

Human Journals **Research Article** August 2021 Vol.:19, Issue:2 © All rights are reserved by A. Boughriet et al.

Removal of (Natural and Radioactive) Cobalt by Synthetic Zeolites from Brick: Adsorption Isotherm, Mechanism, and Performance (in Batch and Column)



⁹. Chaire Unesco « Sur la gestion de l'eau », Laboratoire Hydrosciences Lavoisier, Université de Bangui, Faculté des Sciences, B.P. 908, République Centrafricaine.

Submitted:	22 July 2021
Accepted:	29 July 2021
Published:	30 August 2021





www.ijsrm.humanjournals.com

Keywords: Brick; Zeolite; Cobalt; Decontamination; Adsorption; Isotherm; Mechanism

ABSTRACT

In this study, the removal of natural and radioactive cobalt(II) from aqueous solutions by a modified brick was presented in a batch system and fixed-bed column system. The brick which is originated from Bangui region (in the Central African Republic) contains metakalinite. By treating the brick with sodium hydroxide at 90°C, metakaolinite was transformed into zeolites. Raw brick and its alkali form were fully characterized by environmental scanning electron microscopy (ESEM), energy-dispersive X-ray spectroscopy (EDS) technique, and X-ray diffraction. Elemental analyses of batch and column solutions were realized by using ICP-AES. Equilibrium adsorption data were fitter with the Redlich-Peterson and Sips models than with the two-parameters adsorption models (Langmuir, Freundlich, and Temkin). However, the studied isotherm was closer to the Langmuir isotherm, suggesting that the adsorption process took place mostly on homogeneous adsorbent surfaces. Batch studies revealed that nearly two balancing ions (Na⁺) in the sodic brick were replaced by one incoming ion (Co²⁺) from the solution. The use of alkali brick in fixed-bed column permitted to show the efficiency of this adsorbent for the capture of cobalt(II) from synthetic water even in the presence of competitive metal ions like Pb(II), Cd(II), and Mn(II). These investigations highlighted that alkali brick could be a suitable material for industrial/nuclear cobalt (and heavy metals) depollution.

1. INTRODUCTION

The stable isotope (⁵⁹Co) exists naturally in the earth's crust. The Co element can also exist in the form of a radioactive isotope and thereby produces ionizing radiation. Nowadays, 26 radioactive Co isotopes are reported in the literature. Sources of environmental cobalt are both natural and anthropogenic [1]. Natural cobalt sources result mostly from volcanoes, forest fires, erosion (wind-blown continental specks of dust), weathering of rocks and soil, seawater spray, extraction by plants, and continental and marine biogenic emissions. Anthropogenic cobalt sources derive mainly from mining, smelting processing of cobalt-bearing ores, electroplating, lithium-ion batteries/paints/ pigments/ and electronics industries, phosphate fertilizers, atmospheric depositions from smelting, refining of metals and burning of fossil fuels, and wastes of nuclear power plants [2-4].

Chemically, this metal can exist in three oxidation states (0, +1, and +3), however, it predominates in form +2 under environmental conditions [5]. At low levels, cobalt(II) is known to be an essential nutrient for humans (as a constituent of vitamin B12) and plants. The maximum permissible concentration of cobalt in drinking water is 0.05 mg/L [6]. Above permissible levels, some uncertainties still exist in the evaluation of health risks [5]. However, it was evidenced an increased risk of symptoms such as polycythemia, respiratory and bronchial asthma, and even lung cancer among hard metal industry workers who are directly exposed to anthropogenic cobalt like hard metal dust or "pure" cobalt particles [5]. Radioactive Co exposures can also pose serious risks for humans: skin burns, liver/kidney/bone diseases, and in case acute Co radiation occurs severe sickness can result in death [3]. It follows that the presence of cobalt in various industrial effluents demands its removal to preclude radioactive/environmental pollution and detrimental effects on the local population.

Research studies related to the techniques of removing cobalt from wastewaters have drawn attention increasingly [7]. Thus, different methods had been used in the past: ion-exchange [8-11]; coagulation/flocculation [12]; precipitation [13-15]; ultrafiltration [16]; bioaccumulation/biosorption [17-22]. However, it is now recognized that adsorption is the most promising procedure for the elimination of cobalt(II) from aqueous solutions owing to its simplicity, low energy consumption, and high efficiency. Numerous researches were thus

undertaken for Co(II) ion removal by employing various natural or synthetic adsorbents, *e.g.*: faujasite zeolite Y [23]; natural and synthetic zeolites [24]; nanocomposites of modified chitosan [25]; dicalcium phosphate dihydrate [26]; natural zeolites [27]; silver and zinc nanoparticles functionalized cellulose [28]; montmorillonite [29]; porous carboxymethyl chitosan beads [30]; TiO₂/Ag₂O nano adsorbents [31]; cross-linked carboxymethyl chitosan hydrogel and resin [32]; 6-((2-(2-hydroxy-1-naphthoyl) hydrazono)methyl) benzoic acid (HMBA) ligand onto mesoporous silica-monoliths [33]. But, for most of these adsorbents, their wider application was often hindered by relatively high-cost treatments and/or secondary pollutions. In recent works, low-cost adsorbents prepared from industrial byproducts including slag [34] and fly ash [35], had been employed successfully for eliminating metallic pollutants from wastewaters.

Among the wide variety of reused industrial wastes, brick was an interesting material when converted into an effective adsorbent for the removal of metallic pollutants from aqueous solutions; Different types of bricks had been utilized as low–cost adsorbents for eliminating toxic metals like Hg(II) [36]; Zn(II) [37]; Cr(VI) [38]; both Cr(VI) and Ni(II) [39]; or Ni(II) alone [40]. In the lab, a brick made in the Central African Republic (CAR), was modified chemically by HCl activation and deposition of ferrihydrite on the brick surface, and used successfully for the removal of divalent cations like; Cd^{2+} , Cu^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+} from aqueous solutions [41-47]. CAR brick was also treated with sodium hydroxide at a specific reaction time and temperature for transforming one of its minerals (metakaolinite) into zeolite(s) [48]. The final material is mainly composed of sand and zeolites. This composite was afterward employed as an efficient adsorbent in wastewater treatments [49-51].

As also expected, brick sensitization should contribute as well to achieving good adsorption capacity towards cobalt(II). To check this, we tested in this work brick-derived zeolites as adsorbents for the removal of cobalt(II) from aqueous solutions. Batch experiments were performed at room temperature and recovered samples were analyzed by scanning electron microscopy. Adsorption equilibrium data were examined by using five well-known isotherm models which were previously established by: Langmuir, Freundlich, Temkin, Redlich-Peterson, and Sips. The applicability and efficiency of modified brick were afterward assessed by column operations by treating synthetic wastewater containing cobalt and other heavy metal ions.

2. MATERIALS AND METHODS

2.1. Zeolitized-brick synthesis and characterization

The raw material used in the experiments was obtained from a brick made locally by craftsmen in the Bangui region (Central African Republic). This brick contains mainly quartz (60-65 w%) and metakaolinite (20-26 w%) and, to a lesser extent, iron oxide/hydroxide, illite, and titanium dioxide [42]. The brick was broken into grains and seized and the 0.7-1.0 mm fraction was selected. 10 g of this fraction were treated with 40 mL of sodium hydroxide (0.6 mol.L⁻¹) at room temperature for one night under slow shaking at a speed of 120 rpm. This procedure was afterward followed by a fixed-temperature increase of the mixture at 90°C for a constant reaction time of six days. The recovered grains were afterward rinsed several times with MilliQ water and dried at 90°C for 24 hours.

2.2. Chemicals

All chemicals employed in the experiments were analytical grades. Sodium hydroxide, Cd(NO₃)₂.4H₂O, Co(NO₃)₂.6H₂O, Mn(NO₃)₂.4H₂O, and Pb(NO₃)₂ were supplied by DISLAB (France).

2.3 Isotherm study

To study the adsorption behavior of cationic cobalt ions on alkaline brick, the experiments for adsorption isotherms were performed at room temperature and under constant stirring conditions. Isotherm study was carried out on brick grains with 0.7 -1.0 mm sizes. In single-component systems, batch experiments were performed in ten 100mL-flasks –each one containing 1 g of brick pellets— in which were added 50 mL of a cobalt(II) solution with a concentration ranging from 5.54x10⁻⁴ to 12.91x10⁻⁴ mol.L⁻¹. These flasks were placed on a mechanical (orbital) shaker (Model: IKA Labortechnik KS 250 basic) and gently shake at a speed of 120 rpm. Adsorption-isotherm experiments lasted one night.

Afterward, suspensions were filtered and recovered solutions were analyzed to determine cobalt concentrations using an ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy;

Model: Varian Pro axial view) spectrometer. The cobalt uptake and percentage removal were calculated using the relationships:

$$Q_e = \frac{(C_o - C_e).V}{m} \tag{1}$$

$$\% adsorption = \frac{(C_o - C_e)}{C_o} x100\%$$
(2):

where C_o (mg.L⁻¹) and C_e (mg.L⁻¹) are the initial and equilibrium concentrations of divalent cobalt, respectively; V (L) is the volume of the aqueous solution used in batch experiments, and m (g) is the mass of alkaline brick added in the solution.

2.4. Fixed-bed column experiments

The continuous flow adsorption experiment was conducted in a fixed-bed glass column with an inner diameter of 12.5 mm, a height of 25 cm, and a 160-250 μ m porosity sintered-pyrex disk at its bottom to prevent any loss of material. A bed depth of 6.9 cm (8.06 g) was investigated at a constant flow rate of 5 mL/min. Before being used in the experiments, at least 500 mL of Milli-Q water was passed through the column. The schematic diagram of the fixed-bed column reactor used was previously illustrated [44].

In a multi-component system (Cd²⁺, Co²⁺, Mn^{2+,} and Pb²⁺), the initial concentration of each metal in the influent was 1.78×10^{-4} mol.L⁻¹. The divalent-metal solution was pumped through the column at the desired flow rate using a peristaltic pump (LaboModerne France Type KD1170) in an up-flow mode. During this column experiment, the effluent pH was measured continuously using a pH meter that was connected to a computer; and effluent samples exiting the bottom of the column were collected at different time intervals and analyzed for metal contents using ICP-AES. Flow to the column continued until the effluent metal concentration at time t (C_t) reached the influent metal concentration (C₀): Ct/C₀ \approx 0.99. The performance of the packed bed was described in the present work using the concept of the breakthrough curve.

2.5. Heavy metal speciation in experimental adsorption medium

The Visual MINTEQ 3.0 equilibrium speciation computer software was used to calculate the concentrations of the various cobalt species/hydroxyl complexes generated in the experimental reacting solution at room temperature. The conditions of cobalt (Co^{2+}) -speciation calculation were used as: $[Co^{2+}] = 10^{-3} \text{ mol.L}^{-1}$ and $[NO_3^{-}] = 2[Co^{2+}] = 2x10^{-3} \text{ mol.L}^{-1}$ (by taking the $Co(NO_3)_2$ salt) at different medium pH values ranging from 2 to 12.

2.6. Electron microscopy analysis

Micrographic of representative specimens of the brick before and after chemical treatment were recorded by using an environmental scanning electron microscope (ESEM, Quanta 200 FEI). Elemental analysis was performed using ESEM/EDS (ESEM, model: QUANTA–200–FEI, equipped with an Energy Dispersive X-Ray Spectrometer EDS X flash 3001 and monitored by QUANTA–400 software elaborated by Bruker). EDS measurements were carried out at 20 kV at low vacuum (1.00 Torr) and the maximum pulse throughput was 20 kcps. Different surface areas ranging from 0.5 to 3.5 mm² were targeted on alkali-brick grains and examined by ESEM/EDS. For that, a narrow beam scanned selected areas of brick pellets for chemical analysis. Atomic quantifications and mathematical treatments were undertaken using QUANTA-400 software to determine the averaged elemental composition of the surface brick and to detect chemical/elemental variabilities.

3. RESULTS

3.1. Characterization of the brick adsorbent

Raw brick: The ESEM micrograph of untreated brick exhibits porous and non-uniform morphological/textural surfaces with major fissures and cracks, except for some microspecimens that were well-identified as quartz (Fig. 1A). The ESEM micrograph displays regions of different contrasts with white and gray tones which indicate the diversity of compounds forming the sample.



Figure 1: ESEM images of raw brick (A) and alkali brick (B).

The ESEM technique combined with the EDS spectroscopy was used to yield elemental analyses of raw brick.



Figure 2: Energy dispersive X-rays spectra of raw brick and alkali brick.

For that, ESEM/EDS analyses were performed in large circled regions (about 70µm diameter); And globally, ESEM/EDS study revealed the occurrence of (i) aluminium (Al), oxygen (O), and silicon (Si) as major elements; and (ii) calcium (Ca), iron (Fe), magnesium (Mg), manganese (Mn), potassium (K) and titanium (Ti) as minor elements (as shown in the EDS spectrum of raw brick; see Fig. 2).

Fig. 3 exemplifies the XRD patterns of raw-brick powder. The results showed that the material contains quartz as the principal crystalline mineral and, to a lesser extent, illite and rutile.



Figure 3: X-ray diffractograms of raw brick and alkali brick.

Quartz was identified on the basis of the following '20' reflection angles (the Miller indices, hkl, are given in the parenthesis): 20.9° (100); 26.6° (011); 36.5° (110); 39.5° (102); 40.3° (111); 42.4° (200); 45.8° (201); 50.2° (112); and 54.9° (022) [ICSD Collection Code: 89276]. Because of the smaller amounts of illite and rutile in the brick, these two minerals were recognized only on the basis of some of their intensive reflection angles: *illite*: 17.9° (004), 19.8° (021), and 34.3° (034) [ICDD (International Centre for Diffraction data): 00-009-0343]; *rutile*: 27.4° (110), 36.1° (101), and 54.3° (211) [ICSD Collection Code: 168140].

Alkali brick: After chemical treatment of raw brick with sodium hydroxide at 90°C for 6 days, the morphology of the material was changed significantly into aggregated cubic and spherical shapes, suggesting the formation of zeolites (Fig. 1B). The size of new specimens varied from 8 μ m to 10 μ m for cubic ones and from 3 μ m to 6 μ m for spherical ones (Fig. 4).





Cubic crystals were found to be comparable with those observed previously for the A-type zeolite [52, 53]. As for spherical shape crystals, they were found to be morphologically similar to those reported in the literature for zeolite NaP [54-57].

The EDS spectrum of an alkali-brick sample (see Fig. 2) _which was recorded by targeting a large circled region (~70µm) was compared with that of raw brick, evidencing the appearance of a new peak ascribed to sodium in addition to the major elements (Al, O, and Si) and minor elements (Ca, Fe, Mg, Mn, K, and Ti). Afterward, different grains (cubic and spherical) shown in Fig. 4 were targeted and analyzed quantitatively by ESEM/EDS. We found: 14.77 \pm 2.67 atomic % for sodium; 14.97 \pm 2.05 atomic % for aluminium; and 16.12 \pm 1.46 atomic % for silicon. It was noticed that the averaged elemental composition of targeted grains corresponded well enough to those of zeolites with atomic ratios Si: Al close to 1. In addition, the presence of high amounts of sodium on the targeted surfaces confirmed the formation of sodic zeolites.

The identification of the fabricated product was also made by using the X-ray diffraction (XRD) technique. Fig. 3 exemplifies the XRD patterns of alkali-brick powder. The results confirmed that the synthesized material is mainly a composite of sand (quartz: **Q**) and zeolites LTA (noted here: **A**) and NaP (noted here : **P**). The distinguishing peaks of zeolite LTA at $2\theta = 7.2^{\circ}$, 12.5° , 16.1° , 30.0° , and 30.8° can be imputed to lattice plans of (200), (222), (420), (644 and 820) and (822 and 660), respectively [58]. The distinguishing peaks of zeolite NaP at $2\theta = 12.5^{\circ}$, 17.7° , 21.7° , 28.1° , and 33.4° can be imputed to lattice plans of (101), (200 and 002), (211, 112 and 121), (310, 301, and 103) and (132, 213, 312, and 321), respectively [58].

The structural transformations observed were due to the conversion of metakalinite (chemical formulae: 2SiO₂.Al₂O₃) present in the brick into zeolitic frameworks under alkaline conditions [59-65]. The general chemical formula of brick-derived zeolites can then be written as [66, 67]:

$$(Na^{+})_{x}(AlO_{2}^{-})_{x}.(SiO_{2})_{y}. zH_{2}O$$
 (3);

where x and y correspond to the number of "AlO₄" and "SiO₄" tetrahedra per crystallographic unit cell, respectively; and z the number of water molecules per unit cell. The chemical formula leads to negative charges (x-) which are balanced by extra framework cations (Na⁺ ions with total positive charges: x+). The x/y ratio for brick-derived zeolites which is equal to about 0.93, is almost maximal according to the well-known Lönwenstein's rule [68], thus justifying the relevant ion-exchange capacity of this material.

3.2. Adsorption isotherms

Adsorption isotherms are known to be useful tools for understanding the aqueous surface behavior of adsorbents when interacting with organic or inorganic ionic species, and for predicting adsorbate-adsorption capacity. On this view, batch experiments were performed in the present work for studying the equilibrium isotherm of cobalt(II) adsorption on alkali brick. Experimental data were fitted by using five adsorption isotherm equations established by: (i) Langmuir, Freundlich, and Temkin (as two-parameters adsorption models); and Redlich–Peterson and Sips (as three-parameters adsorption models).

3.2.1. Application of two-parameters adsorption models

Langmuir isotherm This model assumes that adsorption sites are identically homogeneous and adsorption on such a surface is a monolayer. Langmuir equation is expressed as [69]:

$$Q_e = \frac{Q_{\max}.K_L.C_e}{(1+K_L.C_e)} \tag{4}$$

where Q_e is the equilibrium cobalt(II) concentration per unit mass of the adsorbent (mg.g⁻¹); C_e is the equilibrium cobalt(II) concentration in the solution (mg.L⁻¹); Q_{max} is the monolayer adsorption capacity of the adsorbent (mg.g⁻¹), and K_L is the Langmuir adsorption constant (L.mg⁻¹). Eq.(4) can be rearranged to the common linear form:

$$\frac{C_e}{Q_e} = \frac{1}{K_L \cdot Q_{\text{max}}} + \frac{C_e}{Q_{\text{max}}}$$
(5)

The dimensionless constant (R_L), is an essential parameter of the Langmuir model by predicting the nature of adsorption:

$$R_L = \frac{1}{(1 + K_L \cdot C_e)} \qquad \qquad \text{HUMAN}$$
(6);

where the term C_e is taken as the highest initial cobalt(II) concentration (mg.L⁻¹). The R_L value indicates that the adsorption process is either unfavourable (R_L > 1), linear (R_L = 1), favourable (0 < R_L < 1) or irreversible (R_L = 0).





1.6 1.4 $R^2 = 0.9579$

Freundlich isotherm: This model assumes that Co^{2+} ions are adsorbed on heterogeneous surfaces and adsorption is multilayer. Freundlich equation is expressed as [70]:

$$Q_e = K_F \cdot C_e^{1/n_F} \tag{7};$$

where K_F (mg.g⁻¹) and n are the Freundlich adsorption isotherm constants. The linearized form of Eq.(7) is given by:

$$\log(Q_e) = \log(K_F) + (\frac{1}{n_F}) \cdot \log(C_e)$$
 (8).

The value of $1/n_F$ suggests the nature of adsorption as: favourable ($0 < 1/n_F < 1$); unfavourable ($1/n_F > 1$) : or irreversible ($1/n_F = 1$).

Temkin isotherm This model assumes that the heat of adsorption decreases linearly during the adsorption process due to increasing interaction between adsorbent and adsorbate. Temkin equation is expressed as [71]:

$$Q_e = B.\ln(A_T.C_e) \qquad \text{with } B = RT/b_T \qquad (9)$$

where B represents the Temkin constant which depends upon the adsorption heat, b_T (in J.mol⁻¹); R (8.314 J.mol⁻¹.K⁻¹) is the gas constant; T is the absolute temperature (K), and A_T is the equilibrium bond constant (L.mg⁻¹). Eq.(9) can also be written as ::

$$Q_e = 2.303B.\log(A_T) + 2.303B.\log(C_e)$$
(10).

The graphs using the linearized Langmuir, Freundlich and Temkin equations are shown in Fig. 5. From the slopes and intercepts of plots, Langmuir, Freundlich and Temkin isotherms parameters were calculated and listed in Table 1. The goodness-of-fit between the model and experimental observations was ascertained in terms of residual root mean square error (RMSE) and the Reduced Chi-squared (χ_{red}^2) using Eqs.11) and (12), respectively:

$$RMSE = \sqrt{\left(\frac{1}{N-P}\right) \cdot \sum_{j=1}^{N} \left(Q_{j, \exp} - Q_{j, cal}\right)^2}$$
(11);

$$\chi_{red}^{2} = \sum_{j=1}^{N} \frac{(Q_{j, exp.} - Q_{j, cal.})^{2}}{N - P}$$
(12);

where $Q_{j,exp.}$ and $Q_{j,cal.}$ represent the experimental and the predicted (or calculated) values of equilibrium adsorption capacity, respectively (mg.g⁻¹); j is the integer index denoting the successiveness of experimental data; N is the number of data experimental points; and P corresponds to the number of isotherm model parameters.

Two-parameters adsorption models					
Langmuir	Freundlich		Temkin		
$Q_{max}(mg.g^{-1}) = 2.63$	$K_F(mg.g^{-1}) = 1.337$		$A_{\rm T}({\rm L.mg}^{-1}) = 19.05$		
$K_L(L.mg^{-1}) = 0.554$	$n_{\rm F} = 4.885$		B = 0.4130		
$R_L = 0.023 - 0.052$	$1/n_F = 0.2047$		$b_{\rm T}(\rm J.mol^{-1}) = 5898.55$		
Statistics	Statistics		Statistics		
$R^2 = 0.9785$	$R^2 = 0.9428$		$R^2 = 0.9579$		
RMSE = 0.074	RMSE = 0.099		RMSE = 0.081		
$\chi_{red}{}^2 = 0.0054$	$\chi_{red}{}^2 = 0.0098$		$\chi_{red}{}^2=0.0065$		
Three-parameters adsorption models					
Redlich-Peterson		Sips			
$K_{RP}(L.g^{-1}) = 1.8217$		$K_{S}(L.g^{-1}) = 0.5777$			
$\alpha_{RP} (L.mg^{-1})^{\beta RP} = 0.823$		Qs = 2.8557			
$\beta_{RP} = 0.944$		$\beta_S = 0.778$			
Statistics		Statistics			
$R^2 = 0.9972$		$R^2 = 0.9972$			
RMSE = 0.072		RMSE = 0.073			
$\chi_{red}^2 = 0.0052$		$\chi_{red}^2 = 0.0054$			

Table 1: Equilibrium model parameters for a	dsorption of cobalt(II) by alkali brick pellets
(0.7-1.0 mm diameter) at room temperature.	

Overall, the applications of two-parameters adsorption models to our system revealed that: (i) the correlation coefficient obtained from Langmuir isotherm model ($R^2 = 0.9785$) was higher than that from Freundlich and Temkin ones ($R^2 = 0.9428$ and 9579, respectively), see Table 1; and (ii) when modeling from Langmuir model, the residual root mean square error (RMSE) and reduced Chi-squared (χ_{red}^2) were lower than those from Freundlich and Temkin ones, see Table 1. All these findings suggested that the Langmuir equation was more suitable to fit experimental data than Freundlich and Temkin's equations. R_L was between 0 and 1, demonstrating that Co(II) adsorption onto alkali brick was a favorable process. In addition, the relatively low R_L values obtained further indicated that strong interactions would exist between Co^{2+} ions and the active sites of the brick. The value of 1/n in Freundlich isotherm is 0.2047, confirming that the Co(II)-adsorption process is favorable. The maximum cobalt(II) adsorption capacity calculated from the Langmuir isotherm model ($Q_{max} = 2.63 \text{ mg.g}^{-1}$) was close enough to the experimentally obtained values of adsorption capacity ($1.51 < Q_{eq} < 2.58 \text{ mg.g}^{-1}$; Q_{eq} values found for the different performed batch experiments at equilibrium adsorption time).

3.2.2. Application of three-parameters adsorption models

The three-parameter Redlich-Peterson and Sips isotherm models are considered as combinations of the Langmuir and Freundlich isotherm models. They were widely employed in the past for studying homogeneous and heterogeneous adsorption systems [72].

Redlich-Peterson isotherm: This model which is a compromise between Langmuir and Freundlich models contains three adjustable parameters. Redlich-Peterson (R-P) equation is expressed as [73]:

$$Q_e = \frac{K_{RP}.C_e}{(1+\alpha_{RP}.C_e^{\beta_{RP}})}$$
(13)

where K_{RP} (L.g⁻¹), α_{RP} (L.mg⁻¹)^{βRP}, and β_{RP} represent the Redlich–Peterson (R-P) isotherm constants. If $\beta_{RP} \approx 1$, the system adsorption is close to the Langmuir isotherm; and if $\beta_{RP} \approx 0$, the process occurs according to the Freundlich model [74, 75]. Note that the K_{RP}/α_{RP} ratio is indicative of the adsorption capacity.

Sips isotherm The non-linear Sips isotherm equation is expressed as [76]:

$$Q_{e} = \frac{Q_{S}.K_{S}.C_{e}^{\beta_{S}}}{(1+K_{S}.C_{e}^{\beta_{S}})}$$
(14)

where Q_S , K_S , and β_S are the Sips constants. K_S (L.g⁻¹) is related to the adsorption energy; and the Sips exponent, β_S , describes either the homogeneity or heterogeneity of the adsorption process.

The isothermal modeling equations used in this study, Eqs. (13) and (14), are given as non-linear equations. Modeling data were then fitted to experimental results using non-linear regression analysis. The best-fitting was calculated by minimizing RMSE and γ_{red}^2 values by using an algorithm programmed in Scilab 6.0.2 software. R-P and Sips results are listed in Table 1. As indicated in this table, the three - parameters isotherm models, R-P and Sips, provided a very good fit ($R^2 = 0.9972$, RMSE = 0.072 - 0.073, and $\gamma_{red}^2 = 0.0052-0.0054$). The maximum adsorption capacity predicted by the R-P and Sips models was 2.21 mg.g⁻¹ (calculated from the K_{RP}/α_{RP} ratio) and 2.85 mg.g-1, respectively. These two adsorption capacity values are close enough to the maximal/experimental one (2.58 mg.g-1). The regression coefficient (\mathbb{R}^2), the residual root mean square error (RMSE), and the Reduced Chi-squared (χ_{red}^2) which were obtained for the five isotherm models, showed clearly that the equilibrium data were fitter with the Redlich-Peterson and Sips models than with the two-parameters adsorption models (Langmuir, Freundlich, and Temkin). However, the Redlich-Peterson parameter, β_{RP} , was found to be close to 1 ($\beta_{RP} = 0.944$). This suggested that the studied isotherm was closer to the Langmuir isotherm, and the adsorption of Co^{2+} ions on the brick was more mono-layer than multi-layer. Additionally, the calculated value of the Sips constant ($\beta_s = 0.778$) is also close enough to unity, confirming that the adsorption process occurred mostly on homogeneous adsorbent surfaces.

3.3. Adsorption mechanism

3.3.1. Aqueous chemical speciation of cobalt(II)

Divalent metal ions in aqueous solution hydrolyze to form a series of mononuclear and polynuclear hydroxyl complexes according to [77]:

$$xMe^{2+} + yH_2O \leftrightarrow Me_x(OH)_y^{2-y} + yH^+$$
(15);

where Me^{2+} represents the free ion of the divalent metal; and K_{xy} is the formation constant of hydroxy complex (with x and y varying both from 1 to 4).

To calculate the concentrations of hydrolysis cobalt(II) compounds at pH values ranging from 2 to 12, we used the Visual MINTEQ 3.0 equilibrium speciation computer software. Fig. 6 represents the % evolution of cobalt(II)-hydroxy complexes versus pH.



Figure 6: Effect of pH on the chemical speciation of cobalt(II) in an aqueous solution. Metal concentration: 10⁻³ mol.L⁻¹.

Note that, in the distribution diagram only metal species with percentages \geq of 1% are taken into consideration. As shown in Fig. 6, free metal ion remains the dominant species up to reach a maximal pH value of about 7.5. This observation is related to the acid properties of Co²⁺ ions in water, indicating particularly that Co(OH)⁺ is the first hydroxy complex appearing in the medium with pH increase according to:

$$\operatorname{Co}^{2+} + \operatorname{H}_2 O \leftrightarrow \operatorname{Co}(OH)^+ + H^+$$
 (16).

The equilibrium constant for the hydrolysis reaction (16) and corresponding to the formation of the mononuclear hydroxy complex, $Co(OH)^+$, was found to be equal to $log(K_{11}) = 9.65$ [77].

The drawing of the two vertical dashed lines in Fig. 6 represents the minimal and maximal pH values measured during (batch) adsorption experiments. As seen in this figure, the free form of cobalt(II) (\geq 98%) prevailed in the reaction medium during all the course of batch experiments. Consequently, it was stated that only the free ionic form of cobalt should interact predominantly with the active sites of the modified brick.

3.3.2. Heterogeneous reaction stoichiometry

To gain information about the stoichiometric aspect of the ion-exchange mechanism on alkali brick, the Na⁺/Co²⁺ exchange reaction was examined under static (batch) conditions. At the end of each batch experiment, the equilibrium concentration of Na released in the solution was plotted against that of cobalt(II) adsorbed onto brick pellets (Fig. 7). As can be seen in this figure, the slope of the curve (which corresponds to the molar ratio [Na]_{released}/[Co]_{exchanged}) was around 2.100 with a relatively good correlation coefficient (R² = 0.932). This suggested that the studied heterogeneous reaction took place stoichiometrically according to an "ion-exchange" process where nearly two balancing ions (Na⁺) in the sodic brick were replaced by one incoming ion (Co²⁺) from the solution. Therefore, the reaction for the Co²⁺--Na⁺ system might be schemed by the following equation:

$$2 (\mathrm{Na}^{+})_{\mathrm{brick}} + (\mathrm{Co}^{2+})_{\mathrm{solution}} \rightarrow (\mathrm{Co}^{2+})_{\mathrm{brick}} + 2 (\mathrm{Na}^{+})_{\mathrm{solution}}$$
(17).

The "stoichiometric" molar atomic ratio, 2Na/Co, was considered in this work as being the theoretical exchange capacity of the modified brick towards cobalt(II).





3.3.3. Cobalt-enriched spots



A detailed ESEM/EDS micro-observation within a cross-section of an alkali-brick sample was performed after cobalt(II) adsorption, see Fig. 8. The examination of the line scannings for Al, Co, Na, and Si indicated increasing levels of sodium alongside alumino-silicate aggregates (zeolite crystals), whereas Na levels decrease significantly on Si-rich aggregates (quartz). Moreover, several cobalt-rich "hotspots" were identified in the particles. As shown in Fig. 8, the areas where EDS cobalt signals were observed typically contain Na-bearing alumino-silicates but are strongly depleted in silicates. In other words, in the modified brick cobalt was preferentially bound to zeolite crystals.



Figure 8: ESEM/EDS micro-observation within a cross-section of alkali-brick particles after cobalt(II) adsorption.

3.4. Synthetic-wastewater treatment in a fixed-bed column

During the column experiment, each metal concentration in the synthetic water was 1.78.10⁻⁴ mo.L⁻¹, the column contained 8.06 g of brick pellets, and the adsorbent height was about 6.9 cm. Metal levels in the effluent were analyzed at various service times. The breakthrough curves obtained after passing synthetic wastewater containing the dicationic metals Cd(II), Co(II), Mn(II), and Pb(II) through a prepared alkali-brick column are shown in Fig. 9.



Figure 9: Breakthrough curves of Cd(II), Co(II), Mn(II), and Pb(II) present in synthetic wastewater through a packed alkali-brick column.

In this column experiment highlighting Cd-Co-Mn-Pb competition, the packed brick column was firstly saturated with Mn^{2+} and Co^{2+} ions followed successively by Cd^{2+} ions and Pb^{2+} ions (Fig. 9). The amount of cobalt that was still present in the effluent, as compared with the permissible limit recommended for this metal in drinking water by the World Health Organization (WHO). It was noticed that, although the synthetic water contained strongly competing (and very toxic) metals like lead(II) and cadmium(II), the effluent Co(II) concentration remained below the WHO

maximum contaminant level of 0.05 mg.L⁻¹ [6] after passing an influent volume of about 900 mL (Fig. 10). Thereby, under the fixed experimental column conditions used here, it could be declared that 1 kg of prepared adsorbent should enable the treatment of up to \approx 110 L of such strongly polluted water into potable water.



Figure 10: Detailed breakthrough curves highlighting Cd-Co-Mn-Pb competition, and permissible limit recommended for cobalt in drinking water by WHO.

3.5. Making the cost of alkali brick

From the above batch data, it is reasonable to infer that the modified brick can be fruitfully employed as an alternative adsorbent for treating waters that were contaminated with natural cobalt and/or industrial (radioactive) Co isotopes. In addition, the making cost of this material is low. Indeed, the brick which is provided by African craftsmen (in the Central African Republic) and used here as starting material weighs about 5 kg and its price is 75 CFA (i.e. 0.11 Euro; 1 CFA =~ 0.0015 Euro); while solid sodium hydroxide which is provided by local soap factories and used here as reagent costs 30000 CFA / 25 kg (*i.e.* 45 Euros). Knowing that 4 liters of a NaOH solution at a concentration of ~0.6 mol.L⁻¹ are necessary to treat 1 kg of ground brick, we

estimate the cost for synthesizing 1 kg of adsorbent at ca 0.20 Euro (without taking into account labor costs which are very low in this country). This cost evaluation shows clearly that the modified brick ought to be a good low-cost adsorbent for wastewater treatment.

3.6. Comparison with other adsorbents and environmental benefits

The uptake capacity of alkali brick towards Co^{2+} ions was compared with that reported in the literature with different zeolites or mesoporous materials (Table 2).

Table 2:	Comparison	of	Co(II)	sorption	capacity	from	the	literature	using	different
adsorbent	S.									

Adsorbents	Q _{max} (mg/g)	References			
Natural zeolites	2.40-2.70	Chmielewska and Lesny (1992) [78]			
Natural zeolites	14.38	Erdem et al. (2004) [79]			
Natural bentonite	9.91	Kubilay et al. (2007) [80]			
	12.240-	Leseph et al. (2020) [35]			
rAU-type zeontes	30.211	Joseph et al. (2020) [55]			
Montmorillonite	6.92	Hu et al. (2018) [29]			
Modified montmorillonite	22.3	Bhattacharyya and Sen Gupta (2009) [81]			
Modified kaolinite	9	Bhattacharyya and Sen Gupta (2009) [81]			
Mesoporous silica	6.62	Salmani et al. (2020) [82]			
Expanded perlite	1.05	Ghassabzadeh et al. (2010) [83]			
Barley straw ash	4.15	Arshadi et al. (2014) [84]			
Modified-SBA-15-	5 0	Mureseanu et al. (2008)			
mesoporous silica	5.8	[85]			
Crab shell	20.47	Vijayaraghavan et al. (2005) [86]			
Hydroxyapatite	20.19	Smiciklas et al. (2006) [87]			
Animal bones	29.2	Dimovic et al. (2009) [88]			
Carbon-nanotube/iron-	10.61	Wong at al. (2011) [20]			
oxide composites	10.01	w ang et al. (2011) [89]			
Modified-chitosan	16.50-	Abdelbasir et al. (2021) [25]			
nanocomposites	37.35	Audelbasil et al. (2021) [23]			
Alkali brick	2.63	This work			

The Q_{max} value obtained for alkali brick is somewhat lower than those generally found in the literature, however, this material remains an interesting adsorbent for producing potable water because of its easy accessibility, making and maintenance. Furthermore, after metal saturation

the desorption of brick pellets can easily be carried out by passing through the purification system a concentrated solution of sodium chloride followed by a diluted solution of sodium hydroxide. Thus, it was previously demonstrated that during the treatment of ferrous ions-contaminated groundwaters by alkali brick, the saturated material was regenerated five times and it still showed good removal ability [50]. It is also important to note that the presence of sand (60-65 wt%) as a support material in the brick contributes strongly to assure a good permeability and to facilitate the flow of water through brick beds during adsorption column experiments [49].

CONCLUSION

The purpose of this research was to modify a metakaolinite-rich brick in the aim to synthesize zeolites for Co^{2+} ions adsorption. Synthetic zeolites were identified as crystalline LTA and NaP forms by the ESEM/EDS and XRD techniques. Detailed isotherm studies revealed that equilibrium data were fitter with the three-parameters adsorption models (Redlich-Peterson and Sips) than with the two-parameters adsorption models (Langmuir, Freundlich and Temkin). However, the Redlich-Peterson and Sips parameters (β_{RP} and β_{S}) were close to unity, suggesting that the Co(II) adsorption onto alkali brick was more mono-layer than multi-layer and occurred mostly on homogeneous adsorbent surfaces. Column experiments indicated that the modified brick was highly effective to capture cobalt(II) even in the coexistence of competitive metal ions like Pb(II), Cd(II) and Mn(II).

Industrial sectors that are involved in the production or use of cobalt in its natural and/or radioactive forms, and have no alternative, can implement easily the proposed method to remove this metal from their processing effluents before their discharge into the immediate environment. Since the reported adsorbent specifically shows relatively good adsorption performance for cobalt(II) or other toxic metals like lead(II) and cadmium(II, it would be applied efficiently and inexpensively to treat effluents with high concentrations of heavy metals.

Author contribution statement

Nicole Poumaye: Contributed reagents, materials; Performed the experiments; Analyzed and interpreted the data.

Oscar Allahdin: Contributed reagents, materials, analysis tools; Analyzed and interpreted the data.

Michel Wartel: Conceived and designed the experiments; Analyzed and interpreted the data.

Abdel Boughriet: Analyzed and interpreted the data; wrote the paper.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ACKNOWLEDGMENTS

The present investigations were undertaken successfully owing to the cooperation between the University of Lille (France) and the University of Bangui (Central African Republic). This collaboration (being still underway) and the Grant-in-Aid to Ms. N. Poumaye for her Doctoral-Thesis preparation had been financially supported by the Embassy of France to Bangui. The authors gratefully thank David Dumoulin (Chemical Engineer) and Véronique Alaimo (Chemical Technician) for helping us usefully in certain delicate chemical and/or analytical/spectroscopic analyses.

REFERENCES

[1] D.G. Barceloux. Cobalt. Clinical Toxicology 37(2) (1999) 201-216.

[2] I.C. Smith, B.L. Carson. Trace Metals in the Environment. Ann Arbor, MI, Ann Arbor Science Publishers, 1981.[3] ATSDR. Toxicological profile for cobalt. Atlanta, GA, United States Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, 2004.

[4] K.B. Shedd. Cobalt In: U.S. Geological Survey, 2020.

[5] World Health Organization (WHO). Cobalt and Inorganic Cobalt Compounds, prepared by J. H. Kim, H. J. Gibb, P. D. Howe. (Concise International Chemical Assessment Document 69), M. Sheffer (Ed., Ottawa), 2006, 1-55.

[6] World Health Organization (WHO). International year of fresh water. General Assembly Resolution A/RES/55/196, 2003. Official website: www.wateryear2003.org

[7] Md. A. Islam, D. W. Morton, B. B. Johnson, B. K. Pramanik, B. Mainali, M. J. Angove. Opportunities and constraints of using the innovative adsorbents for the removal of cobalt(II) from wastewater: A review. Environmental Nanotechnology, Monitoring & Management 10 (2018) 435–456. https://doi.org/10.1016/j.enmm.2018.10.003

[8] J.S. Kim, M.A. Keane. The removal of iron and cobalt from aqueous solutions by ion exchange with Na-Y zeolite: batch, semi-batch and continuous operation. J. Chem. Technol. Biotechnol. 77 (2002) 633–640.

[9] S. Rengaraj, K.-H. Yeon, S.-Y. Kang, J.-U. Lee, K.-W. Kim, S.-H. Moon. Studies on adsorptive removal of Co (II), Cr (III) and Ni (II) by IRN77 cation-exchange resin. J. Hazard. Mater. 92 (2002) 185–198.

[10] S. Rengaraj, S.-H. Moon. Kinetics of adsorption of Co (II) removal from water and wastewater by ion exchange resins. Water Res. 36 (2002) 1783–1793.

[11] S. M. Al-Jubouria, S. M. Holmes, 2020. Immobilization of cobalt ions using hierarchically porous 4A zeolitebased carbon composites: Ion-exchange and solidification. Journal of Water Process Engineering 33, 101059, 1-10. https://doi.org/10.1016/j.jwpe.2019.101059

[12] E. Assaad, A. Azzouz, D. Nistor, A. Ursu, T. Sajin, D. Miron, F. Monette, P. Niquette, R. Hausler. Metal removal through synergic coagulation–flocculation using an optimized chitosan–montmorillonite system. Appl. Clay Sci. 37 (2007) 258–274.

[13] F. L. Becker, D. Rodríguez, M. Schwab. Magnetic removal of cobalt from waste water by ferrite coprecipitation (11th International Congress on Metallurgy & Materials SAM/CONAMET 2011). Procedia Materials Science 1 (2012) 644 – 650. doi:10.1016/j.mspro.2012.06.087

[14] S. Dhiman, B. Gupta. Partition studies on cobalt and recycling of valuable metals from waste Li-ion batteries via solvent extraction and chemical precipitation. Journal of Cleaner Production 225 (2019) 820-832. https://doi.org/10.1016/j.jclepro.2019.04.004

[15] Z.T. Ichlas, M.Z. Mubarok, A. Magnalita, J. Vaughan, A.T. Sugiarto. Processing mixed nickel-cobalt hydroxide precipitate by sulfuric acid leaching followed by selective oxidative precipitation of cobalt and manganese. Hydrometallurgy 191 (2020)105185, 1-7. https://doi.org/10.1016/j.hydromet.2019.105185

[16] V.D. Karate, K. Marathe. Simultaneous removal of nickel and cobalt from aqueous stream by cross flow micellar enhanced ultrafiltration. J. Hazard. Mater. 157 (2008) 464–471.

[17] M. Ashfaq, S. Ali, M. Asif Hanif. Bioaccumulation of cobalt in silkworm (Bombyx mori L.) in relation to mulberry, soil and wastewater metal concentrations. Process Biochemistry 44 (2009) 1179–1184. doi:10.1016/j.procbio.2009.05.006

[18] A. Bhatnagar, A.K. Minocha, M. Sillanpää. Adsorptive removal of cobalt from aqueous solution by utilizing lemon peel as biosorbent. Biochemical Engineering Journal 48 (2010) 181–186. doi:10.1016/j.bej.2009.10.005

[19] H.M. Saleh, T.A. Bayoumi, H.H. Mahmoud, R.F. Aglan. Uptake of cesium and cobalt radionuclides from simulated radioactive wastewater by Ludwigia stolonifera aquatic plant. Nuclear Engineering and Design 315 (2017) 194–199. http://dx.doi.org/10.1016/j.nucengdes.2017.02.018

[20] Q. Zhang, S. Zhuang, J. Wang. Biosorptive removal of cobalt(II) from aqueous solutions using magnetic cyanoethyl chitosan beads. Journal of Environmental Chemical Engineering 8 (2020) 104531, 1-10. https://doi.org/10.1016/j.jece.2020.104531

[21] D. M.S.A. Salem, M. N. Moawad, A. A.M. El-Sayed. Comparative study for bioremediation of cobalt contaminated aqueous solutions by two types of marine macroalgae. Egyptian Journal of Aquatic Research, (2021) in press. https://doi.org/10.1016/j.ejar.2021.02.002

[22] CH.A.I. Raju, J. Anitha, R. Mahalakshmi Kalyani, K. Satyanandam, P. Jagadeesh. Sorption of cobalt using marine macro seaweed graciliariacorticatared algae powder. Materials Today: Proceedings, (2021) in press. https://doi.org/10.1016/j.matpr.2020.12.009

[23] L. Sellaoui, E. P. Hessou, M. Badawi, M. Schadeck Netto, G. Luiz Dotto, L. F. Oliveira Silva, F. Tielens, J. Ifthikar, A. Bonilla-Petriciolet, Z. Chen.Trapping of Ag⁺, Cu²⁺, and Co²⁺ by faujasite zeolite Y: New interpretations of the adsorption mechanism via DFT and statistical modeling investigation. Chemical Engineering Journal, (2021) in press. https://doi.org/10.1016/j.cej.2020.127712

[24] M. Jiménez-Reyes, P.T. Almazan-Sanchez, M. Solache-Ríos. Radioactive waste treatments by using zeolites. A short review. Journal of Environmental Radioactivity 233 (2021) 106610, 1-12. https://doi.org/10.1016/j.jenvrad.2021.106610

[25] S. M. Abdelbasir, A. M. El-Shewaikh, S. M. El-Sheikh, O. I. Ali. Novel modified chitosan nanocomposites for Co(II) ions removal from industrial wastewater. Journal of Water Process Engineering 41 (2021) 102008, 1-13. https://doi.org/10.1016/j.jwpe.2021.102008

 [26] E. L. Vivas, K. Cho. Efficient adsorptive removal of Cobalt(II) ions from water by dicalcium phosphate dihydrate. Journal of Environmental Management 283 (2021) 111990, 1-10. https://doi.org/10.1016/j.jenvman.2021.111990

[27] T.P. Belova. Adsorption of heavy metal ions (Cu²⁺, Ni²⁺, Co²⁺ and Fe²⁺) from aqueous solutions by natural zeolite. Heliyon 5 (2019) e02320, 2-6. https://doi.org/10.1016/j.heliyon.2019.e02320

[28] A. Ali, A. Mannan, I. Hussain, I. Hussain, M. Zia. Effective removal of metal ions from aquous solution by silver and zinc nanoparticles functionalized cellulose: isotherm, kinetics and statistical supposition of process. Environ. Nanotechnol. Monit. Manage. 9 (2018) 1–11.

[29] W. Hu, S. Lu, W. Song, T. Chen, T. Hayat, N.S. Alsaedi, C. Chen, H. Liu. Competitive adsorption of U (VI) and Co (II) on montmorillonite: a batch and spectroscopic approach. Appl. Clay Sci. 157 (2018) 121–129.

[30] W. Luo, Z. Bai, Y. Zhu. Fast removal of Co (ii) from aqueous solution using porous carboxymethyl chitosan beads and its adsorption mechanism. RSC Adv. 8(2018) 13370–13387.

[31] M. E. Mahmoud, E. A. Saad, A. M. El-Khatib, M. A. Soliman, E. A. Allam. Adsorptive removal of radioactive isotopes of cobalt and zinc from water and radioactive wastewater using TiO2/Ag2O nanoadsorbents. Progress in Nuclear Energy 106 (2018) 51–63. https://doi.org/10.1016/j.pnucene.2018.02.021

[32] W. Luo, Z. Bai, Y. Zhu. Comparison of Co (II) adsorption by a cross-linked carboxymethyl chitosan hydrogel and resin: behaviour and mechanism. New J. Chem. 41 (2017) 3487–3497.

[33] Md. R. Awual, M. Ismael, T. Yaita. Efficient detection and extraction of cobalt(II) from lithium ion batteries and wastewater by novel composite adsorbent. Sensors and Actuators B 191 (2014) 9–18. http://dx.doi.org/10.1016/j.snb.2013.09.076

[34] Q. Thi Ngoc Le, E. L. Vivas, K. Cho. Oxalated blast-furnace slag for the removal of Cobalt(II) ions from aqueous solutions. Journal of Industrial and Engineering Chemistry 95 (2021) 57–65. https://doi.org/10.1016/j.jiec.2020.12.003

[35] I. V. Joseph, L. Tosheva, A. M. Doyle. Simultaneous removal of Cd(II), Co(II), Cu(II), Pb(II), and Zn(II) ions from aqueous solutions via adsorption on FAU-type zeolites prepared from coal fly ash. Journal of Environmental Chemical Engineering 8 (2020) 103895, 1-9. https://doi.org/10.1016/j.jece.2020.103895

[36] N.S. Labidi. Removal of mercury from aqueous solutions by waste brick. Inter. J. Environ. Res. 2(3) (2008) 275-278. https://applications.emro.who.int/imemrf/Int_J_Environ_Res_2008_2_3_275.pdf

[37] A. Witharana, M. Jayaweera, J. Manatunge. Zinc adsorption by low cost sorbent materials: Clay title, brick, sawdust and rice husk. International Conference on Sustainable Built Environment (ICSBE-2010), Kandy, 13-14 Decembre 2010: pp. 21-28.

[38] N. Gandhi, D. Sirisha, K.D. Chandra Sekhar. Adsorption studies of chromium by using low cost adsorbents. Our Nature 11(1) (2013) 11-16.

[39] P.V. Hemalatha, P.V.V. Prasada Rao. Adsorption batch studies on calcined brick powder in removing chromium and nickel ions. Inter. J. Adv. Res. Chem. Sci. 1(6) (2014) 14-21. https://www.arcjournals.org/pdfs/ijarcs/v1-i6/3.pdf

[40] R.H. Krishna, A.V.V.S. Swamy. Physico-chemical key parameters, Langmuir and Freundlich isotherm and Lagergren rate constant studies on the removal of calcined brick. Inter. J. Eng. Res. Dev. 4(1) (2014) 29-38. https://idc-online.com/technical_references/pdfs/chemical_engineering/Physico%20Chemical.pdf

[41] S.C. Dehou, J. Mabingui, L. Lesven, M. Wartel, A. Boughriet. Improvement of Fe(II)-adsorption capacity of FeOOH-coated brick in solutions, and kinetics aspects. J. Water Resourc. Protection 4 (2012) 464-473. http://dx.doi.org/10.4236/jwarp.2012.47054

[42] S.C. Dehou, M. Wartel, P. Recourt, B. Revel, J. Mabingui, A. Montiel, A. Boughriet. Physicochemical, crystalline and morphological characteristics of bricks used for ground waters purification in Bangui region (Central African Republic). Appl. Clay Sci. 59-60 (2012) 69-75. https://doi.org/10.1016/j.clay.2012.02.009

[43] O. Allahdin, S.C. Dehou, M. Wartel, P. Recourt, M. Trentesaux, J. Mabingui, A. Boughriet. Performance of FeOOH-brick based composite for Fe(II) removal from water in fixed bed column and mechanistic aspects. Chem. Eng. Res. and Design 9 ((2013) 2732-2742. https://doi.org/10.1016/j.cherd.2013.04.006

[44] O. Allahdin, M. Wartel, P. Recourt, B. Revel, B. Ouddane, G. Billon, J. Mabingui, A. Boughriet. Adsorption capacity of iron oxyhydroxide-coated brick for cationic metals and nature of ion surface interactions. Appl. Clay Sci. 90 (2014) 141–149. https://doi.org/10.1016/j.clay.2014.01.008

[45] O. Allahdin, M. Wartel, J. Mabingui, A. Boughriet. Kinetics of divalent Metals (Cd²⁺, Cu²⁺, Pb²⁺, Zn²⁺) adsorption onto a modified brick. Am. Chem. Sci. J. 4(5) (2014) 687-705. DOI:10.9734/ACSJ/2014/9275

[46] O. Allahdin, M. Wartel, J. Mabingui, A. Boughriet. Implication of electrostatic forces on the adsorption capacity of a modified brick for the removal of divalent cations from water. Am. J. Anal. Chem. 6 (2015) 11-25. http://dx.doi.org/10.4236/ajac.2015.61002

[47] O. Allahdin, B. Bagoua, M. Wartel, J. Mabingui, A. Boughriet. Effects of chemical activation on surface sites of the brick: pH-dependence on metal adsorption. International J. New Technol. Res. 2(1) (2016) 22-31.

[48] N. Poumaye, O. Allahdin, G. Tricot, B. Revel, G. Billon, P. Recourt, M. Wartel, A. Boughriet. MAS NMR investigations on a metakaolinite-rich brick after zeolitization by alkaline treatments. Microporous and Mesoporous Materials 277 (2019) 1-9.

[49] N. Poumaye, O. Allahdin, M. Wartel, A. Boughriet. Insights into characterization and adsorptive behaviour of zeolitized brick in water toward cadmium (A very toxic heavy metal to humans). Int. J. Pharm. Pharmaceut. Res. 13(3) (2018) 1-29. https://ijppr.humanjournals.com/insights-into-characterization-and-adsorptive...

[50] N. Poumaye, O. Allahdin, L. Lesven, M. Wartel, A. Boughriet. Adsorption of Iron (II) on Sodic Zeolites—Bearing Brick (In Batch): Insights into Interfacial Chemical Processes and Thermodynamic Equilibria. International Journal of Science and Research Methodology 11(3) (2019) 88-119. https://ijsrm.humanjournals.com/adsorption-of-iron-ii-on-sodic...

[51] A. Boughriet, N. Poumaye, O. Allahdin, M. Wartel. Kinetic and diffusional aspects of heavy metals adsorption onto zeolitized brick. Advanced Materials and Technologies Environmental Sciences 3(4) (2019) 281-297.

[52] M.K. Seliem, S. Kormarneni, Equilibrium and kinetic studies for dissociation of iron from aqueous solution by synthetic Na-A zeolites: Statistical modelling and optimization. Microporous and Mesoporous Materials 228 (2016) 266-274. https://doi.org/10.1016/j.micromeso.2016.04.010

[53] S. Tontisirin, Synthesis and characterization of co-crystalline zeolite composite of LSX/A. Microporous and Mesoporous Materials 239 (2017) 123-129. https://doi.org/10.1016/j.micromeso.2016.09.051

[54] M. Sathupunya, E. Glari, S. Wongkasemjit, ANA and GIS zeolite synthesis directly from alumatrane and silatrane by sol-gel process and microwave technique. J. Eur. Ceram. Soc. 22 (2002) 2305-2314. https://doi.org/10.1016/S0955-2219(02)00042-0

[55] H.-L. Zubowa, H. Kosslick, D. Müller, M. Richter, L. Wilde, R. Fricke. Crystallization of phase-pure zeolite NaP from MCM-22-type gel compositions under microwave radiation. Microporous and Mesoporous Materials 109 (2008) 542–548. https://doi.org/10.1016/j.micromeso.2007.06.002

[56] S. Khabuanchalad, P. Khemthong, S. Prayoonpokarach, J. Wittayakun. Transformation of zeolite NaY synthesized from rice husk silica to NaP during hydrothermal synthesis. Suranaree J. Sc. Technol. 15 (2008) 225-231.

[57] J. Behin, H. Kazemian, S. Rohani. Sonochemical synthesis of zeolite NaP from clinoptilolite. Ultrasonics Sonochemistry 28 (2016) 400-408. https://doi.org/10.1016/j.ultsonch.2015.08.021

[58] M.M.J. Treacy, J.B. Higgins, Collection of Simulated XRD Powder Patterns for Zeolites (4th Revised Edition), Elsevier, New York (2001), pp. 174-175 and 212-215. DOI:10.1016/B978-0-444-53067-7.X5470-7

[59] M. Murat, A. Amokrane, J.P. Bastide, L. Montanaro, Synthesis of zeolites from thermally ctivated kaolinite. Some observations on nucleation and growth. Clay Minerals 27 (1992) 119-130.

[60] D. Akolekar, A. Chaffee, R.F. Howe, The transformation of kaolin to low-silica X zeolite. Zeolites 19(5-6) (1997) 359-365.

[61] L. Heller-Kallai, I. Lapides, Reactions of kaolinites and metakaolinites with NaOH—comparison of different samples (Part 1). Applied Clay Science 35(1-2) (2007) 99-107.

[62] M.K. Seliem, S. Komarneni, Equilibrium and kinetic studies for adsorption of iron from aqueous solution by synthetic Na-A zeolites: Statistical modeling and optimization. Microporous and Mesoporous Materials 228 (2016) 266-274. https://doi.org/10.1016/j.micromeso.2016.04.010

[63] J. Temuujin, K. Okada, K.J.D. MacKenzie, Zeolite formation by hydrothermal treatment of waste solution from selectively leached kaolinite. Materials Letters 52 (2002) 91-95.

[64] E.B.G. Johnson, S.E Arshad, Hydrothermally synthesized zeolites based on kaolinite: A review. Applied Clay Science 97-98 (2014) 215-221.

[65] L. Ayele, J. Pérez-Pariente, Y. Chebude, I. Diaz, Synthesis of zeolite A from Ethiopian kaolin. Microporous and Mesoporous Materials 215 (2015) 29-36.

[66] N.E. Zimmermann, M. Haranczyk, History and utility of zeolite framework-type discovery from a data-science perspective, Cryst. Growth Des. 16 (2016) 3043-3048.

[67] T. Abdullahi, Z. Harun, M.H. Dzarfan Othman, A review on sustainable synthesis of zeolite from kaolinite resources via hydrothermal process, Adv Powder Technol. 28 (2017) 1827-1840.

[68] W. Loewenstein, The distribution of aluminium in the tetrahedral of silicates and aluminates. Am. Mineral. 39 (1954) 92-96.

[69] I. Langmuir, The constitution and fundamental properties of solids and liquids, Part I Solids, J. Am. Chem. Soc.
 38 (1916) 2221–2295. https://doi.org/10.1021/ ja02268a002

[70] H.M.F. Freundlich, Over the adsorption in solution, J. Phy. Chem. 57 (1906) 385-471.

[71] M.I. Temkin. Adsorption equilibrium and the kinetics of processes on non homogeneoussurfaces and in the interaction between adsorbed molecules, Zh. Fiz. Chim. 15 (1941) 296–332.

[72] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, Chem. Eng. J. 156 (2010) 2–10, https://doi.org/10.1016/j.cej.2009.09.013

[73] O. Redlich, D.L. Peterson. A useful adsorption isotherm, J. Phys. Chem. 63 (1959) 1024–1026, https://doi.org/10.1021/j150576a611

[74] N. Ayawei, A.N. Ebelegi, D. Wankasi. Modelling and interpretation of adsorption isotherms, J. Chem. (2017) 1–11. https://doi.org/10.1155/2017/3039817

[75] M.A. Al-Ghouti, D.A. Da'ana. Guidelines for the use and interpretation of adsorption isotherm models: A review, J. Hazard. Mater. (2020) 122383–122404. https:// doi.org/10.1016/j.jhazmat.2020.122383

[76] R. Sips. Combined form of Langmuir and Freundlich equations, J. Chem. Phys. 16 (1948) 490-495.

[77] D. Barnum. Hydrolysis of cations. Formation and standard free energies of formation of hydroxyl complexes. Inorg. Chem. 22 (1983) 2297-2305.

[78] E. Chmielewska, J. Lesny. Adsorption of cobalt on some natural zeolites occurring in CSFR. Journal of Radioanalytical and Nuclear Chemistry 166(1) (1992) 41-53. https://doi.10.1007/BF02167997

[79] E. Erdem, N. Karapinar, R. Donat. The removal of heavy metal cations by natural zeolites. Journal of Colloid and Interface Science 280 (2004) 309–314.

[80] S. Kubilay, R. Gürkan, A. Savran, T. Sahan. Removal of Cu(II), Zn(II) and Co(II) ions from aqueous solutions by adsorption onto natural bentonite. Adsorption 13 (2007) 41–51.

[81] K.G. Bhattacharyya, S. Sen Gupta. Calcined tetrabutylammonium kaolinite and montmorillonite and adsorption of Fe(II), Co(II) and Ni(II) from solution. Appl. Clay Sci. 46 (2009) 216–221.

[82] M. H. Salmani, M. H. Ehrampoush, H. Eslami, B. Eftekhar. Synthesis, characterization and application of mesoporous silica in removal of cobalt ions from contaminated water. Groundwater for Sustainable Development 11 (2020) 100425, 1-9.

[83] H. Ghassabzadeh, M. Torab-Mostaedi, A. Mohaddespour, M.G. Maragheh, S.J. Ahmadi, P. Zaheri. Characterizations of Co (II) and Pb (II) removal process from aqueous solutions using expanded perlite. Desalination 261 (2010) 73–79.

[84] M. Arshadi, M.J. Amiri, S. Mousavi. Kinetic, equilibrium and thermodynamic investigations of Ni(II), Cd(II), Cu(II) and Co(II) adsorption on barley straw ash. Water Res. Ind. 6 (2014) 1–17.

[85] M. Mureseanu, A. Reiss, I. Stefanescu, E. David, V. Parvulescu, G. Renard, V. Hulea. Modified SBA-15 mesoporous silica for heavy metal ions remediation. Chemosphere 73 (2008) 1499–1504.

[86] K. Vijayaraghavan, M. Thilakavathi, K. Palanivelu, M. Velan. Continuous sorption of copper and cobalt by crab shell particles in a packed column. Environmental Technology 26 (2005) 267–276.

[87] I. Smiciklas, S. Dimovic, I. Plecas, M. Mitric. Removal of Co^{2+} from aqueous solutions by hydroxyapatite, Water Research 40 (2006) 2267–2274.

[88] S. Dimovic, I. Smiciklas, I. Plecas, D. Antonovic, M. Mitric. Comparative study of differently treated animal bones for Co^{2+} removal. Journal of Hazardous Materials 164 (2009) 279–287.

[89] Q. Wang, J. Li, C. Chen, X. Ren, J. Hu, X. Wang. Removal of cobalt from aqueous solution by magnetic multiwalled carbon nanotube/iron oxide composites. Chem. Eng. J. 174 (2011) 126–133.



