Review

Modeling the sorption of metal ions from aqueous solution by iron-based adsorbents

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ABSTRACT

The possibility of using iron-based adsorbents (i.e. akaganéite or goethite) to remove heavy metal ions from aqueous solutions was the aim of the present review paper. Synthesized material was used in two forms, i.e. in fine powder of nanocrystals and in the form of grains (as granular). The main examined parameters were the quantity of sorbent, the presence of ionic strength, the pH value of solution and the metals speciation, including the presence of complexing agents. The removal efficiency of the packed-bed column was examined and compared. Typical adsorption models were discussed and the bed depth–service time equation has been applied to the sorption results in order to model the column operation.

Contents

1. Introduction

Although filtration is one of the principal unit operations in the treatment of potable water, the filtration of effluents is rather less practiced; usual examples are the achievement of supplemental removal of suspended solids from wastewater of biological and chemical treatment processes, and also the removal of chemically precipitated phosphorus. Sorptive filtration was found [1] to be a promising technique, as today there is a tendency for combined and compact processes, offering both the need for effluent treatment due to environmental reasons, plus the recovery of metal values that otherwise perhaps will be lost, and perhaps more importantly water reuse. Adsorption by activated carbon has a long history of use in treating municipal, industrial and hazardous wastes.

Polluted wastewater discharged directly into rivers, poses a great risk to the aquatic ecosystem, while discharge into the sewage system affects bio-sludge activity negatively. As a result of the standards specified in the Water Resources Act, industry takes precautions against these risks by treating dangerous components in a partial stream, i.e. before being mixed with other types of wastewater. So, research was focused, among others, to the development of highly selective bonding agents with fast reaction kinetics for the removal of heavy metal ions [2]. Equilibrium data also are often collected and fitted to known isotherms, such as that

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of Langmuir, Freundlich, Langmuir–Freundlich, Radke–Prausnitz, Brunauer–Emet–Teller, Dubinin–Kaganer–Radushkevich, etc. [3–5].

Several adsorbents can be applied for removal of heavy metals from wastewater; the choice of these depends on their adsorption capacity, availability and cost. Hydrous oxides and oxyhydroxides have been known recently to control trace elements removal, although their use has been limited, mostly due to competition from the commercially available ones in several phases, particle sizes and surface areas, oxides of aluminum or active carbon [6]. These oxyhydroxides are available only as fine powders or are generated in aqueous suspensions as a hydroxide floc or gel. In these forms they retain their desirable sorptive properties for trace elements, but are limited to reactor configurations that incorporate large sedimentation basins or filtration units for subsequent separation. Under such conditions, the separation and regeneration of these materials can be difficult. These disadvantages can be overcome if the oxide is available in granulated form, thereby permitting its use in fixed-bed design. In addition, the comparative insolubility of iron oxides permits their use under greater extremes of pH than most other oxide materials. Such a characteristic is important for regeneration, and for the removal of anionic and cationic contaminants, for which simple pH adjustment is often sufficient.

The fixed-bed operation constitutes the appropriate configuration mode for large-scale applications as those of water and wastewater treatment. Fixed-bed sorption filters filled with an iron-based sorbent were used to remove a range of heavy metals [7]. The homogeneous surface diffusion model and two of its derivatives were used to model anion breakthrough curves with granular ferric hydroxide adsorption filters [8].

Some of the reasons for selecting the iron-based bonding materials were that they are cheap, easily synthesized and they present low risks of adding a further pollutant to the system. In situ production and use of ferric hydroxides for zinc and chromium removal from aqueous solution has been experienced [9], as also the application of mineral fines such as pyrite [10]. In the case of fine particulate matter, flotation has been extensively studied (in our Lab) as a downstream separation method. Mention of zero-valent iron, for instance as permeable reactive barriers to treat contaminated groundwater, should be made, too [11]. Ding et al. [12] have studied the adsorption of arsenate, chromate, phosphate, lead and zinc ion on amorphous black ferric oxyhydroxide. Badruzzaman et al. [13] have used granular ferric hydroxide to identify and quantify mass transport processes of arsenate adsorption in packed-beds. The adsorption of arsenate and salicylic acid onto granulated ferric hydroxide in fixed-bed adsorbents were also experimentally investigated and modeled by Sperlich et al. [14]. The research of Lehmann et al. [15] was focused on the sorption of chromate anions and zinc cations from dilute aqueous solutions using a packed-bed of synthesized granulated goethite. The examined parameters during their investigation were the initial pH value of column, the quantity of sorbent in the column and the influence of a strong chelating agent. Moreover, synthetic goethite from ferric nitrate nonahydrate dissolved in ammonia solution, was used by Matis et al. [16] for pentavalent arsenic removal.

It is noted that a part of the current paper has been recently presented in an Advanced Research Workshop on water treatment technologies for the removal of high toxicity pollutants [17].

1.1. Theory: modeling sorption

Sorption, by definition, is a general term describing the attachment of charged species (like the toxic metal ions) from a solution to a co-existing solid surface. Sorption kinetics may be controlled by

several independent processes that can act in series or in parallel. These processes fall in one of the following general categories:

1. bulk diffusion
2. external mass transfer (film diffusion)
3. chemical reaction (chemisorption) and
4. intraparticle diffusion

Kinetic analyses not only allow estimation of sorption rates but also lead to suitable rate expressions characteristic of possible reaction mechanisms [18]. This extensive study was applied to a biosorbent, *Aeromonas caviae* biomass, a waste often present in groundwater and generally in aquatic environments, proved suitable to remove both metal cations and oxyanions. Evidence was provided that the metals biosorption is a complex process. One is tempted to argue that sorption may be more correctly described by more than one models, as is often the case with the sorption of metal ions. Perhaps, the questioning on surface kinetics is also known, concluding that it is good enough to use the simplest available correlating rate expression [19].

A number of surface complexation approaches have been developed such as the Constant Capacitance, Stern, Diffuse Double Layer and Triple Layer Models [20]. Nevertheless, the fundamental concepts upon which all these are based remain, more or less, the same:

1. sorption of minerals onto surface takes place at specific coordination sites,
2. sorption reactions can be described quantitatively using mass law equations,
3. surface charge results from the sorption reactions themselves,
4. the effect of surface charge on sorption can be taken into account by applying a correction factor, derived from the electrical double layer (EDL) theory to mass law constants for surface reactions.

The latter has been termed as generalized two-layer model, by integrating also surface precipitation for higher concentrations of metal ions. An attempt was made to apply this model for arsenic ions sorption onto goethite [21].

1.2. Theory: packed–bed sorption

During operation of a fixed-bed adsorption column the service time of the system can be related to the bed depth for a given set of experimental conditions. The initial solute (pollutant) concentration fed to the column, is desired to be reduced in the final effluent to a pre-determined value, usually imposed by the respective environmental regulation laws. At the beginning of sorbing operation, when the sorbent material is still unused, the exit concentration is actually lower, than the permitted one. As sorption proceeds and the sorbent material is being gradually saturated, the effluent concentration increases and reaches the so-called "breakthrough" point. Various methods for the designing of fixed-bed columns have been suggested, such as the length of unused bed (LUB) theory, the empty bed residence time procedure, etc., as reviewed in reference [22]. The respective theory for the model as applied to gas adsorption was also presented [23].

The major aim when sizing adsorptive columns is the ability to predict the service time until the column effluent exceeds a pre-defined solute (pollutant) concentration. The Bed Depth Service Time model relates the service time of a fixed-bed with the height of adsorbent in the bed, hence with its quantity, because quantity is directly proportional to the bed height. The measurement of sorbent quantity is more precise than the determination

Table 1
Models of prediction of breakthrough curves, according to Singh et al. [29].

Model equation	Equation number
Bohart and Adams	(2) $\ln\left(\frac{C_0}{C} - 1\right) = \ln\left[\exp\left(kN_0\frac{Z}{U}\right) - 1\right] - kC_0 t \quad t = \frac{N_0}{C_0 U_0}Z - \frac{1}{kC_0}\ln\left(\frac{C_0}{C} - 1\right)$
Thomas	(3) $\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_T q_0 m_c}{Q} - k_T C_0 t$
Yoon and Nelson	(4) $\ln\left(\frac{C}{C_0 - C}\right) = k_{YN}t - t_{0.5}k_{YN}$
Clark	(5) $\ln\left[\left(\frac{C_0}{C}\right)^{n-1} - 1\right] = -rt + \ln A$
Wolborska	(6) $\ln\frac{C}{C_0} = \frac{\beta C_0}{N_0}t - \frac{\beta Z}{U}$

of the respective volume, especially for the case of granules. Therefore, sorbent quantity is being preferably used, instead of the bed height. An appropriate equation was proposed by Chang and Ku [24].

$$t = \frac{q_0}{C_0 V}M - \frac{1}{kC_0}\ln\left(\frac{C_0}{C_t} - 1\right) = aM + b \qquad (1)$$

where t is the service time (min), q_0 the adsorption capacity (mol/g), C_0 the initial concentration of adsorbate (mM), V the applied flowrate (L/min), M the quantity of sorbent inside the column (g), k the rate constant of adsorption (L/min/mol), and C_t the respective effluent concentration of adsorbate (mM) at time t. In fact, the original work on the BDST model is from a long way back in 1920, carried out by Bohart and Adams [25].

A solid diffusion controlled model was used to describe the fixed-bed operation in another case [26]. Also, apart from the BDST, a mass transfer model, the Thomas and the Yoon–Nelson models have been tried elsewhere [27]. The fixed-bed adsorption of p-nitrophenol on activated carbon was examined by Wolborska [28]—see Table 1.

Despite the apparent simplicity of fixed-beds they are difficult to design accurately because the progress of the mass transfer zone (MTZ) introduces time into the equations [30]. To solve the problem rigorously it is necessary, in most practical applications, to solve sets of partial differential equations that describe the mass and heat transfer phenomena. Several short-cut design techniques exist but they can vary considerably in their accuracy. The uncertainties, which arise and the simplifications that are often required inevitably introduce conservatism into the bed sizing calculations. In turn, this leads to equipment sizes and adsorbent inventories being larger than the minimum requirements.

It is fortunate that in most fixed-bed adsorption processes of commercial interest the shape of the mass transfer zone remains unaltered as it progresses through the majority of the bed, because this leads to substantial simplifications in design. For a favourable isotherm, particularly one of Type I [31,32], the mass transfer wave spreads from shock front as it progresses through the initial region of the bed. The shape of the isotherm causes the MTZ to take an asymptotic pattern form and become stable at some distance from the inlet.

For the BDST method the assumption is that the adsorption rate is proportional to both the residual adsorbent capacity and the remaining adsorbate concentration. This equation, which describes in general how the MTZ progresses through a single fixed-bed of adsorbent, can be adapted to include series of fixed-beds and moving bed systems [30].

The application of different flowrates of wastewater through the column can be calculated by multiplying the original slope by the ratio between the original and new flowrate, because changing the flowrate linearly is not expected to have any effect on the ordinate intercept [33]. A variation in feed concentration of metals can be determined by performing some correcting calculations, according to Hutchins [34]; so, various modifications of the BDST model exist. Correlation of the model incorporating a time-dependent term has been developed by McKay and coworkers [35]. The typical (from

gas absorption, distillation, extraction, etc.) transfer unit approach, with NTU and HTU, was also applied for the case [22,30].

2. Materials and methods

The synthesis of iron oxyhydroxides and hydroxides was reported, by the use of a novel, simple and low-cost method [36]. The preparation involves the hydrolysis of aqueous solutions of ferric salts followed by membrane purification and freeze-drying of the products. Three different iron precursors have been tested (iron(III) chloride, nitrate and sulfate) and combined to three different volatile precipitating agents (ammonium carbonate and carbamate, as well as ammonia solution). The obtained products were akaganéite, goethite and iron(III) hydroxide. Irrespective of the starting materials used, all three products, although different in chemical nature, presented some very interesting and unique features; they consisted of nanoparticles with mean sizes ranging from 1 to 10 nm and they had very high surface areas and pore sizes in the meso- and micropore regions. The produced materials were examined by powder X-ray diffraction for crystalline phase identification, TEM and XRD for particle size estimation and nitrogen sorption for surface area, pore volume and pore size distribution measurement (Table 2).

Since the same compounds were previously produced in many other published works, starting from the same materials, with much bigger particle size and considerably lower surface areas, it can be concluded that the particular method used in this work, namely membrane purification followed by freeze-drying, makes the critical difference and drives the preparation towards the synthesis of valuable nanocrystalline products.

The preparation of akaganéite (β-FeO(OH)) as well as the investigation of relative surface properties of the produced iron oxyhydroxide gel was the aim of the initial paper in this area [37]. Akaganéite was prepared by precipitation from an aqueous solution of iron(III) chloride (0.506 M with respect to Fe^{3+}). For the hydrolysis process an aqueous solution of ammonium carbonate ($0.23\,g\,L^{-1}$) was used. The chloride ions were removed through a cellulose membrane by osmosis. The obtained material was freeze-dried in a bench-scale instrument. It is noted that after thermal treatment at 473 and 673 K akaganéite was transformed to iron oxide hydroxide (FeOOH) and finally to hematite (α-Fe$_2$O$_3$). The use of a volatile agent for the hydrolysis process, the special method of chloride ion removal, as well as the freeze-drying technique, led to the production of a material consisting of nanocrystals with high surface area and defined pore size distribution (see Fig. 1). Very finely divided particles might well exhibit properties not predictable from those of the bulk. The prepared material consisted of nanocrystals 2–6 nm in size, with a high specific surface area ($330\,m^2\,g^{-1}$) and narrow pore size distribution (1–6 nm) with a maximum at 3.6 nm. The surface area was slightly decreased for the sample calcined at 373 K, while the total pore volume of $0.35\,cm^3\,g^{-1}$ was preserved.

The method used in this work favoured the synthesis of β-FeO(OH) without the use of an additive (i.e. urotropin). Contrary

Table 2
Physical characteristics of prepared samples.

Sample	Predominant species	Part. size (nm) (Scherrer)	Part. size (nm) (BET)	SSA (BET) $(m^2\,g^{-1})$	Pore volume $(cm^3\,g^{-1})$	Predominant pore diameter (nm) (BJH model)
Cn–Cl	Akaganéite	3–6	4–6	330	0.35	2.5, 3.6
Cm–Cl	Akaganéite	2–4	6–8	358	0.30	2.2, 3.6
NH–Cl	Iron(III) hydroxide	1.5–4	1–2	352	0.26	2.0, 3.6
Cn–N	Goethite	4–6	2–4	316	0.22	1.7, 3.6
Cm–N	Goethite	1.5–4	3	311	0.22	1.9, 3.6
NH–N	Iron(III) hydroxide	1–2	2–3	307	0.22	1.5, 3.6
Cn–S	Goethite	4–6	8–10	284	0.42	2.5, 6.2
Cm–S	Goethite	1.5–4	4–6	280	0.47	2.5, 8.8
NH–S	Iron(III) hydroxide	1–2	3–5	270	0.22	1.5, 3.6

Copyright Elsevier 2003, reprinted with permission from Bakoyannakis et al. [36].
Abbreviations used in sample names: Cn: ammonium carbonate, NH: ammonia solution, Cl: ferric chloride, N: ferric nitrate, S: ferric sulfate (the last 3 as hydrous salts).
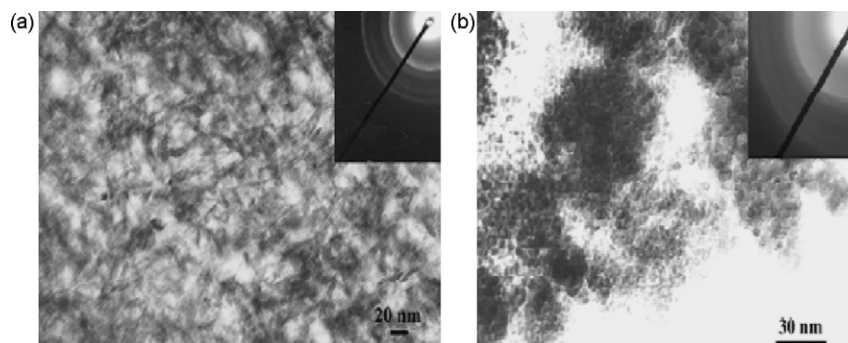

Fig. 1. TEM images: (a) goethite, (b) akaganéite.

to what has been reported about the competitive activity of OH^- versus Cl^- ions, as the pH of the hydrolysis process was increased up to 8, the obtained material was well confirmed to be nanocrystalline akaganéite with considerable features and morphology. This finding may be of significance for magnetic material applications, where the quest for higher magnetic recording densities and better magnetic colloids demand very small particles.

Goethite was the other examined and very interesting material that was carried out by precipitation from nonahydrated iron nitrate salt solution hydrolyzed by ammonium carbonate [36]. Goethite consisted of nanocrystals 1.5–6 nm in size, with a high specific surface area ($316\,m^2\,g^{-1}$) and narrow pore size distribution (1–6 nm) with a maximum at 3.6 nm and total pore volume of $0.22\,cm^3\,g^{-1}$.

3. Discussion of results

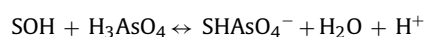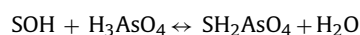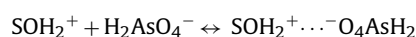### 3.1. Batchwise sorption: influence of main parameters

In recent years, contamination of ground and surface water with heavy metals has become a major concern. The knowledge of the oxidation state of pollutant ions is often a prerequisite for the application of efficient treatment methods, as in the case of arsenic. The inhibition of conventional metal precipitation, due to the presence of chelating or complexing compounds, as acetate, citrate and tartrate ions, ammonia, EDTA, etc., which may be present in most real wastewater streams, is another problem for examination. Thermodynamic equilibrium diagrams and software packages (such as Mineql+) have been employed to construct aqueous speciation diagrams for the metals under investigation and then, interpret the removal mechanism involved.

In Fig. 2 the chemical speciation is presented for an aqueous solution containing simultaneously hexavalent chromium and EDTA species. Although an interaction between Cr(VI) and EDTA

species is not feasible, it can be suggested, based on their distribution, that a strong competition for the same sorption sites is possible to take place between CrO_4^{2-} and $EDTAH_2^{2-}$ anions. This competition results in lower efficiency regarding the adsorption of chromate in the case of the Cr(VI)/EDTA mixed solution, compared to single Cr(VI) solution. Inversely, in the case of Zn(II) aqueous solution the addition of EDTA caused an increase of adsorption efficiency [15]. Same conclusion was found for chelated copper [24].

Moreover, batch tests were performed in order to examine the removal of arsenate oxyanions from dilute aqueous solution with sorption onto synthetic akaganéite, β-FeO(OH) [38]. The effect of the sorbent and pollutant concentration, the contact time, temperature, solution pH value, and ionic strength variation on the treatment process was mainly investigated during this study. Typical sorption isotherms were determined, which were found to fit sufficiently the typical Langmuir equation. The mechanism of sorption was examined by electrokinetic, X-ray diffraction, Fourier transmission infrared and scanning electron microscopy measurements and the authors concluded that arsenate could specifically adsorb on akaganéite surface. The presence of arsenate ions reduced the negative zeta-potential values of solely sorbent particles in the pH range 3–11. Positive identification of sorbed arsenate species was provided using the FTIR technique. Electrostatic effects on oxide surfaces could, in certain instances, account for the enhancement of adsorption in multi-adsorbate systems. The removal of pentavalent arsenic oxyanions was also achieved by goethite [16].

Basic surface reactions describing the mechanism and occurring during the respective tests are the following:
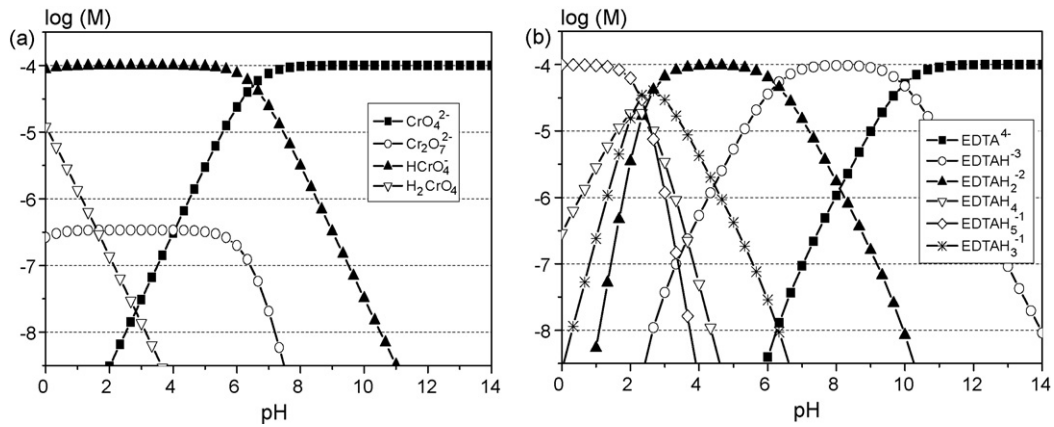
$$SOH_2^+ + H_2AsO_4^- \leftrightarrow SOH_2^+ \cdots^- O_4AsH_2$$

$$SOH + H_3AsO_4 \leftrightarrow SH_2AsO_4 + H_2O$$

$$SOH + H_3AsO_4 \leftrightarrow SHAsO_4^- + H_2O + H^+$$

Fig. 2. Speciation in an aqueous solution containing Cr(VI) and EDTA (0.1 mM) as a function of pH. Copyright Elsevier 2001, reprinted with permission from Lehmann et al. [15].

$$SOH + H_3AsO_4 \leftrightarrow SAsO_4{}^{2-} + H_2O + 2H^+$$

The increased ionic strength of solution resulted in a marked shift in the position of the pH edge towards the alkaline region, and also improved the removal of arsenic in the range between 7 and 12 (Fig. 3). This improvement was attributed to certain depression of negative solid surface charges in the alkaline region, caused by the presence of inorganic electrolyte; therefore, enhancing the interactions between surface sites and arsenic oxyanions, as it was previously described for the case of aluminum oxides [39]. For the lower, acidic pHs (4.5–7), the adsorption percentage of arsenic removal was constant and almost quantitative, i.e. not depending on pH values and unresponsive to ionic strength variations.

The effect of ionic strength on cation and anion adsorption onto oxides provided a measure of the relative bonding affinity of these ions for surface hydroxyl groups. For the case of anions, which bound relatively strongly to the surface of oxides, the change of ionic strength (0.001–1.0 M) was found to show little effect on fractional adsorption. In the case of more weakly bonding anions, the amount adsorbed was reduced with increasing ionic strength; these results were consistent with model predictions [40].

The aforementioned material, akaganéite nanocrystals, was also investigated for cadmium cations removal [41]. The effects of adsorbent amount, initial cadmium concentration, pH value of solution, concentration of background electrolyte ions and temperature vari-

ation on the treatment process of cadmium removal by akaganéite were investigated. Cadmium removal was shown to decrease with the increase of the electrolyte ions in solution. The adsorption isotherm of cadmium on akaganéite (for a solution without electrolyte ions in solution) was expressed by the Langmuir as well as the Freundlich model. All the obtained evidence leads to a mechanism of weak chemisorption (i.e. specific adsorption) possibly describing the removal process. The small concentration of negatively charged surface sites (at pH lower than 8) limits the extent of physical adsorption.

Basic surface reactions occurring during the respective column tests:

$$SOH + Cd^{2+} \leftrightarrow SOCd^+ + H^+ \qquad (\text{physical adsorption})$$

$$SOH + CdOH^+ \leftrightarrow SOCdOH + H^+ \qquad (\text{chemisorption})$$
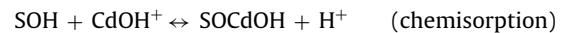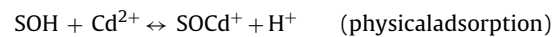
The influence of pH on the sorption of cations was presented (Fig. 4). These experiments were conducted at solution pHs where chemical precipitation of cadmium as hydroxide did not take place, as concluded by the respective aqueous speciation diagram, so that the metal removal was due only to sorption. The speciation diagram of akaganéite was also constructed, showing that the adsorbent surface is positively charged at low pH (<4); hence, under these conditions Cd^{2+} ions cannot be sorbed onto akaganéite due to repulsive forces. The increased cadmium adsorption coincided with the
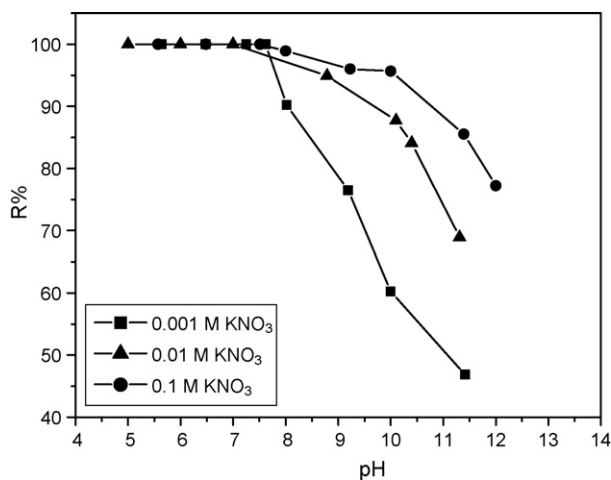

Fig. 3. Effect of pH on As(V) removal by akaganéite for different ionic strengths. Copyright Elsevier 2003, reprinted with permission from Deliyanni et al. [38].
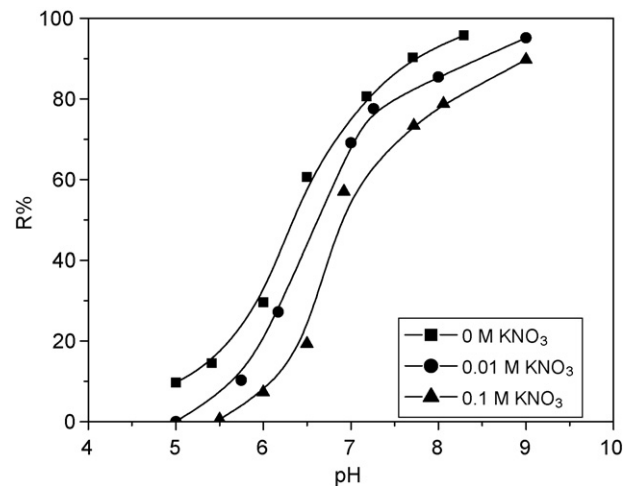

Fig. 4. Influence of pH on Cd ion removal by akaganéite for different ionic strengths. Copyright Elsevier 2005, reprinted with permission from Deliyanni and Matis [41].
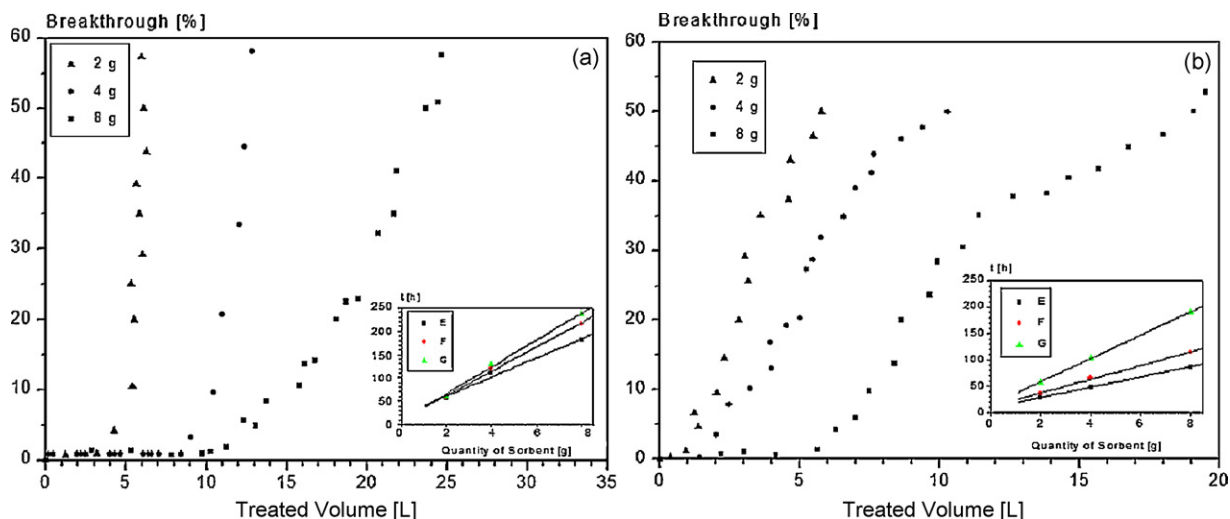
Fig. 5. Breakthrough curves for chromates removal (0.1 mM concentration at pH 3.5) different sorbent quantities and as an inset, iso-removal lines (for 20, 35 and 50% breakthrough); (b) in presence of EDTA (0.1 mM).
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increase discharging of the surface as pH was increased. In the same figure, the effect of the concentration of background electrolyte (KNO$_3$) on metal removal is also presented, showing that the latter is reduced with the concentration rise of the electrolyte, perhaps due to competition between cadmium and potassium ions.

Similar results were obtained for Zn removal [42]. The effect of cationic surfactant on the adsorption of arsenites onto akaganéite nanocrystals, was also successfully studied [43]. The efficient removal of As(III) is quite difficult and usually, an oxidation step is necessary [44]. The adsorbent modification was accomplished either by surfactant adsorption on the material or its coprecipitation and the respective comparison followed. FTIR and XPS analysis gave useful information on the removal process and the synthesized adsorbent [45].

3.2. Packed-bed sorption

The sorption modeling of hexavalent chromium oxyanions and zinc cations, in the presence of complexing agents, on goethite fixed-beds was earlier reported [15]; The Bed Depth Service Time (BDST) model has been applied to the experimental results. Goethite was initially synthesized according to a standard method, from ferric nitrate nonahydrate dissolved in ammonia solution and aged in potassium hydroxide. The resulted powdered material was subsequently granulated/crystallized (following a method developed at the Technical University of Berlin by Driehaus) [15]. During previously performed batch equilibrium experiments the maximum adsorption capacity for granulized goethite was found for Cr(VI) and for Zn(II) [46].

Fig. 5 is a typical example of experimentation in this area. The contact time, a major design parameter, is usually expressed as the empty bed residence time, EBRT or EBCT [35]. From the iso-removal lines, being inplots in the figure, regarding column operation under constant experimental conditions (except of sorbent dosage), the main parameters of BDST equation can be calculated. From the slope of the lines the adsorption capacity can be calculated, while from the intercept the rate constant of adsorption. From the respective linear equation, the necessary quantity of sorbent for a pre-selected service time period can be directly calculated until a defined breakthrough concentration. The results of performed experiments are usually summarized in the form of a table [15].

In order to obtain the full bed capacity, the value at 50% breakthrough is often used, based on the approximate assumption that the S-shaped breakthrough is symmetrical about the 50% break-point. However, this is frequently not the case and can be due to a number of causes, such as irreversibility of the sorption process at high sorbent solid-phase loadings, uneven flow patterns through the bed and the long time taken by the system to reach equilibrium. Special care should be exercised when determining the applicability of short-cut methods for a particular design problem [30].

Column experimental data in terms of COD for a textile industry effluent have been correlated using the BDST model [47]. The results from the model were then used to design a pilot adsorption rig at the plant. The performance of the pilot plant column was accurately predicted by scale-up from the bench-scale columns. Elsewhere [48], the service time of adsorbent beds (of calcined bauxite) under different flowrate and influent concentration of arsenates were also predicted using the BDST model and were compared with experimental observations; the observed data on service time and breakthrough curve correlated well with the theoretical values.

In Table 3 results for the adsorption capacities from the application of BDST for sorption of toxic ions are presented [6]. Akaganéite presented a greater adsorption capacity than that of goethite, although the pH of the treated solution in the case of goethite was adjusted to 3.5 or 5.

Table 3
Adsorption capacities from the application of the BDST model on sorption of toxic ions.

q_0 (mmol g^{-1})	Case	Reference
0.0109	Adsorption of zinc cations on goethite	[15]
0.095	Adsorption of cadmium cations on akaganéite	[8]
0.395	Adsorption of arsenate anions on akaganéite	[8]
0.297	Adsorption of chromate anions on goethite	[15]
4.890	Adsorption of lead cations on silica gel	[50]
0.450	Adsorption of zinc cations on water Fern Azola	[51]

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Note: The experimental conditions (i.e. solution pH) were not quite comparable. The adsorption of lead was conducted at low flowrate.

3.3. Comments and scientific discussions of others

The adsorption of chelated copper on activated carbon was found to vary over the entire solution pH range, possibly because the electrostatic interactions between the activated carbon surface and the dominant species are highly pH dependent [24]. Based on the column adsorption characteristics of both copper and EDTA species, it was further presumed that the concentrated hydrogen ion on the carbon surface might be exchanged with the copper ion of the adsorbed chelate, $CuEDTA^{2-}$, in acidic solutions. An interesting phenomenon observed was that the adsorption behaviour of copper and EDTA was significantly different for higher carbon dosages. The BDST design model that was used could adequately describe the adsorption behaviour of chelated copper species. Although experimental results indicated that further improvement of the aforementioned equation has been necessary, this model offered an alternative method to estimate the exhaust time of activated carbon.

The EBRT is one of the simplest and most straightforward methods for sizing fixed-bed adsorbers. The minimum bed depth can be obtained by conducting an economic analysis that optimises the adsorbent exhaustion rate and the EBRT operating line diagram. The optimised data used for the EBRT plot can be obtained from the new BDST model and correlated different flowrates, influent concentrations and adsorbent particle sizes. The original BDST model assumes a constant bed capacity throughout the column operation, which may not be true in most cases [35]. A time-dependent bed capacity factor has been proposed and applied to the BDST model. The modified BDST model provided a description of the experimental results for the bed depth and service time at different operating parameters, such as flowrate and particle size. The improvement in the sum of the squares of the errors values for the EBRT results based on the modified BDST equation significantly improved the fixed-bed EBRT optimization model. The problems of obtaining a solid-phase loading concentration to design are not only confined to the BDST and EBRT applications.

Ion exchange of Pb^{2+} on clinoptilolite in fixed-bed and batch operations was studied and simple models on experimental data have been applied. Theoretically, the equilibrium isotherm, the capacity and the diffusion coefficient for a specific ion exchange or adsorption system were independent of the experimental method used for their determination. Also, in a fixed-bed reactor the operating capacity and the diffusion coefficient were expected to be independent of the flowrate. However, some experimental results (obtained in the related literature concerning ion exchange and adsorption systems) and the results of this study put the basic theory under question. According to these experiments, the operating capacity was depending on the flowrate, and was different from that measured in batch systems. Paterson's model was used to describe batch kinetics, the Langmuir isotherm was used to correlate equilibrium data and a solid diffusion controlled process was used to describe the fixed-bed operation. Furthermore, the equilibrium isotherm was likely to be influenced by the type of reactor used for its measurement (fixed-bed and batch reactor). Finally, the diffusion coefficient may be different when measured in fixed-bed or batch reactor. These results could be explained only if the type of experimental setup used influenced the equilibrium isotherm. The hydrodynamic differences between the two types of reactors were leading to a different physicochemical behaviour.

Experimental findings with granular ferric hydroxide adsorbing arsenate were discussed in the context of intraparticle surface diffusion affecting packed-bed treatment system design and application of rapid small-scale column tests, to simulate the performance of pilot- or full-scale systems at the bench-scale [13]. Future development and design of arsenic treatment systems were proposed by these authors to consider internal diffusion as a rate-limiting process. For example, modified or new nanostructured adsorbent materials for removing arsenic could be designed with a larger percentage of macropores to increase adsorption kinetics, which would allow higher loading rates. Numerous analogies and commonalities appear to exist between emerging nanostructured adsorbent treatment systems involving porous metal oxides for the removal of inorganic contaminants and the application of carbonaceous adsorbents for the removal of organic compounds.

Breakthrough curves for the adsorption of arsenate and salicylic acid onto granulated ferric hydroxide in fixed-bed adsorbers were experimentally determined and modeled using the homogeneous surface diffusion model [14]. The results suggested that this model was applicable for the adsorption of salicylic acid onto this adsorbent, but not directly applicable to modeling arsenate adsorption. The non-ideal breakthrough curve behaviour of arsenate pointed on a time-dependent surface diffusion coefficient. The reason for this unexpected observation was not clarified. Surface precipitation was discussed as one possible mechanism. An experimental alternative to both modeling as well as time-consuming laboratory and/or pilot studies was the use of rapid small-scale column tests. The obtained results agreed well with the experimental breakthrough curves, and therefore, the tests were believed to be a powerful method not only to predict full-scale breakthrough curves, but also as a research tool.

In another study [5], the thermodynamic and kinetic investigations of Cr(VI) adsorption on the Thuja oriantalis particles were studied using the Langmuir, Freundlich, Radke–Prausnitz BET and D–R isotherm models. The kinetic studies showed that the pseudo second order rate equations were able to provide a realistic description of adsorption kinetics of Cr(VI). Isotherm studies indicated that the Freundlich and D–R isotherm models were found suitable, but the BET, Langmuir and Radke–Prausnitz isotherm models were not able to describe the adsorption equilibrium of Cr(VI). The value of adsorption energy gave an idea of the nature of adsorption. The activation energy of the Cr(VI) adsorption was calculated using Arrhenius equation. The adsorption dependence of Cr(VI) on temperature was investigated and the thermodynamic parameters ΔH°, ΔS° and ΔG° were calculated. The results show an endothermic heat of adsorption and negative free energy value, indicating that the process of Cr(VI) adsorption was favoured at high temperatures.

The result of certain investigations [48] revealed that the modified calcined bauxite was efficient in removing As(V) from aqueous environment with an adsorption capacity of $627.3\,mg\,L^{-1}$ in the continuous flow system. A bed depth of mere 1.3 cm of a fixed 10 cm bed of adsorbent could produce effluent of As(V) concentration less than $0.01\,mg\,L^{-1}$ from an influent of $2\,mg\,L^{-1}$ at a flowrate of $8\,mL\,min^{-1}$. The BDST approach used in the analysis of column performance and evaluation of characteristic parameters exhibited good correlation with experimental results. The theoretical breakthrough curves obtained from continuously mixed batch reactor by Langmuir isotherm data and experimental breakthrough curves exhibited identical trends. The pH of the treated water was found to be ~7 (which is within the drinking water range). The quality of the effluent water, and the consistent adsorption capacity under various operating conditions, rendered it as a potential adsorbent for scavenging.

Experimental and theoretical investigations were carried out on As(III) adsorption from aqueous solution onto iron oxide-coated cement (IOCC) in a continuous fixed-bed column at various bed depths, flowrates and initial As(III) concentrations [27]. The results obtained are as follows: these studies showed that IOCC was an effective adsorbent in removing As(III) from the aqueous environment and the sorption of As(III) was strongly dependent on the bed depth, flowrate and initial As(III) concentration. With the increase in flowrate the breakthrough curves became steeper, the break-

through time and As(III) removal percentage decreased. The total quantity of As(III) adsorbed increased with the increase in inlet As(III) concentration but removal percentage decreased. The effectiveness of the column increased when lower flowrates and higher bed depths were used. The breakthrough data predictions by the BDST approach slightly deviated from the experimental results above breakpoint due to complexity of the adsorption process. The mass transfer model on the other hand could not provide a very good correlation between the data obtained from the batch and the column experiments. Further, the Thomas and Yoon–Nelson models provided very good descriptions of the breakthrough curves at all the process parameters studied and were proposed for use in column design. The mechanism of lead removal in the column included ion exchange and physisorption.

Synthetic iron–nickel oxide magnetic particle in co-sedimentation was suitable for selective adsorbing and recycling hexavalent chromium from the binary Cr(VI) and Ni(II) liquid in wastewater [4]. The effect from co-existing ions was really weak, except from phosphate. Langmuir isotherm was employed successfully to describe adsorption equilibrium of Cr(VI) and the maximum adsorption capacity was about $30\,mg\,g^{-1}$. The ion exchange of $HCrO_4^-$ ion with OH^- was the major mechanism in adsorption process, because the adsorption energy was about 10–$21\,kJ\,mol^{-1}$, energy spectra and FTIR image presented peak of Cr, forming an outer-sphere complex during the process and the adsorption capacity was strongly depended on ionic strength. The regeneration (using solution of $0.1\,mol\,L^{-1}$ NaOH) was also examined, indicating that the economic benefit of using this magnetic oxide particle was better in the treatment of wastewater containing Cr(VI) and Ni(II) compared to the conventional methods.

The simultaneous heavy metals removal (i.e. from stormwater and industrial wastewaters) was studied using columns of iron-based sorbents [7]; the effect of humic acid and light on the removal was elucidated. Using the data obtained from the column experiments and the Thomas model, the following conclusions were drawn: the results suggested that the adsorbent was highly efficient for simultaneous adsorption of As, Cd, Cr, Cu, Ni, and Zn from aqueous solutions with estimated breakthrough capacities of 10.57, 21.85, 15.96, 12.86, 17.54, and $11.07\,\mu mol\,g^{-1}$ for As, Cd, Cr, Cu, Ni and Zn, respectively. The presence of $100\,mg\,L^{-1}$ humic acid significantly suppressed the removal of all heavy metals, and the suppression was the highest for Cr with 81%. The columns run at the dark demonstrated moderately suppressed heavy metal removal in the absence of humic acid, while the suppression was minor in the presence of humic acid.

Breakthrough curves for the adsorption of arsenate, phosphate, dissolved organic carbon, and salicylic acid onto granular ferric hydroxide were predicted using the homogeneous surface diffusion model [8]. The applicability of two simplifications of this model was limited and depended on the values of the dimensionless Biot and Stanton numbers. Arsenate adsorption onto GFH showed very slow surface diffusion coefficients, leading to high Biot numbers. In most cases, the linear driving force model and the constant pattern homogeneous surface diffusion model were not able to describe arsenate breakthrough in the fixed-bed filters; limits of their applicability were defined. When designing fixed-bed adsorbers, model selection based on known or estimated Biot and Stanton numbers was possible.

In a recent study, activated carbon packed-bed was used to analyze the column dynamics in the adsorption process [29]. The influence of the bed height, inlet pollutant (furfural) concentration, flowrate and column diameter on breakthrough curves have been investigated. Higher uptake of furfural was observed at highest bed height. It was found that the time to breakthrough decreased with an increase in inlet concentration. The larger the latter is, the steeper was the slope of the breakthrough curve and smaller was the time to breakthrough. The amount of furfural adsorbed onto the unit bed height increased with an increase in flowrate leading to faster saturation at a higher value. It was also found that the adsorbent usage rate decreased with an increase in EBCT. The plot of 50% breakthrough versus bed height curve did not pass through the origin indicating the adsorption of furfural onto this adsorbent occurred through complex mechanism. The adsorption capacity as calculated from the slope of 50% plot. Adams–Bohart, Thomas, Yoon–Nelson, Clark and Wolborska models were applied to the experimental data for the prediction of the breakthrough point. Error analysis showed that Yoon–Nelson model was most suitable for the tracing of breakthrough curve at the experimental condition.

4. Concluding remarks

The United Nations warns that the world's use of water is not sustainable. Globally, agriculture claims 70% of the world's supply of fresh water, leaving little for industry. Nevertheless, the latter in certain countries (i.e. China) heavily contaminates water, where the government acknowledged that more than 300 million people do not have access to safe drinking water. The need for fresh sources of drinking water is becoming more and more urgent worldwide, including many areas and/or countries across the Mediterranean Sea.

Environmental sustainability is a stand to stay within forecasted limits in the resources and renewability capacity of the Earth [49]. The technology for this further includes using the principles of industrial ecology to locate ways to use wastes and recycle products as source materials for other processes to make and close material cycles. The understanding and application of sustainability from a chemical engineering viewpoint was presented [50]. A steel industry waste material was tried, among various low-cost adsorbents (many non-conventional), for the removal of Cr(VI) from aqueous solution [51].

The possibility of using a packed-bed (in column configuration) of akaganéite to remove oxyanions like As(V) and cations like Cd from aqueous solutions was the aim of an aforementioned study [6]. Synthesized akaganéite was used in two forms, i.e. in fine powder (of nanocrystals) and in the form of grains (as granular). The main examined parameters were: (a) the quantity of sorbent in the column, and (b) the presence (or not) of ionic strength.

A sorption process as alternative removal technique was proposed and examined in order to evaluate the removal efficiency of a new adsorbent. The BDST model was fitted to the experimental results. From the obtained breakthrough curves the following were concluded:

1. In all cases the sorbent mass increase resulted in better removal efficiency.
2. Nanostructured akaganéite presented higher removal efficiency than granular akaganéite.
3. The effect of ionic strength was positive as it was expected from batch experiments, for the case of arsenate.
4. The removal efficiency of akaganéite (both nanostructured and granular) for anionic arsenate was more pronounced than that of cationic cadmium species.

From the obtained breakthrough curves and from the calculation of model parameters, the following classification of removal efficiency could be depicted:

$$As(V)_{Akn-I=0.1} > As(V)_{Akg-I=0.1} > As(V)_{Akn-I=0} > As(V)_{Akg-I=0}$$

$$> Cd(II)_{Akn-I=0} > Cd(II)_{Akg-I=0}$$

where Ak_n denoted the nanostructured akaganéite, Ak_g the granular akaganéite and I the ionic strength in presence of KNO_3. The BDST model, finally, was found to be a simple but effective methodology for designing and controlling the removal of toxic ions for waters. Empirical (short-cut) methods are still used extensively for the design of fixed-beds.

Acknowledgements

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