

# Study of the nanostructure of the mixed adsorption layer of heavy metal and diclofenac on the surfaces of synthetic zeolites and their carbon composites



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Applied adsorbents: zeolite-carbon composites (Na-X(C), Na-P1(C)) were obtained by hydrothermal reaction of an aqueous solution of sodium hydroxide and a by-product of coal combustion - high-carbon fly ash (HC FA). Then, pure synthetic zeolites (Na-X, Na-P1) were derived from post-reaction waste rich in silicon and aluminum. They were used for adsorptive removal of heavy metals (lead(II), zinc(II)), poly(acrylic acid) (PAA) and the anti-inflammatory drug diclofenac (DCF) from mixed systems. In order to describe the mechanisms of binding of adsorbate molecules and ions to the surface of the solids studied, electrokinetic measurements were carried out. To determine the isoelectric point (iep) and zeta potential of the examined suspensions, electrophoretic mobility measurements were performed using a Nano ZS zetameter (*Malvern Instruments, Cambridge, UK*) equipped with an immersion dip cell. To determine the point of zero charge (pzc) and surface charge density of the studied suspensions, potentiometric titrations were carried out. An automatically controlled kit was used with a computer equipped with the program "titr\_v3", which calculates the surface charge density values as a function of the pH of the solution based on the volume difference of the titrant added to the test solution and the maintenance electrolyte providing the specified pH value [1].

Table 1. Points of zero charge 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)
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

The results of potentiometric titrations are summarized in Table 1, while the dependency of the zeta potential as a function of pH is presented on the example of zeolite Na-P1 in Figure 1a and 1b.

In the studied systems, under adsorption experimental conditions (pH 5), the investigated solid assumes a positive sign of charge. Thus, it can be concluded that the adsorption of both diclofenac and poly(acrylic acid) is favored electrostatically due to the anionic character of these substances. On the other hand, the opposite tendency occurs for the positively charged small cations of lead(II) and zinc(II), which repel with the positively charged surface of the zeolitic materials. The addition of organic substances lowers the pzc of the examined suspensions and the addition of small metal cations lowers this parameter even more.

An increase in zeta potential is evident during the DCF addition to the system (in the pH range 3-7). The addition of Pb or Zn cations to Na-P1 suspension results in a smaller increase in the zeta potential than in the corresponding suspension with DCF itself. In contrast, the addition of PAA as well as PAA together with Pb(II) or Zn(II) results in a decrease in the zeta potential values. However, this decrease is smaller in the case of mixed systems containing additionally metal cations.

Based on electrokinetic studies, it can be concluded that adsorbates bind to the surface of solids not only through electrostatic interactions, but also with the participation of hydrophobic forces and hydrogen bonds. The formation of complexes between adsorbates in mixed systems: anionic organic substances and divalent heavy metal cations is also significant

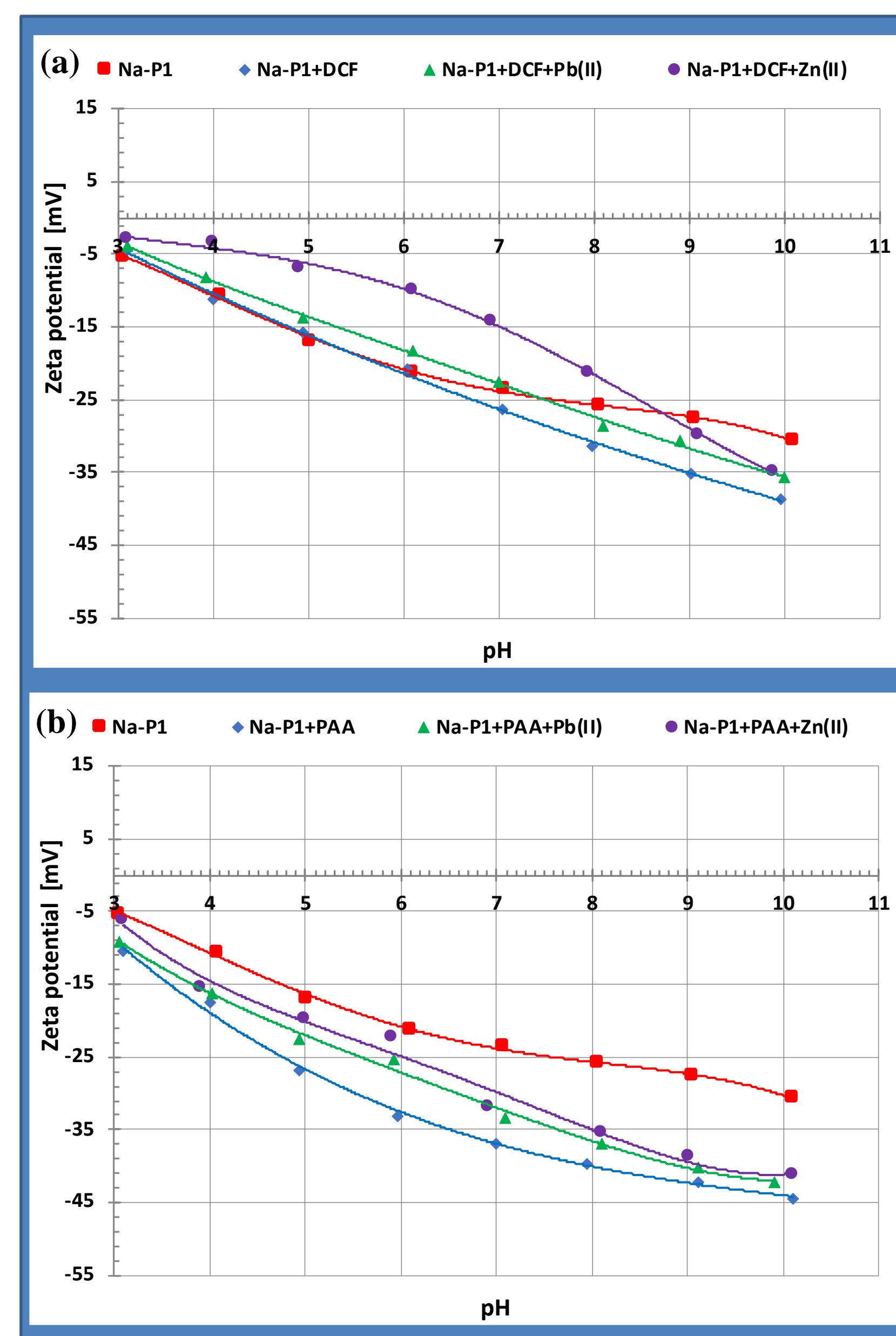


Figure 1. Zeta potential of Na-P1 particles as a function of pH without and in the presence of: (a) DCF, (b) PAA and Zn(II) or Pb(II) ions;  $C_{Pb(II)/Zn(II)}$  10 ppm,  $C_{PAA}$  50 ppm,  $C_{DCF}$  50 ppm.

1. Janusz, W., 1999. Electrical double layer at the metal oxide–electrolyte interface in “interfacial forces and fields: theory and applications”, M. Dekker, New York, vol 85, Chapter 4.

