this rule refers only to the systems containing small inorganic ions.

### Stability of zeolitic materials suspensions without and in the presence of organic compounds and heavy metal cations

The stability of suspensions is directly related to the structure of electrical double layer. It varies according to the proportion of ions present in the specific layers (of Stern, Helmholtz etc.). The stability of the examined suspensions was investigated by spectrophotometric method. Figures 5a, b, c, d, e present the absorbance over time for the systems of HC FA, Na-X, Na-X(C), Na-P1 and Na-P1(C) with and without adsorbates. At the pH close to pzc, the systems exhibit decreasing stability, which is visible in the absorbance curves. Their analysis indicated that in most cases the stability decreases after the addition of adsorbates. The most stable suspension without additives is noted for the Na-P1(C) composite (Fig. 5e). The stability deteriorates considerably in the systems containing PAA + Zn(II) and DCF + Zn(II) (especially over time). For the other systems investigated, the stability decreases with the addition of adsorbates, although a slight increase is sometimes observed in the systems containing only DCF or DCF with metals. Various effects can occur in such complex solutions. Polymer bridges can be formed when one long chain of the polymer adsorbs onto at least two solid particles. This phenomenon is called flocculation and leads to formation of sedimenting aggregates (Gelardi and Flatt, 2016). The segments of polymer chain create 'loops' and 'tails' on the solid surface, and the bridging is possible when their length exceeds the range of electrostatic repulsive forces occurring between the particles. Additionally, the surface cannot be entirely covered by the adsorbed polymer. In the mixed adsorption layers, the steric and electrosteric mechanisms are mainly responsible for the suspension stabilization (Wiśniewska et al., 2013b). The most unstable system proved to be the one with Na-P1 zeolite without and with the addition of heavy metals and/or diclofenac or poly (acrylic acid). The lack of adequate stabilization of suspensions results in more efficient separation of the solid with the adsorbates from the solution. This phenomenon was observed in the examined systems

and thus it can be considered that the zeolites and its carbon composites form easily separable suspensions (Wiśniewska et al., 2021a, b; Riddick, 1968).

## Conclusions

Energy waste—high carbon fly ash, was transformed and used as adsorbents to remove other environmental pollutants. Both Na-X, Na-P1 zeolites and their Na-X(C), Na-P1(C) carbon composites are effective materials for simultaneous separation of hazardous heavy metal ions and undesirable organic molecules from aqueous solutions. The highest adsorbed amounts of heavy metals are observed for Na-X, i.e., 322.1 mg/g of Pb(II), 332.5 mg/g of Zn(II). In the case of Na-P1 zeolite, these amounts were 332.9 mg/g and 103.6 mg/g for Pb(II) and Zn(II), respectively. The adsorption in the multicomponent systems of pollutants is different. The main mechanism governing the adsorption process in such systems are: the competition for adsorbent active sites and the formation of complexes between adsorbates with opposite ionic nature. Each of these phenomena contributes to the reduction of the adsorption of heavy metal ions. In the DCF presence, the Pb(II) adsorption on Na-X decreased to 98.7 mg/g, whereas that on Na-P1 to 99.7 mg/g. However, the heavy metal addition increases the adsorption of the selected drug. With Pb(II) ions, the DCF adsorbed amount on Na-X increased from 6.68 mg/g to 12.86 mg/g, and that on Na-X(C) raises from 8.49 mg/g to 21.95 mg/g. The zeolites and its carbon composites generally form easily separable suspensions. Moreover, the synthesized adsorbents can be successfully regenerated with hydrochloric acid.

Based on these results, it can be stated that the described treatment of toxic fly ash is a very suitable way to prevent its accumulation in the environment. The synthesized fly ash-based zeolitic adsorbents are effective materials for simultaneous separation of heavy metals and organic molecules from wastewater.

**Author contributions** Conceptualization, R.P.; methodology, M.M., K.S.K., M.W. and R.P.; software, M.M. and R.P.; validation, K.S.K., R.P. and M.W.; formal analysis, R.P., M.F. and M.W.; investigation, M.M., K.S.K., M.W. and R.P.; resources, R.P.; data curation, M.W., M.F. and R.P.; writing—original draft preparation, M.M., K.S.K. and M.F.; writing—review and editing, M.M., K.S.K. and M.W.; visualization, R.P. and M.M.; supervision, M.W. and R.P.; project administration, R.P.; funding acquisition, R.P. All authors have read and agreed to the published version of the manuscript.

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## Declarations

**Competing interests** The authors have not disclosed any competing interests.

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## References

- Ahmaruzzaman M (2010) A review on the utilization of fly ash. *Prog Energy Combust Sci* 36(3):327–363
- Akgerman A, Zardkoohi M (1996) Adsorption of phenolic compounds on fly ash. *J Chem Eng Data* 41(2):185–187
- Alam J, Akhtar MN (2011) Flyash as a resource material in construction industry: a clean approach to environment management. *Int J Emerg Trends Eng Dev* 1(1):1–14
- Al-Khateeb LA, Hakami W, Salam MA (2017) Removal of non-steroidal anti-inflammatory drugs from water using high surface area nanographene: kinetic and thermodynamic studies. *J Mol Liq* 241:733–741
- Axpe E, Chan D, Offeddu GS, Chang Y, Merida D, Henandez HL, Appel EA (2019) A multiscale model for solute diffusion in hydrogels. *Macromolecules* 52(18):6889–6897
- Bailey SE, Olin TJ, Bricka RM, Adrian DD (1999) A review of potentially low-cost sorbents for heavy metals. *Water Res* 33(11):2469–2479
- Bandura L, Panek R, Madej J, Franus W (2021) Synthesis of zeolite-carbon composites using high-carbon fly ash and their adsorption abilities towards petroleum substances. *Fuel* 283:119173
- Banerjee SS, Joshi MV, Jayaram RV (2005) Removal of Cr(VI) and Hg(II) from aqueous solutions using fly ash and impregnated fly ash. *Sep Sci Technol* 39(7):1611–1629
- Blanchard G, Maunaye M, Martin G (1984) Removal of heavy metals from waters by means of natural zeolites. *Water Res* 18(12):1501–1507
- Chen B, Chen S, Zhao H, Liu Y, Long F, Pan X (2018) A versatile  $\beta$ -cyclodextrin and polyethyleneimine bi-functionalized magnetic nano-adsorbent for simultaneous capture of methyl orange and Pb(II) from complex wastewater. *Chemosphere* 216:605–616
- Davis TA, Volesky B, Mucci A (2003) A review of the biochemistry of heavy metal biosorption by brown algae. *Water Res* 37(18):4311–4330
- Dwivedi A, Jain MK (2014) Fly ash—waste management and overview: a review. *Recent Res Sci Technol* 6(1):30–35
- Fijałkowska G, Szewczuk-Karpisz K, Wiśniewska M (2019) Chromium(VI) and lead(II) accumulation at the montmorillonite/aqueous solution interface in the presence of polyacrylamide containing quaternary amine groups. *J Mol Liq* 293:111514

- Fijałkowska G, Szewczuk-Karpisz K, Wiśniewska M (2020a) Anionic polyacrylamide as a substance strengthening the Pb(II) immobilization on the kaolinite surface. *Int J Environ Sci Technol* 17:1101–1112
- Fijałkowska G, Szewczuk-Karpisz K, Wiśniewska M (2020b) Anionic polyacrylamide influence on the lead(II) ion accumulation in soil—the study on montmorillonite. *J Environ Health Sci Eng* 18(2):599–607
- Franus W, Wdowin M, Franus M (2014) Synthesis and characterization of zeolites prepared from industrial fly ash. *Environ Monit Assess* 2014(186):5721–5729
- Gelardi G, Flatt RJ (2016) Working mechanisms of water reducers and superplasticizers. In: Flatt R (ed) *Science and technology of concrete admixtures*. Woodhead publishing, New York, pp 257–278
- Hu X, Cheng Z, Sun Z, Zhu H (2017) Adsorption of diclofenac and triclosan in aqueous solution by purified multi-walled carbon nanotubes. *Pol J Environ Stud* 26(1):87–95
- Huang L, Zhou Y, Guo X, Chen Z (2015) Simultaneous removal of 2,4-dichlorophenol and Pb(II) from aqueous solution using organoclays: isotherm, kinetics and mechanism. *J Ind Eng Chem* 22:280–287
- Janusz W (1999) Electrical double layer at the metal oxide–electrolyte interface. In Dekker M (ed) *Interfacial forces and fields: theory and applications*. New York, vol 85, Chap. 4
- Jodeh S, Abdelwahab F, Jaradat N, Warad I, Jodeh W (2016) Adsorption of diclofenac from aqueous solution using *Cyclamen persicum* tubers based activated carbon (CTAC). *J Assoc Arab Univ Basic Appl Sci* 20(1):32–38
- Jutakradsada P, Prajaksud C, Kuboonya-Aruk L, Theerakulpisut S, Kamwilaisak K (2016) Adsorption characteristics of activated carbon prepared from ground coffee. *Clean Technol Environ Policy* 18:639–645
- Khader EH, Mogammed TJ, Mirghaffari N, Salman AD, Jzszakova T, Abdullah TA (2022) Removal of organic pollutants from produced water by batch adsorption treatment. *Clean Technol Environ Policy* 24:713–720
- Kusum SA, Pour-Ghaz M, Ducoste JJ (2020) Reducing Fat, Oil, and Grease (FOG) deposits formation and adhesion on sewer collection system structures through the use of fly ash replaced cement-based materials. *Water Research* 186:116304
- Li S, Gan Y, Shah SJ, Wang R, Gong W, Wei R, Ji H, Zhao Z, Zhao Z (2021) Engineering NSAIDs imprinted UiO-66s for markedly enhanced adsorption of coexisting diclofenac sodium and Cu(II) and their synergistic adsorption mechanism. *Chem Eng J* 426:131440
- Lin Z, Weng X, Owens G, Chen Z (2019) Simultaneous removal of Pb(II) and rifampicin from wastewater by iron nanoparticles synthesized by a tea extract. *J Clean Prod* 242:118476
- M'Pandou A, Siffert B (1987) Polyethylene glycol adsorption at the TiO<sub>2</sub>-H<sub>2</sub>O interface: distortion of ionic structure and shear plane position. *Colloids Surf A* 4:159–172
- Maheshwari U, Mathesan B, Gupta S (2015) Efficient adsorbent for simultaneous removal of Cu(II), Zn(II) and Cr(VI): kinetic, thermodynamics and mass transfer mechanism. *Process Saf Environ Prot* 98:198–210
- Mazaheri H, Ghaedi M, Hajati S, Dashtian K, Purkait MK (2015) Simultaneous removal of methylene blue and Pb<sup>2+</sup> ions using ruthenium nanoparticle-loaded activated carbon: response surface methodology. *RSC Adv* 5(101):83427–83435
- Merrikhpour H, Jalali M (2013) Comparative and competitive adsorption of cadmium, copper, nickel, and lead ions by Iranian natural zeolite. *Clean Technol Environ Policy* 15:303–316
- Nibou D, Mekatel H, Amokrane S, Barkat M, Trari M (2010) Adsorption of Zn<sup>2+</sup> ions onto NaA and Na-X zeolites: kinetic, equilibrium and thermodynamic studies. *J Hazard Mater* 173:637–646
- Oshima H (1994) A simple expansion for Henry's function for the retardation effect in electrophoresis of spherical colloidal particles. *J Colloid Interface Sci* 168:269–271
- Oter O, Akcay H (2007) Use of natural clinoptilolite to improve water quality: sorption and selectivity studies of lead(II), zinc(II), and nickel(II). *Water Environ Res* 79(3):329–335
- Panek R, Wdowin M, Bandura L, Wisła-Walsh E, Gara P, Franus W (2017) Changes in the textural parameters of fly ash-derived Na-P1 zeolite during compaction processes. *Mineralogia* 48(1–4):3–22
- Panek R, Medykowska M, Szewczuk-Karpisz K, Wiśniewska M (2021a) Comparison of physicochemical properties of fly ash precursor, Na-P1(C) zeolite-carbon composite and Na-P1 zeolite—adsorption affinity to divalent Pb and Zn cations. *Materials* 14(11):3018
- Panek R, Medykowska M, Wiśniewska M, Szewczuk-Karpisz K, Jedruchiewicz K, Franus M (2021b) Simultaneous removal of Pb<sup>2+</sup> and Zn<sup>2+</sup> heavy metals using fly ash Na-X zeolite and its carbon Na-X(C) composite. *Materials* 14(11):2832
- Riddick TM (1968) Control of colloid stability through zeta potential. Livingston Pub Co Edition, Wynnewood PA
- Sahoo PK, Kim K, Powell MA, Equeenuddin SM (2016) Recovery of metals and other beneficial products from coal fly ash: a sustainable approach for fly ash management. *Int J Coal Sci Technol* 3(3):267–283
- Skwarek E, Janusz W, Sternik D (2014) Adsorption of citrate ions on hydroxyapatite synthesized by various methods. *J Radioanal Nucl Chem* 299:2027–2036
- Sotelo JL, Ovejero G, Rodríguez A, Álvarez S, Galán J, García J (2014) Competitive adsorption studies of caffeine and diclofenac aqueous solutions by activated carbon. *Chem Eng J* 240:443–453
- Sun D, Zhang X, Wu Y, Liu X (2010) Adsorption of anionic dyes from aqueous solution on fly ash. *J Hazard Mater* 181(1–3):335–342
- Szewczuk-Karpisz K, Bajda T, Tomczyk A, Kuśmierz M, Komaniecka I (2022) Immobilization mechanism of Cd<sup>2+</sup>/HCrO<sub>4</sub><sup>-</sup>/CrO<sub>4</sub><sup>2-</sup> ions and carboxin on montmorillonite modified with *Rhizobium leguminosarum* by trifolii exopolysaccharide. *J Hazard Mater* 428:128228
- Ternes TA (1998) Occurrence of drugs in German sewage treatment plants and rivers. *Water Res* 32(11):3245–3260
- Tomczyk A, Szewczuk-Karpisz K (2022) Effect of biochar modification by vitamin c, hydrogen peroxide or silver nanoparticles on its physicochemistry and tetracycline removal. *Materials* 15(15):5379
- Tomul F, Arslan Y, Başoğlu FT, Babuçoğlu Y, Tran HN (2019) Efficient removal of anti-inflammatory from solution by Fe-containing activated carbon: adsorption kinetics, isotherms, and thermodynamics. *J Environ Manage* 238:296–306
- Usman M, Ahmed A, Ji Z, Yu B, Shen Y, Cong H (2021) Environmentally friendly fabrication of new β-Cyclodextrin/ZrO<sub>2</sub> nanocomposite for simultaneous removal of Pb(II) and BPA from water. *Sci Total Environ* 784:147207
- Wang G, Xiao H, Zhu J, Zhao H, Liu K, Ma S, Zhang S, Komarneni S (2021) Simultaneous removal of Zn<sup>2+</sup> and p-nitrophenol from wastewater using nanocomposites of montmorillonite with alkyl-ammonium and complexant. *Environ Res* 201:111496
- Wdowin M, Franus M, Panek R, Bandura L, Franus W (2014) The conversion technology of fly ash into zeolites. *Clean Technol Environ Policy* 16:1217–1223
- Wiśniewska M, Nosal-Wiercińska A, Dąbrowska I, Szewczuk-Karpisz K (2013a) Effect of the solid pore size on the structure of polymer film at the metal oxide/polyacrylic acid solution interface—Temperature impact. *Micropor Mesopor Mater* 175:92–98
- Wiśniewska M, Urban T, Grządka E, Zarko VI, Gun'ko V.M. (2013) Comparison of adsorption affinity of polyacrylic acid for surfaces of mixed silica–alumina. *Colloid Polymer Sci* 292(3):699–705

- Wiśniewska M, Chibowski S, Urban T (2015) Impact of polyacrylamide with different contents of carboxyl groups on the chromium (III) oxide adsorption properties in aqueous solution. *J Hazard Mater* 283:815–823
- Wiśniewska M, Nowicki P, Szewczuk-Karpisz K, Gęca M, Jędruchiewicz K, Oleszczuk P (2021a) Simultaneous removal of toxic Pb(II) ions, poly(acrylic acid) and Triton X-100 from their mixed solution using engineered biochars obtained from horsetail herb precursor—Impact of post-activation treatment. *Sep Purif Technol* 276:119297
- Wiśniewska M, Nowicki P, Urban T (2021b) Influence of surfactants with different ionic character on the structure of poly(acrylic acid) adsorption layer on the activated biocarbons surface—electrokinetic and stability studies. *J Mol Liq* 332:115872
- Zhang H, Li R, Zhang Z (2022) A versatile EDTA and chitosan bifunctionalized magnetic bamboo biochar for simultaneous removal of methyl orange and heavy metals from complex wastewater. *Environ Pollut* 293:118517
- Zhou C, Gao Q, Luo W, Zhou Q, Wang H, Yan C (2015) Preparation, characterization and adsorption evaluation of spherical mesoporous Al-MCM-41 from coal fly ash. *J Taiwan Inst Chem Eng* 52:147–157

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