Characterization of a Synthetic Zeolite P as a Heavy Metal Bonding Agent*

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A new treatment process aimed at water and metal reuse was developed for the selective separation of heavy metals from wastewater to reduce costs and mitigate the environmental impact of wastewater pollutants. The process was divided into the following three stages: heavy metal bonding by a bonding agent, wastewater filtration to separate the loaded bonding agent, and bonding agent regeneration. Synthetic zeolite P, selected as a bonding agent, was characterized. The results of bonding kinetics, maximum loading capacity, and bonding agent regeneration potential are presented.

Toxic metal cations or their oxoanions (*e.g.* lead, chromium, arsenic, zinc, cadmium, copper, nickel, and selenium in concentrations up to 500 mg dm^{-3}) are present in many industrial wastewater streams (the metal-working, semiconductor and copper industries, mine water, *etc.*) and must be removed prior to water discharge or water recycling. Direct discharge of this wastewater into surface water bodies presents a considerable danger to the ecosystem while discharge into the sewage system results in an adverse effect on biosludge activity, culminating in contamination of excess sludge.

The standards defined in various European Laws on Water Resources have compelled industry to implement preventative measures to combat such environmental impacts, one measure being the treatment of toxic components in a separate partial stream prior to being combined with other types of wastewater. State-of-the-art processes, such as chemical precipitation, ion-exchange bed filtration, adsorption bed filtration, and membrane processes: electrodialysis (ED), nanofiltration (NF), and reverse osmosis (RO) have numerous shortcomings for treating this type of wastewater (*e.g.* slow kinetics, inadequate selectivity) [1, 2]. Furthermore, problems are encountered in metal reuse procedures as well as in the disposal of concentrates or sludge.

In view of this, a new treatment process inspired by the possibility of water and metal reuse has been developed to reduce costs and mitigate environmental impact. The process is divided into the following three stages [3]:

1. The heavy metal is bound by adding a metal bonding agent (BA) to the wastewater.

2. Ultra-filtration/micro-filtration (variant 1, low-contaminated water) or a new hybrid process involving flotation and membrane filtration (variant 2, highly contaminated water) is applied to separate the loaded bonding agent.

3. Regeneration of the bonding agent (Fig. 1).

Implementation of this process requires the use of new bonding agents characterized by high bonding capacity and rapid bonding of heavy metals (fast kinetics), and selectivity even in the presence of other metal ions (*e.g.* Ca^{2+}, Mg^{2+}). These BA properties allow the development of smaller units for wastewater treatment meeting the individual standards for water reuse (or discharge).

Zeolites are known for their good adsorption behaviour in the liquid phase [4—6]. In the present study, a synthetic zeolite P, developed by INEOS Silicas (U.K.), was characterized and used for heavy metal separation from wastewater containing copper, nickel, and zinc ions.

EXPERIMENTAL

The synthetic zeolite P (Na$_{48}^+$(AlO$_2^-$)$_{48}$(SiO$_2$)$_{48}$ · xH$_2$O) [7] was earmarked as the bonding agent to be studied. Typical particle size of the BA sample was 2 μm and its surface area about 30 m^2 g^{-1}.

Zeolites are prepared by crystallizing an aluminosilicate gel to form very uniform structures with channels of 0.3 nm to 1 nm in diameter. Therefore,

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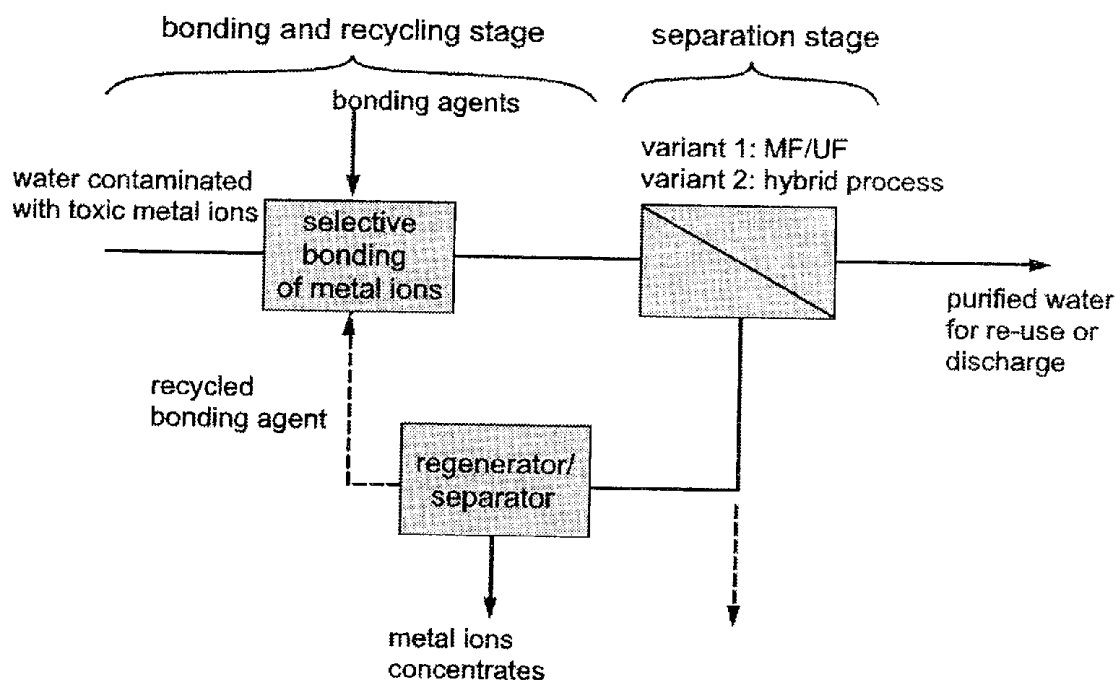
Fig. 1. Flow diagram of the new separation processes for removing toxic metals from contaminated wastewater.
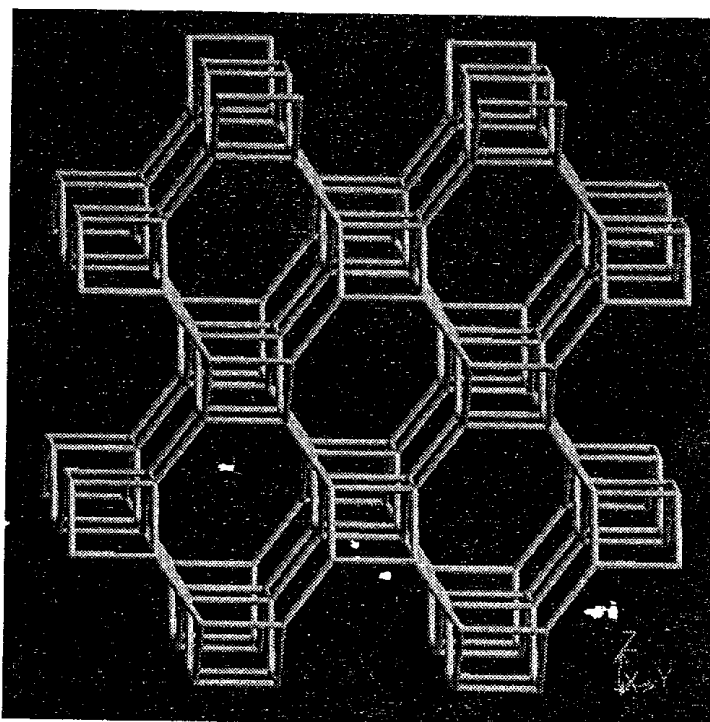

Fig. 2. Structure of the synthetic zeolite P [7].

two key differences compared to silicas are: significantly smaller pores and the totally uniform pore size (Fig. 2). Another difference is the negative surface charge of zeolites and the associated cations (usually Na$^+$), which are exchangeable for other ions.

Pore size is controlled by changing the zeolite crystal structure (indicated by the suffix letter: A, P, Y, X, etc.) and/or by changing the exchangeable ion for one of a different size; e.g. Zeolite P (also referred to as "MAP" – maximum aluminium P) has a pore di-

ameter of 0.2 nm. Zeolite pore volume tends to be low ($ca.$ 0.3 cm^3 g^{-1}) and only small molecules or ions will be able to enter its pore structure.

The treatment and characterization of the BAs were conducted as follows: A certain amount of the powdered bonding agent was dried in a vacuum-drying cabinet at 50 °C for 24 h under vacuum conditions and then stored in a desiccator.

500 mg dm^{-3} of Mg^{2+} in the form of Mg(NO$_3$)$_2$ and 500 mg dm^{-3} of Na$^+$ in the form of NaNO$_3$

added to 250 cm³ of the model solution which was used in the experiments to determine the kinetics of heavy metal bonding on BA. If necessary, the pH value of the solution was adjusted by NaOH or HNO₃ and a certain amount of bonding agent was added. Subsequently, the slurry was placed in a shaker (frequency approximately 400 min⁻¹). Samples of 1 cm³ were taken for analysis at given time intervals. Each sample was diluted with a proper amount of fully desalinated water and then routed through a membrane filter (Millipore with 0.45 μm pore diameter). Immediately after filtration all the samples were subjected to heavy-metal photometric analysis using cuvette tests (Dr. Lange – Photometer LASA 100).

During zeolite P bonding capacity measurements, the metal concentration in the solution was varied. Subsequently, 1 g cm⁻³ of bonding agent was added to the solution and left for 24 h until a steady state was established.

The pH stability of the bonding agent was determined via contact with solutions of different initial pH values. Since the structure of the bonding agent comprises Al^{3+} ions, these ions are released into the solution when the zeolite structure is altered. The content of Al^{3+} in the corresponding slurry was used for indirect BA stability measurement.

RESULTS AND DISCUSSION

The binding kinetics of commercially available bonding agents was studied in preliminary experiments to obtain information in this respect. Findings showed that none of these agents had sufficiently fast kinetics. One prerequisite of the new process is that approximately 90 % of the metal ions must be removed within roughly ten minutes.

The new bonding agent displayed very fast adsorption kinetics for heavy metals even at concentrations of more than 250 mg dm⁻³ for both copper and
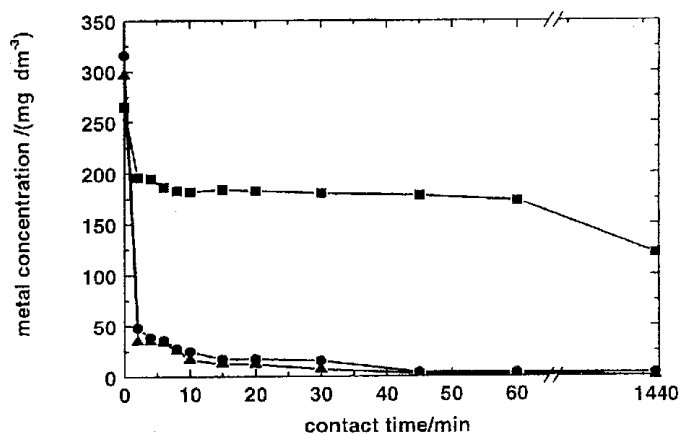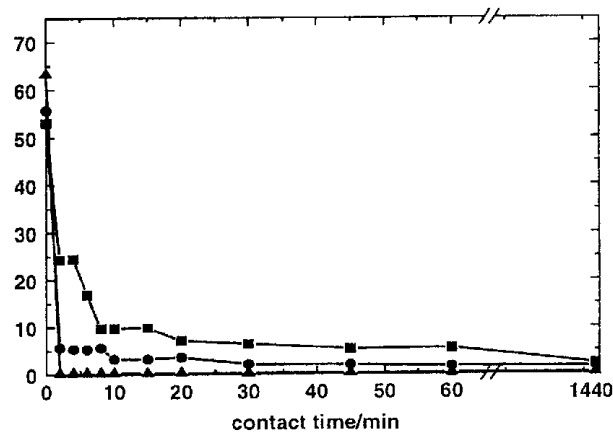
Fig. 4. Kinetics of liquid-phase adsorption of ● copper, ■ nickel, and ▲ zinc on synthetic zeolite P in the presence of competing metal ions. Initial heavy metals concentration: 250 mg dm⁻³, competing Mg^{2+} and Na^+ ions concentration: 500 mg dm⁻³ each, and BA load: 4 g dm⁻³.

Fig. 5. Kinetics of liquid-phase adsorption of ● copper, ■ nickel, and ▲ zinc on synthetic zeolite P in the presence of competing metal ions. Initial heavy metals concentration: 60 mg dm⁻³, competing Mg^{2+} and Na^+ ions concentration: 500 mg dm⁻³ each, and BA load: 4 g dm⁻³.

zinc, poorer results were obtained for nickel adsorption (Fig. 3). The presence of competing metal ions, e.g. Mg^{2+} and Na^+ at concentration of 500 mg dm⁻³ each, has only insignificant influence on the kinetics of copper and zinc adsorption on the synthetic zeolite (Fig. 4). The results of adsorption from solutions with lower initial metal concentration (approximately 60 mg dm⁻³) are shown in Fig. 5. At given conditions, also nickel adsorption was fast enough and almost complete.

The ability of a new zeolite P to bind metal ions was confirmed by determining its adsorption capacity, which was obtained by measuring the corresponding adsorption isotherms (Fig. 6). The adsorption capacity of the bonding agent towards the metal ions studied decreased in the order $Zn^{2+} \geq Cu^{2+} \gg Ni^{2+}$.
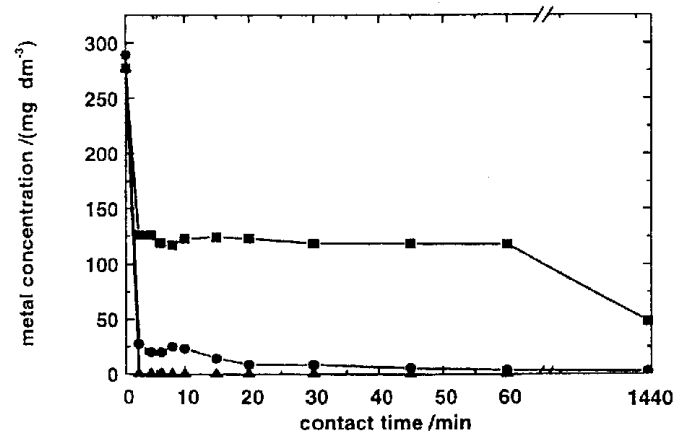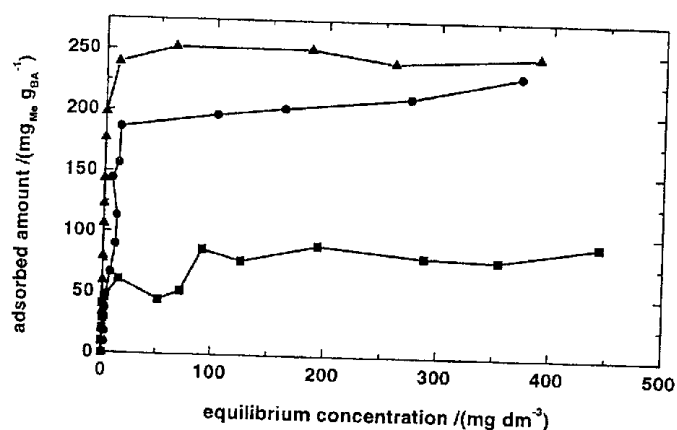
Fig. 3. Kinetics of liquid-phase adsorption of ● copper, ■ nickel, and ▲ zinc on synthetic zeolite P. Initial heavy metals concentration: 250 mg dm⁻³ and BA load: 4 g dm⁻³.

Fig. 6. Adsorption isotherms of ● copper, ■ nickel, and ▲ zinc on synthetic zeolite P in the absence of competing ions.

Table 1. Composition of the Model Wastewater Similar to that of the Real Industrial Wastewater according to the Information from an Industrial Partner

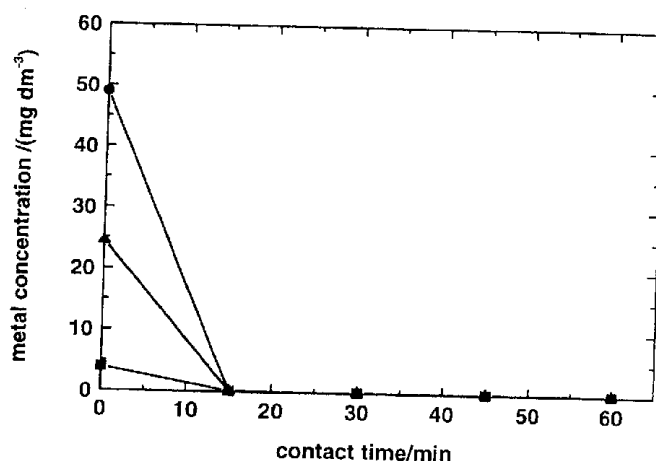| Parameters	Concentration in the wastewater	Required concentration
	mg dm^{-3}	mg dm^{-3}
Ni^{2+}	3	< 0.1
Zn^{2+}	25	< 0.1
Cu^{2+}	50	< 0.1
SO$_4^{2-}$	400	–
pH	2.2	6—8

Fig. 8. Treatment of the model wastewater with a composition similar to the real industrial wastewater (BA load: 4 g dm^{-3}, initial pH adjusted with NaOH: 6.3). ▲ Zinc, ■ nickel, ● copper.

Table 2. pH Stability of the Synthetic Zeolite P

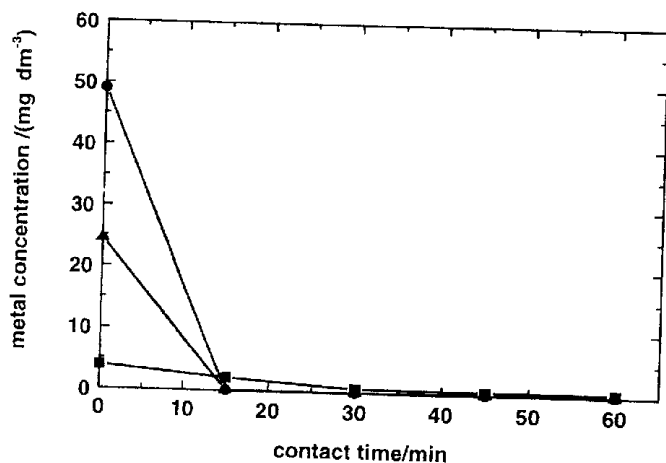| pH of the BA slurry	Al concentration/(mg dm^{-3}) in the BA slurry	Dissolved BA/%
2	830	100
3	830	100
4.3	771	93
5.2	2.1	< 0.5
6.2	2.2	< 0.5
7.1	1.7	< 0.5

Fig. 7. Treatment of the model wastewater with a composition similar to the real industrial wastewater (BA load: 4 g dm^{-3}, initial pH without adjustment: 2.2). ▲ Zinc, ■ nickel, ● copper.

About 250 mg of Zn^{2+}, 200 mg of Cu^{2+}, and roughly 90 mg of Ni^{2+} were adsorbed per gram of the synthetic zeolite P from a corresponding metal ion solution.

In view of these promising results, tests were performed using model industrial wastewater, which was prepared according to the information provided by a copper foil producer for this type of wastewater (Table 1).

No other chemicals were added to compensate for the low pH value (2.2) of the solution. However, pH value increased to above 5 once the zeolite was added. First results showed that, after 15 min, the required values for zinc and copper (< 0.1 mg dm^{-3}) were reached using 4 g of BA per dm^3 of model solution. During this period, nickel was reduced to roughly 4 mg dm^{-3} (Fig. 7).

In a final test, the pH of the model solution was initially increased to 6.3 using sodium hydroxide. Once the BA was added, the concentration of nickel, copper, and zinc dropped to below 0.1 mg dm^{-3} within 15 min (Fig. 8). All required concentrations for these metals (> 0.1 mg dm^{-3}) were reached.

Regeneration of bonding agents containing metal ions is commonly performed via contact with strong mineral acids. This procedure is accompanied by a strong decrease in the pH value. Unfortunately, the tests on the pH stability of the BA showed that at pH values lower than 5 not only metal ions, but also Al^{3+} from the zeolite structure was washed out by the solution used for regeneration. Results of the BA stability vs. pH value of the solution are shown in Table 2.

Table 3. Regeneration of the Synthetic Zeolite P Loaded with 57.2 mg of Zn (BA Concentration: 4 g dm^{-3})

Regeneration time/min	Zn concentration/(mg dm^{-3}) in the solution	Regenerated BA/%
0	< 0.2	–
15	35.6	62.2
30	42.2	73.4
45	44.0	76.9
60	45	78.7
1440	56	97.9

Therefore, it was not possible to use the standard regeneration method, which involves a pH shift to a value lower than 3. A 20 mass % NaCl solution was used and pH was only adjusted down to 5 using HCl in the first regeneration tests. The results obtained using this regeneration method showed that more than 95 % of the adsorbed metal ion was recovered. Therefore, the bonding agent could be regenerated almost entirely (Table 3).

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