Removal of Zn(II), Cu(II) and Cd(II) from aqueous solution using gyrolite

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This study presents a gyrolite as adsorbent for removal of Zn\(^{2+}\), Cu\(^{2+}\) and Cd\(^{2+}\) ions from aqueous solutions. Adsorption reactions were found more intensive in alkaline solution (pH 10.61) because almost all (98-99%) zinc, copper and cadmium ions are adsorbed in 30 s. Ion-exchange equilibrium is reached only after 3 min in acidic (pH 5.86) medium. Alkaline solution substitution isomorphism was found typical to gyrolite because 20% of heavy metals ions participate in ion exchange reaction and other part of ions were present in gyrolite by chemosorption. At acidic solution, cation exchange mechanism proceed differs because all heavy metal ions participate only in ion exchange reaction. Crystal structure of gyrolite is stable in solutions (pH, 5.81-10.61). XRD, STA, FTIR and SEM methods characterized sorption products.

Keywords: Calcium-silicate-hydrate, Cation exchange reactions, Gyrolite, Heavy metals

Introduction

Population and industrialization increase have resulted in an increase in heavy metals content in environment\(^1\),\(^2\). Most of them come from anthropogenic sources of pollution, mainly through effluents from industries (tannery, metallurgy, dyes, explosives, ceramics, paints, textile, fertilizers) as well as landfills\(^3\)-\(^6\). Heavy metals can be absorbed by living organisms through food crops\(^7\)-\(^9\). Impact of heavy metals on environment can be a serious threat to the stability of ecosystem\(^5\),\(^10\). Some heavy metals (Cd, Pb, Hg) even at a very low level can result in reduced growth and development, cancer, organ damage, and in extreme cases, death. A number of metal ions (Na\(^+\), K\(^+\), Ca\(^{2+}\), Mn\(^{2+}\), Fe\(^{3+}\), Co\(^{2+}\), Cu\(^{2+}\) and Zn\(^{2+}\)) are essential for biological systems. However, each element (too high conc.) can cause considerable health problems\(^5\). Among various methods (chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical treatment technologies, etc)\(^11\)-\(^15\), adsorption is now recognized as an effective and economic method for heavy metal wastewater treatment\(^16\),\(^17\). Adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process\(^11\),\(^18\). Calcium silicate hydrates (C–S–H) have a large number of structural sites available for cation and anion binding\(^19\). Tits et al\(^20\) showed that C–S–H phases are capable of taking up bivalent cations, Sr\(^{2+}\) via exchange processes with Ca\(^{2+}\). Gyrolite, a C–S–H, rarely occurs as a natural mineral in association with zeolites as a low-temperature hydrothermal replacement product of basic igneous rock\(^21\). Adsorption of Cu\(^{2+}\) onto gyrolite has been studied\(^2\). Importantly, additives increase capacity of C–S–Hs to extract heavy metal ions from water\(^22\),\(^23\). It has been determined\(^24\) that when Na\(^+\) ions are inserted into crystal structure of gyrolite, its cation exchange capacity increases to 92.30 mg Cu\(^{2+}\)/g, which is almost twice better as of (Al+Na)-substituted to bermorite (53.22 mg Cu\(^{2+}\)/g).

This study evaluates application of gyrolite as adsorbent for removal of Zn\(^{2+}\), Cu\(^{2+}\) and Cd\(^{2+}\) ions from aqueous solutions.

Experimental Section

Reagents used for gyrolite synthesis were fine-grained SiO\(_2\)·nH\(_2\)O (Reaktiv, Russia; ignition losses, 21.28%; specific surface area, \(S_a = 1155\) m\(^2\)/kg by Blaine) and calcium oxide (CaO was burned at 950°C...
for 0.5 h; \( S_a = 548 \text{ m}^2/\text{kg}; \) purity, 96.54\%). Pure gyrolite was synthesized\(^4\) from a stoichiometric composition (\( \text{CaO}/\text{SiO}_2 = 0.66 \)) of \( \text{CaO} \) and a \( \text{SiO}_2\cdot n\text{H}_2\text{O} \) mixture, cured for 48 h at 200°C. Dry primary mixture was mixed with water in stainless steel vessels [water/solid (W/S) ratio of suspension = 10.0]. Product was filtered, dried at 50 ± 5°C, and put through a sieve (80 µm mesh).

### Ion Exchange Experiments

Ion exchange experiments were carried out at 25°C in a Grant SUB14 thermostatic absorber by stirring gyrolite (1 g) in two different aqueous solutions [Solution 1 (S1) & Solution 2 (S2)] for 120 min. Initial concentration of heavy metal ions for both solutions [S1 (pH, 5.86; \( \text{NH}_4\text{OH}, 0 \text{ ml} \)) & S2 (pH, 10.61; \( \text{NH}_4\text{OH}, 25 \text{ ml} \)) was same as follows: \( \text{Zn}^{2+}, 142.23 \text{ mg/dm}^3 \), \( \text{Cu}^{2+}, 25.8 \text{ mg/dm}^3 \) and \( \text{Cd}^{2+}, 2.17 \text{ mg/dm}^3 \). \( \text{NH}_4\text{OH} \) in S2 prevented \( \text{Me(OH)}_2 \) precipitation and maintained alkalinity. Exchange% was determined based on concentration variations in cations in solution and in gyrolite. Saturated adsorbent was rinsed with distilled water, dried at 50 ± 5°C, and dissolved in HCl (1:1). Concentration of \( \text{Ca}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+} \) and \( \text{Cd}^{2+} \) ions was determined using a Perkin-Elmer Analyst 4000 spectrometer.

### Table 1—Amount of adsorbed heavy metal ions

<table>
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<tr>
<th>No</th>
<th>pH</th>
<th>Me(^{2+})</th>
<th>0.5 min</th>
<th>1 min</th>
<th>3 min</th>
<th>10 min</th>
<th>25 min</th>
<th>120 min</th>
<th>Determined in adsorbent*</th>
<th>Average**</th>
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<td></td>
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<td>Calculated by data of differential and integral kinetic curves, mg/g</td>
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<td>1</td>
<td>5.86</td>
<td>Zn(^{2+})</td>
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<td>11.2</td>
<td>11.8</td>
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<td>Cu(^{2+})</td>
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<td>2.4</td>
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</table>

*concentration of incorporated cations into gyrolite structure, **medium value of cations concentration in solution and in adsorbent

Simultaneous thermal analysis (STA) was employed for measuring thermal stability and phase transformation of samples at a heating rate of 15°C/min, at 30-1000°C under air atmosphere. Test was carried out on a Netzsch instrument STA 409 PC Luxx. Ceramic sample handlers and crucibles of Pt-Rh were used. Fourier-Transform Infrared (FT-IR) spectra was carried out with PerkinElmer FT-IR Spectrum X system apparatus. Specimen were prepared by mixing sample (1 mg) with KBr (200 mg). Spectral analysis was performed in the range of 4000-400 cm\(^{-1}\) with spectral resolution of 1 cm\(^{-1}\). Scanning electron microscopy (SEM) (Evo 50) coupled with energy dispersive X-ray spectrometer (EDS) was performed using an accelerating voltage of 20 kV and a working distance of 10 mm for SEM observation and a 200 s accumulation time for EDS analysis.

### Results and Discussion

Cation exchange capacity of gyrolite and intrusion of \( \text{Zn}^{2+} \) ions in its structure was found to depend on solution pH because sorption proceeds less intensively in an acidic solution (pH 5.86) than in an alkaline solution (pH 10.61). When initial concentration of \( \text{Zn}^{2+} \) ions was 142.23 mg/dm\(^3\), almost all ions (>99%) entered into adsorbent already after 0.5 min in an alkaline solution. However, after same duration, only 72% \( \text{Zn}^{2+} \) ions intruded into gyrolite structure in an acidic solution (Table 1). Intrusion of \( \text{Cu}^{2+} \) and \( \text{Cd}^{2+} \) ions into gyrolite structure depends on solution pH too. Intrusion of \( \text{Cu}^{2+} \) and \( \text{Cd}^{2+} \) ions into gyrolite structure occurs faster when

Analytical Methods

X-ray powder diffraction (XRD) data were collected with a DRON–6 X-ray diffractometer with Bragg–Brentano geometry using \( \text{Cu K}_{\alpha} \) radiation and graphite monochromator, operating at 30 kV and 20 mA. Step-scan covered angular range 2-60° (2\( \theta \)) in steps of 2\( \theta = 0.02^\circ \). \( S_a \) of raw materials was determined by Blaine’s method with air permeability apparatus (Model 7201, Toni Technik Baustoffprüfsysteme GmbH).
medium is alkaline. Maximum amount of Cu$^{2+}$ and Cd$^{2+}$ ions intrusion reached already after 0.5 min. Meanwhile, ion-exchange equilibrium is reached only after 3 min when medium was acidic (Table 1).

Ca$^{2+}$ ions were released from crystal lattice of gyrolite into solution. Decrement of pH values in solution accelerates desorption of Ca$^{2+}$ ions (Fig. 1). Amount of released Ca$^{2+}$ ions was higher than 15 mg Ca$^{2+}$/g after 3 min in solution at pH 5.86 (Fig. 1a). Meanwhile, using a solution with higher pH value (pH 10.61), Ca$^{2+}$ ions were leached out after 3 min as 1.6 mg Ca$^{2+}$/g (Fig. 1b). Concentration of Ca$^{2+}$ ions increases slightly with increase of adsorption duration. Thus adsorption of metal ions by gyrolite is irreversible. After adsorption experiment, gyrolite powder was dried and poured into decarbonized water for leaching test. It was determined that zinc, copper and cadmium ion concentration in solution after 120 min at 25°C did not exceed over 0.1%. It was estimated that substitution isomorphism is typical to gyrolite in alkaline solution (pH 10.61) because 20% of heavy metals ions participate in ion exchange reaction as

$$\text{Gyrolite-Ca}^0 + \text{Me}^{2+} \leftrightarrow \text{gyrolite-Me}^0 + \text{Ca}^{2+} \quad \cdots (1)$$

This explains that ions in gyrolite remain because of chemosorption interaction (Fig 2a). Thus an acidic solution cation exchange mechanism proceed differ because all heavy metals ions participate only in ion exchange reaction (Ca$^{2+} \leftrightarrow \text{Me}^{2+}$). The main reason is
pH of initial cation metal solutions. However, pH of solution rapidly increases when gyrolite was mixed with solution. This change is attributed to the degree of release of Ca$^{2+}$ ions from the structure of gyrolite solid in solution during reaction. Thus solution pH with lower initial pH 5.86 increases with increasing adsorption duration (Fig 3a). Variation of pH by alkaline solution was not considerable (Fig. 3b). Thus, gyrolite is quite stable in solution with lower pH. In order to identify stability of gyrolite and a new solid phase, sorption products were characterized with numerous instrumental analysis methods.

**Analytical Methods**

XRD analysis showed that structure of gyrolite remains stable in solution at pH 5.86, although intensity of typical diffraction peaks slightly decrease due to calcium ions desorption into solution (Fig. 4, curve 2). At higher initial pH (10.61) after adsorption, crystallinity of gyrolite has not changed because intensity of diffractions peaks with d-spacing (2.233; 1.1264; 0.8370; 0.4196; 0.3731; 0.3512; 0.2804; 0.2139 nm) remain the same (Fig. 4, curve 3). SEM and STA analysis results confirmed that crystal structure of gyrolite remains stable after adsorption process under all conditions of experiments. On DSC curves, after sorption process, the same thermal effects (endothermic effect at 143°C of water dehydratation and exothermic effect at 855°C of recrystallization into wollastonite) were identified (Fig. 5, curves 2, 3) as in pure gyrolite (Fig. 5, curve 1). EDS analysis indicates that heavy metal ions incorporate into
Adsorbents (synthetic gyrolite)

Waste water, pH>5.81
(Zn$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ ions)

Adsorption reaction

Mixing time: 3-5 min

Temperature 25°C

Suspending of gyrolite with impure Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$ ions and clean water

Filtration process

Drying time: 40-45 min

Temperature 85°C

Gyrolite with impure Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$ ions

Excess of clean water

Fig. 6—Different analyses of gyrolite after adsorption process (25°C, 120 min) in solutions with pH 10.61: a) SEM micrographs; b) EDS analysis; and c) FT-IR spectrum

Fig. 7—Scheme of removal of Zn(II), Cu(II) and Cd(II) from aqueous solution by using gyrolite
structure of gyrolite, because after 120 min adsorption (pH 10.61), EDS data show 1.09 wt. % of Zn\(^{2+}\) and 0.28 wt. % Cu\(^{2+}\) ions in the structure of crystal compounds (Fig. 6a). FT-IR data shows a sharp peak near 3639 cm\(^{-1}\), which is visible only in gyrolite spectrum, showing distinguished OH positions of gyrolite structure, which are connected with Ca atoms only and are not influenced by hydrogen bonds. Whereas, a wide band near 3456 cm\(^{-1}\) means that molecular water forms hydrogen bonds in interlayers. Bands in the range of 1639 cm\(^{-1}\) frequency are assigned to \(\delta (H_2O)\) vibrations and confirm this presumption. Also, peak at 613 cm\(^{-1}\) was due to Si-O-Si vibrations, and band at ~975 cm\(^{-1}\) due to Si-O stretching mode of nonbrinding oxygens (Fig. 6c).

Based of data obtained in this study, a principal scheme has been designed for removal of Zn(II), Cu(II) and Cd(II) from aqueous solution using gyrolite (Fig. 7). In this scheme, wastewater containing heavy metal ions is supplied to an absorber filled with gyrolite. Recommended duration of adsorption is ~3 min at 25°C. Taking into account the experimental data obtained, adsorption capacity (\(\Sigma x\)) of gyrolite is \(\Sigma x = 14.2\) mg Zn\(^{2+}\)/g, \(\Sigma x = 2.5\) mg Cu\(^{2+}\)/g, \(\Sigma x = 0.21\) mg Cd\(^{2+}\)/g (1.691 kg/100 kg) when sorption time is 3 min at 25°C. At the same time, 10 ml/100 kg excess of clean water is returned in industry. Also, gyrolite with impure heavy metal ions can be supplied to Portland cement industry.

Conclusions

Cation exchange capacity of gyrolite and intrusion of heavy metals ions depend on reaction time and solution pH. Adsorption reactions were found more intensive in an alkaline solution (pH 10.61) because almost all Zn\(^{2+}\), Cu\(^{2+}\) and Cd\(^{2+}\) ions (98-99%) are adsorbed in 30 s. Ion-exchange equilibrium is reached only after 3 min when medium was acidic (pH 5.86). Cation exchange reactions independent of solution pH were irreversible. Alkaline solution substitution isomorphism was found typical to gyrolite because 20% heavy metal ions participate in ion exchange reaction and other part of ions present in gyrolite by chemosorption. At acidic solution, cation exchange mechanism proceed differ because all heavy metals ions participate only in ion exchange reaction. Crystal structure of gyrolite was found stable in solutions (pH, 5.81-10.61) and its stability does not depend on examined adsorption conditions (120 min, 25°C) and concentration of heavy metals ions.

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References