

# COMPOSITE NANOADSORBENTS

Edited by  
George Z. Kyzas  
Athanasios C. Mitropoulos

Micro & Nano Technologies Series



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# Preface

One of the most recent trends in environmental technology is the research turn to adsorbent materials. It is generally accepted that one of the most promising techniques for wastewaters treatment is adsorption. Based on this, numerous adsorbent materials have been synthesized up until now. However, there is a novel concept nowadays, which promotes the use of nanomaterials with the lowest possible cost. The most important aspect of nanomaterial is their special properties associated with nanoscale geometries. The most fundamental characteristic of nanomaterial is the high surface area to volume ratio, which results in a number of unusual physical and chemical properties such as high molecular adsorption, large surface tension force, enhanced chemical and biological activities, large catalytic effects, and extreme mechanical strength, but another unique property of nanomaterial and recently most studied is the quantum size effect that leads to their discrete electronic band structure like those of molecules. The present book “Composite Nanoadsorbents” includes recent progress of selected nanomaterials combining two major classes of recent science: (i) adsorption and (ii) nanotechnology. Two main categories of environmental pollutants majorly discussed are as follows: (i) dyes and (ii) heavy metals. Extensive comparison is described for the composite nanoadsorbents: (i) their adsorption capacity, showing the main models used up till now for the expression of their theoretical maximum capacity; (ii) their kinetic behavior, showing the main models used and some more specific kinetic simulations; (iii) parameters influenced by adsorption (salinity, particle size or mass of adsorbent, etc.); (iii) their reuse potential, given the ultimate goal of each adsorbent to be used in industrial/factorial design; (iv) fixed-bed columns; (v) the surface of the low-cost materials (comments about their characterization); (vi) economic perspectives; and (vii) future trends and applicability. All the above clearly indicate that the “world” of composite nanoadsorbents has various sections. Therefore, the target of this book is wide. Specialists, researchers, and professors from many countries have contributed to this book their research into nanoadsorption. We are grateful to all the authors who have contributed their tremendous expertise to the present book.

George Z. Kyzas, Athanasios C. Mitropoulos  
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## Dedicated to

- Prof. Nikolaos K. Lazaridis (Aristotle University of Thessaloniki, Greece) who showed me the road of Adsorption.
- Prof. Dimitrios N. Bikiaris (Aristotle University of Thessaloniki, Greece) who showed me the road of Composite Materials.
- Prof. Athanasios C. Mitropoulos (Eastern Macedonia and Thrace Institute of Technology, Greece) who showed me the road of Nanotechnology.

The combination of all gave me the expertise in Composite Nanoadsorbent Materials.



# Inorganic Nanoadsorbent: Akaganéite in Wastewater Treatment

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## 1 Introduction

Worldwide environmental problems are becoming more and more acute. The presence of priority pollutants in the effluent streams from several chemical (and metal plating) industries has been a major environmental problem for both industries and neighboring municipalities. It is known that many specific industrial wastewater streams with large flows contain toxic metals in concentrations (up may be to 500 mg/L), which have to be removed prior to water recycling, indirect discharge into the sewage system or direct discharge into surface waters [1]. Serious concerns about possible contamination of ground and surface waters by pollutants leached from abandoned disposal sites but also, in certain cases, from currently operating ones have generated various efforts aimed at remediating contaminated soils. The removal of toxic metals (such as cadmium) was investigated by using hydroxyapatite, an effective inorganic sorbent, at the ultrafine particle size range (average diameter  $\sim 2.5 \mu\text{m}$ ); calcium hydroxyapatite (often denoted as HAP) is the prototype of an inorganic crystalline constituent in human calcified tissues [2]. The interaction between HAP and cadmium ion could not be explained by simple adsorption, indicating that possibly more than one mechanism was simultaneously responsible to some extent for the removal process (e.g., adsorption, ion exchange, surface complexation, precipitation or coprecipitation, etc.).

Inorganic materials used as sorbents exhibit a number of specific advantages, such as easier preparation and lower costs, compared with the respective synthetic organic ion exchangers. Many inorganic adsorbents have been applied including mineral by-products, such as the pyrite fines [3]; pyrite (iron sulfide mineral), was found to act as an efficient Cr(VI) reducing agent. The resulted hydroxo-Cr(III) species were found to be precipitated and hence, removed onto the pyrite particles (at  $-45 \mu\text{m}$  size range). Low-cost by-products from agricultural, household, and industrial sectors have been

indeed recognized as a sustainable solution for wastewater treatment [4]. So, activated carbons prepared after pyrolysis of waste potato peels, were investigated for the removal of cobalt ions from synthetic wastewaters [5].

Inorganic sorbents, including also the inorganic ion exchangers, were said to have received far less attention for the treatment of wastewaters than their organic counterparts, even though they represent a wide range of natural and synthetic minerals [6]. Adsorption is widely popular for removal of heavy metals due to its low cost, efficiency, and simplicity [7]; focus of the review was the use of inorganic adsorbents engineered at the nanoscale.

The combination of flotation following sorption downstream (termed sorptive flotation) for metal cations removal by ion-exchange materials, as the synthetic zeolites, gave promise for an improved metal separation process. Flotation perhaps constitutes an alternative as a solid/liquid separation for sorbents (including the biosorbents), which usually exist at the fine or ultrafine particle size range [8]. The application of this technique for the removal by (prepared) goethite of chromium(VI) and zinc ions was one aim of a published paper [9]; further, adsorbing colloid flotation with ferric hydroxide (as the coprecipitant) could be another method for the above-mentioned metal ions removal. The relation of the aforementioned processes to sustainability has been discussed [10].

Synthetic dyestuffs, which are used extensively in textile, paper, printing industries, and dye houses, constitute another pollutant of concern. The effluents of these industries are highly colored and their disposal into receiving waters causes damage to the environment as they may significantly affect photosynthetic activity in aquatic life [11]. Chemically, many of the reactive dyes belong to the group of anionic monoazo dyes. Many of them are “acid dyes”; name derived from the dyeing process.

The potential of nanomaterials as nanoadsorbents and their many advances was discussed in a recent review [12]. At the nanoscale level, materials are characterized by different physical, chemical, and biological properties than their normal-size equivalents; noting that “nano” is derived from the Greek word for dwarf. The surface area of particles increases with decreasing particle size and as such, nanoscale particles exhibit different optical, electrical, and magnetic properties from the properties exhibited by macroscopic particles [13]. The potential of nanomaterials as nanoadsorbents and their many advances afforded in the separation and pre-concentration of a variety of analytes have been also outlined [14]. A deep insight, bridging the gap among the past, present, and future of the elegant nanosorbents for heavy metals removal from wastewater was also presented [15].

Typical equations that are applied to studies in this area are briefly given in Table 1; while, other sorption isotherm models were elsewhere presented, like the Brunauer-Emmett-Teller, Redlich-Peterson, Dubinin-Radushkevich, Temkin, Toth, Koble-Corrigan, Sips, Khan, Hill, Flory-Huggins, Radke-Prausnitz isotherm, etc. [12]. Work in this scientific field is usually sorption isotherms, process mechanism, kinetics, and thermodynamics, in batch mode or a packed-bed-type unit.

Presumably, the most important and widely used sorbent in water/wastewater technology is activated carbon. Modified activated carbon (microporous or mesoporous)

**Table 1** Typical Equations/Models Often Used in These Studies [5,27]

For the total surface charge (mmol/g):

$$Q_{surf} = \frac{C_A + C_B + [H^+] + [OH^-]}{W}$$

where  $C_A$  and  $C_B$  (mol/L) are the acid and base concentrations, respectively;  $[H^+]$  and  $[OH^-]$  are the equilibrium concentrations of those ions (mol/L), and  $W$  (g/L) is the solid concentration

Kinetics of pseudo-first and -second order:

$$C_t = C_0 - (C_0 - C_e)(1 - e^{-k_1 t})$$

$$C_t = C_0 - (C_0 - C_e) \left( 1 - \frac{1}{1 + k_2 t} \right)$$

where  $k_1$ ,  $k_2$  ( $\text{min}^{-1}$ ) are the rate constants for the pseudo-first, -second-order kinetic model, respectively, and  $C_0$ ,  $C_t$ , and  $C_e$  (mg/L) are the initial, transient, and equilibrium concentrations of adsorbate in the aqueous solution, respectively

Amount  $Q_e$  (mg/g) of solid phase in equilibrium:

$$Q_e = \frac{(C_0 - C_e)V}{m}$$

Column experiments (BDST model):

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

where  $t$  is the service time (min),  $q_0$  the adsorption capacity ( $\text{mol g}^{-1}$ ),  $C_0$  the initial concentration of adsorbate (mM),  $V$  the applied flow rate ( $\text{L min}^{-1}$ ),  $M$  the mass of sorbent inside the bed (g),  $k$  the rate constant of adsorption ( $\text{L min}^{-1} \text{mol}^{-1}$ ), and  $C_t$  the respective effluent concentration of adsorbate (mM) at time  $t$

Sorption isotherms Langmuir and Freundlich:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$$

$$Q_e = K_F C_e^{1/n}$$

where  $Q_m$  (mg/g) is the maximum amount of adsorption;  $K_L$  (L/mg) is the Langmuir adsorption equilibrium constant;  $K_F$  ( $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}$ ) is the Freundlich constant representing the adsorption capacity;  $n$  (dimensionless) is the constant depicting the adsorption intensity

Thermodynamics:

$$K_c = \frac{C_s}{C_e}$$

$$\Delta G^0 = -RT \ln(K_c)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\ln(K_c) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

three main parameters are usually calculated (the change of Gibbs free energy ( $\Delta G^0$ , kJ/mol), enthalpy ( $\Delta H^0$ , kJ/mol) and entropy ( $\Delta S^0$ , kJ/mol K)) based on the isotherms resulted at different temperatures (where  $C_s$  (mg/L) is the amount adsorbed on a solid at equilibrium and  $R$  is the universal gas constant)

was examined, for instance, as adsorbents for the removal of lead ions from water [16]. The modifications involved the following: (i) oxidation, to introduce oxygen-containing functional groups and (ii) treatment with aqueous ammonia, to introduce basic nitrogen functional groups. Oxidation and treatment with ammonia severely affected the porosity of carbons. Pore volumes and surface areas decreased for all modified samples.

A direct comparison between an examined sorbent for a specific wastewater application with those obtained in the literature is generally difficult, due mainly to the varying experimental conditions employed in the studies (see Table 2—here for arsenates).



**Table 2** An Example of Comparison for Pollutant Removal, as Maximum Adsorption Capacity ( $Q_{max}$ , mg/g), From Wastewaters by the Application of Several Adsorbents

Adsorbent	pH	Adsorption Capacity (mg/g)
Mycon/HDTMA	3	57.85
Bauxite	3.5	12.6
Activated bauxite	3.5	6.9
Activated chitosan	2.5	197.6
Fly ash	2.2	34.5
Fly ash	4	27.78
Hydrotalcite	3–7	15.8
Activated alumina	2.6	12.34

From M.X. Loukidou, K.A. Matis, A.I. Zouboulis, M. Liakopoulou-Kyriakidou, Removal of as(V) from wastewaters by chemically modified fungal biomass, *Water Res.* 37 (2003) 4544–4552, Copyright Elsevier.

Adsorption of arsenate oxyanions has been studied by various investigators using a variety of different sorbents, including the biosorbents; like here Mycon (*Penicillium chrysogenum* biomass) that, for this scope, was requiring also pretreatment with a common surfactant. Biosorption, that is, the uptake of heavy metals by dead biomass, has gained credibility recently, as it offers a technically feasible and economical approach. Similar extended tables, for various heavy metals with various experimental data respectively, were given in a recent review paper [15]. The relative comparison of adsorbents should also take into account other parameters, such as simplicity in synthesis, stability in operation, regenerability, availability of raw materials, and of course cost. Cost is, in general, an important parameter, although cost information is seldom reported [6].

## 2 Akaganéite-Type Nanocrystals

Iron oxyhydroxides and oxides are used as model systems for the study of fundamental colloid and surface properties of metal oxides. These compounds are of technological importance as catalytic materials, sorbents, pigments, flocculents, coatings, gas sensors, ion exchangers, etc. Akaganéite [ $\beta$ -FeO(OH)], being a natural oxyhydroxide mineral, has a hollandite-type crystal structure (like BaMnO<sub>2</sub>), containing tunnel-shaped cavities, running parallel to the c-axis, the sites being bound by double rows of fused octahedra, in which chloride ions resides; pointing out that large ions, such as chloride, are necessary for the formation of this tunnel structure [17,18]. Among the various synthetic methods (due mainly to the hydrolysis conditions) available at the time, the following preparation was followed; a simple and low-cost method, with good results—as the latter will be briefly described below.

The sorbent samples were prepared in the lab by precipitation from aqueous solutions of iron(III) chloride, nitrate, and sulfate. For the hydrolysis process, aqueous solutions of ammonium carbonate and carbamate, as well as ammonia solution were used. The preparation of the gels was carried out in a three-necked round-bottom flask, placed in a thermostat.

The precipitating agent was added dropwise, using a dosimetric pump at a constant flow rate. Vigorous mechanical stirring was applied in order to achieve good mixing of the reactants and to prevent a possible agglomeration of the gel. The starting pH of the process was 1.7, while the final one was adjusted to 8. After the addition of the precipitating agent, the stirring was continued (for at least 15 min). The precipitate thus obtained was decanted in a dialysis tubing cellulose membrane, and the latter was placed in a bath of distilled water. Upon standing, the anions of the suspension were removed by osmosis through the membrane. The water of the bath was replaced many times until no more anions were detectable in it. The resulting cake, on the membrane surface, was isolated from the mother liquor and freeze dried, until the temperature of the frozen gel reached the ambient temperature. The material obtained after the freeze-drying process appeared in the form of ultrafine powder [19].

This method yielded unique nanocrystalline products; akaganéite, goethite, and iron(III) hydroxide were obtained, depending on the initial chemicals used for the precipitation step. However, irrespective of the chemicals used, in all cases, the obtained freeze-dried products consisted of nanoparticles with very high surface areas, with no internal porosity and with pore sizes in the range of meso- and micropores. The identity of the crystalline phases was determined by powder XRD, while for the particle size estimation, Scherrer analysis of the XRD spectra and transmission electron microscopy (TEM) micrographs was used. Nitrogen sorption isotherms provided data for surface areas and interparticle distances. The particle size of the nine produced samples (see Table 3) ranged from 1 to 10 nm. Since the same compounds were previously produced in many other published works, starting from the same materials, with much bigger particle size and

**Table 3** Physical Characteristics of Prepared Iron Adsorbent Samples, Depending on the Synthesis Method

Sample <sup>a</sup>	Predominant Sorbent Particle Size	Specific Surface Area Pore Volume Predominant Pore Diameters	(nm) (Scherrer) (nm) (TEM)	(m <sup>2</sup> g <sup>-1</sup> ) (BET)	(cm <sup>3</sup> g <sup>-1</sup> )	(nm) (by two models)
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

<sup>a</sup>Abbreviations used in the sample name: Cn: ammonium carbonate, Cm: ammonium carbamate, NH: ammonia solution, Cl: FeCl<sub>3</sub>6H<sub>2</sub>O, N: Fe(NO<sub>3</sub>)<sub>3</sub>9H<sub>2</sub>O, S: Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>xH<sub>2</sub>O.

From D.N. Bakoyannakis, E.A. Deliyanni, A.I. Zouboulis, K.A. Matis, L. Nalbandian, Th. Kehagias, Akaganéite and goethite-type nanocrystals: synthesis and characterization, Microporous Mesoporous Mater. 59 (2003) 35–42, Copyright Elsevier.

considerably lower surface areas, it was concluded that the particular method used, namely membrane purification followed by freeze drying, made the critical difference and drove the preparation toward the synthesis of valuable nanocrystalline products [20].

## 2.1 Certain Application Examples

A priority pollution problem, the removal of arsenate oxyanions from dilute aqueous solutions by sorption onto synthetic akaganéite was the aim of a study [21]—see Table 4 for a relative comparison. The percentage removal of arsenic for different sorbent concentrations is presented in Fig. 1, when the initial As(V) content was varied. It is obvious that increasing the amount of sorbent, the removal of arsenic was also increased. The sorbent retained its high surface area and crystalline for long and even after its regeneration—that is, by a caustic bath. Since the starting reagents are cheap and common, the sorbent can be characterized as a low-cost and easily available sorbent.

An innovative adsorbent nanocrystalline hybrid surfactant-akaganéite, which was synthesized in the laboratory using  $\text{FeCl}_3$  as the precursor and a cationic surfactant, hexadecyl-trimethylammonium bromide, as modifier showed a significantly higher arsenate adsorption capacity [ $\sim 180 \text{ mg As(V)}/\text{g}$ ] than the pure nanocrystalline akaganéite [of about  $120 \text{ mg As(V)}/\text{g}$ ], presenting also fast kinetics [22]; the latter obeyed a pseudo-second-order rate equation, with correlation coefficient  $R^2$  of the order of 0.999. X-ray photoelectron spectroscopy (XPS) measurements and Fourier transform infrared (FTIR) spectra indicated that arsenate ions rather reacted with surface  $\text{OH}^-$  functional groups than with the surfactant external polar groups of the hybrid sorbent, which meant that the quaternary ammonium surfactant incurred a favorable Donnan effect.

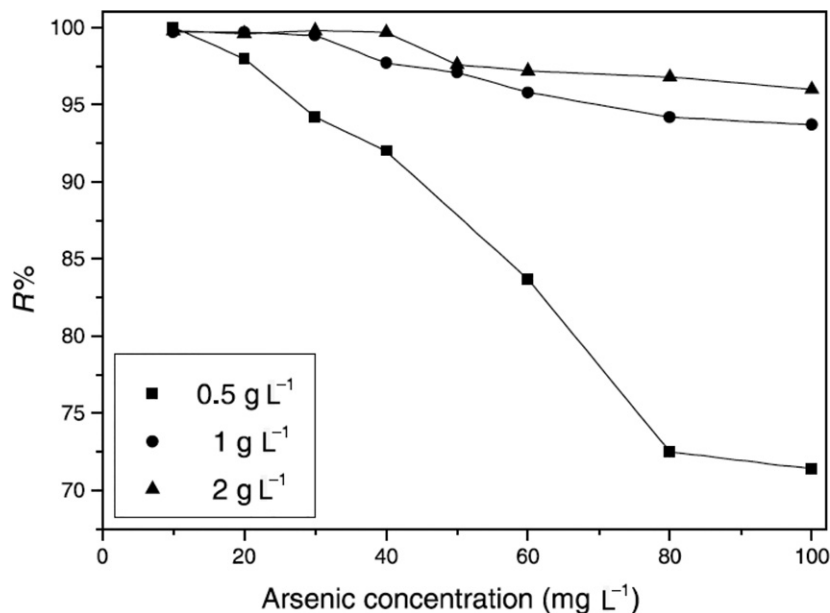
Sorption is, by definition, a general term describing the attachment of charged species (like the toxic metal ions) from a solution to a coexisting solid surface. Sorption kinetics may be controlled by several independent processes that can act in series or in parallel. These processes fall in one of the following general categories: (i) bulk diffusion,

**Table 4** A Comparison of Some Published Maximum Adsorption Capacities of Various Sorbents for As(V) Ions (see also Table 2)

$Q_{\max}$ mmol As(V)/g	pH	Adsorbent
1.79	7.5	Akaganeite
2.01	4	Hydrous iron oxide
1.79		Ferrihydrite
1.34	4	Hydrous ferric oxide (HFO)
0.34	7.5	AmFeOOH
1.25	5.6–6	Goethite
0.15	7	Fly ash
0.37	5	Goethite
0.59	3	Goethite

From E.A. Deliyanni, D.N. Bakoyannakis, A.I. Zouboulis, K.A. Matis, Sorption of as(V) ions by akaganéite-type nanocrystals, Chemosphere 50 (2003) 155–163, Copyright Elsevier.





**FIG. 1** Effect of initial arsenic concentration on As(V) removal for different akaganéite concentrations ( $I = 0.1$  M  $\text{KNO}_3$ , pH 7.5, contact time 24 h and temperature 298 K). Reprinted with permission, copyright Elsevier, E.A. Deliyanni, D.N. Bakoyannakis, A.I. Zouboulis, K.A. Matis, Sorption of as(V) ions by akaganéite-type nanocrystals, *Chemosphere* 50 (2003) 155–163.

(ii) external mass transfer (film diffusion), (iii) chemical reaction (chemisorption), and (iv) intraparticle diffusion [23]. In a thoroughly studied biosorption example (i.e., *Aeromonas caviae* biomass for the removal of cadmium cation and hexavalent chromium oxyanion), it was finally said that the conducted analysis had been rather not capable of providing strong evidence in favor of any of the examined mechanisms, since several diverse kinetic models were successful in fitting the experimental data.

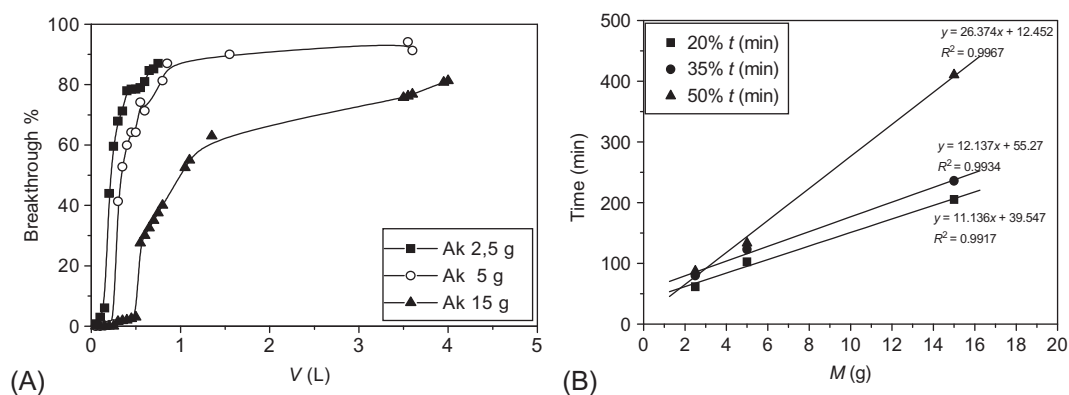
Arsenic occurrence and mobility in natural waters and its removal in water treatment have become the focus of increasing attention, as it is one of the most toxic of contaminants found in the environment; arsenic is occurring in many natural waters, as well as in various industrial wastes, solid or liquid, entering the environment from anthropogenic sources (the Bangladesh crisis with the contamination of water wells, poisoning millions of people, perhaps being the best example). It is known that at pH range between 3 and 6 pentavalent arsenic occurs mainly in the form of  $\text{H}_2\text{AsO}_4^-$ , while the divalent anions  $\text{HAsO}_4^{2-}$  dominate at higher pH values, between 8 and 10.5. While As(III) ions are chemically known to present rather peculiar speciation in aqueous solution, as mainly they remain protonated, as arsenious acid ( $\text{H}_3\text{AsO}_3^0$ ), at pH values lower than around 9; in the alkaline region the form  $\text{H}_2\text{AsO}_3^-$  starts to appear, and in the acidic region the form  $\text{H}_4\text{AsO}_3^+$  is found too, at lower concentrations [24].

The chemical kinetics of the process was studied, described by a pseudo-second-order equation—see also Ho et al. [25]. The Freundlich adsorption isotherm was determined to

examine the mechanism of sorption, which accounts macroscopically for sorption on heterogeneous surfaces. The equilibrium adsorption data of hybrid surfactant-akaganéite were not possibly to be fitted to the Langmuir equation, perhaps due to the heterogeneity of the sorbent surface following the modification.

The examination of akaganéite efficiency for the removal of cadmium cations was elsewhere studied [26]. From the results, it was concluded that sorption depended greatly on the solution pH value, increasing as pH increased; for a change of around 2.5 pH units, cadmium removal varied between 0% and 100%. All the experiments were conducted at solution pH of  $<9.5$ , where it was found by the thermodynamic aqueous speciation diagram of Cd ion, that chemical precipitation of cadmium as hydroxide did not take place (so that cadmium removal was due only to sorption). The obtained evidences led to a mechanism of weak chemisorptions, possibly describing the removal process.

Zinc is also highly toxic and could be damaging to human health. Industries discharging waste streams that contain significant levels of zinc include steel works with galvanizing lines, zinc and brass metal works, zinc and brass plating, viscose rayon yarn and fiber production, ground wood pulp production, and newsprint paper production. Zinc salts are also used in the inorganic pigments industry (e.g., zinc chromate) and high zinc levels have been reported in acid mine drainage. The sorption of zinc ion, existing in the dilute aqueous solution as  $\text{Zn}^{2+}$ , was investigated onto akaganéite, in two formations of nanocrystal and granulated material [27]. Based on the earlier batch experiments and the respective findings, column tests were planned (Fig. 2). The iso-removal lines, of bed service to the respective adsorbent quantity for sorption of 20%, 35%, and 50%, are also presented following the bed depth-service time (BDST) equation in order to model the column operation. Akaganéite, as compared with other sorbent materials, had high sorption capacity—see Table 5.



**FIG. 2** (A) Breakthrough curves in column experiments for different quantities of akaganéite, from an initial solution of 10 mg/L  $\text{Zn}^{2+}$  at pH 6.5. (B) Iso-removal lines for 20%, 35%, and 50% breakthrough; bed depth-service time (BDST) model output, where M is the quantity (in g) of sorbent inside the column. Reprinted with permission, copyright Elsevier, E.A. Deliyanni, E.N. Peleka, K.A. Matis, Removal of zinc ion from water by sorption onto iron-based nano-adsorbent, *J. Hazard. Mater.* 141 (2007) 176–184.

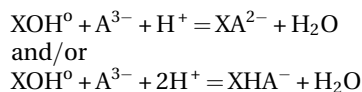
**Table 5** A comparison of some Published Maximum Adsorption Capacities of Various Sorbents for Zn Ions

$Q_{max}$ (mg/g)	$Q_{max}$ (mg/g m <sup>2</sup> )	Sorbent
35	0.106	Akaganeite
3	–	River bed sediment
21.09	0.153	Sea nodule residue
2.9	0.007	Clinoptilolte
1.6	0.002	Philipsite
7.8	0.007	Chabazine
3.9	0.012	Analcime
2.9	0.003	Bentonite
7.8	0.097	Modified montmorillonite
1.2	0.47	Coal
29.4	–	Biosolids
30.7	–	Silico-antimonate ion exchanger

From E.A. Deliyanni, E.N. Peleka, K.A. Matis, Removal of zinc ion from water by sorption onto iron-based nanoadsorbent, J. Hazard. Mater. 141 (2007) 176–184, Copyright Elsevier.

Sorption process was examined in order to evaluate the removal efficiency of the new adsorbent; the BDST model was fitted to the experimental results [28]. From the obtained breakthrough curves, it was concluded that in all cases the sorbent mass increase resulted in better removal efficiency. The effect of ionic strength was positive as it was expected from batch experiments, for the case of arsenate. 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 also the aim of another paper [29]. The nanostructured sorbent presented higher removal efficiency than the granular one. The removal efficiency of akaganéite (in both forms) for anionic arsenate was more pronounced than that of cationic cadmium species.

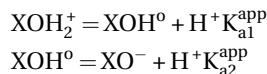
Sorption modeling was investigated by the mechanism of surface complexation, in order to describe the process or even predict the outcome for the expected rate and in general, to develop this detection technique for pollutants. That investigation included the application of goethite mineral as the suitable metal ion (arsenic oxyanions) sorbent, and the use of appropriate computer software (PHREEQC and MINEQL+) [30]. Specific sorption of anions on hydrous oxides occurs via ligand exchange reactions, in which hydroxyl surface groups are replaced by the ions to be sorbed. It is worth noting that all binding sites are considered uniformly available for anion binding, that is, only one type of sites exists. Therefore, anion sorption could be described with the following reactions:



where  $\text{A}^{3-}$  is a hypothetical trivalent anion.



Solids containing hydroxyl functional groups are considered as Brönsted acids which behave amphoterically [30]. The surface ionization reactions responsible for the amphoteric behavior of the oxide minerals studied here can be written as follows:

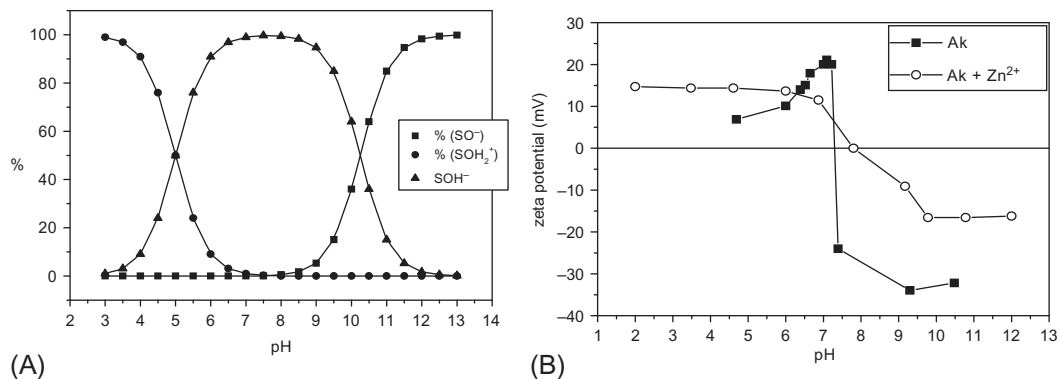


where  $\text{XOH}_2^+$ ,  $\text{XOH}^0$ , and  $\text{XO}^-$  represent positively charged, neutral, and negatively charged surface hydroxyl groups, respectively and  $\text{K}_{\text{a1}}^{\text{app}}$  and  $\text{K}_{\text{a2}}^{\text{app}}$  are apparent acidity constants, derived from the mole balances of these equations. The intrinsic equilibrium constants, which do not depend on surface charge, were introduced later, adding an electrostatic correction factor.

## 2.2 Characterization (Before and After Adsorption)

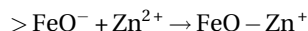
Fig. 3A presents the fractions of  $\text{SOH}_2^+$  and  $\text{SOH}$  groups of akaganéite at various pH produced by pehametric titration. From the speciation of akaganéite, it was concluded that zinc ion cannot be sorbed onto akaganéite at  $\text{pH} < 4$  due to repulsive forces between the positively charged surface of akaganéite at this pH region and  $\text{Zn}^{2+}$  ion. At the pH range of the experiments, an increase of the concentration of the neutral surface species ( $\text{SOH}$ ) was observed, so the adsorption of Zn onto these  $\text{SOH}$  species was performed increasingly [31].

As it is generally accepted, the specific adsorption (i.e., chemisorption) of cations charges positively the colloids surfaces. Considering that the sorbed species are positively charged, the process is carried out easier to negatively charged or neutral sites, which meanwhile following sorption are decreased shifting the pH to higher pH values.



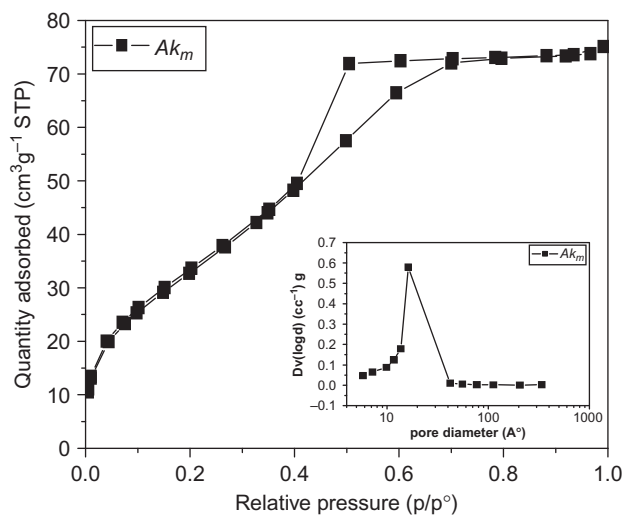
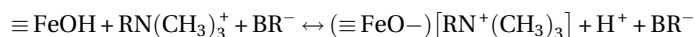
**FIG. 3** (A) Speciation diagram of akaganéite ( $I = 0 \text{ M}$ , temperature =  $25^\circ\text{C}$ ). (B)  $\zeta$ -potential measurements of the nanostructured akaganéite (Ak) as a function of solution pH, in the presence and the absence of the metal ion. Reprinted with permission, copyright Elsevier, E.A. Deliyanni, E.N. Peleka, K.A. Matis, Removal of zinc ion from water by sorption onto iron-based nanoadsorbent, *J. Hazard. Mater.* 141 (2007) 176–184.

In this way, if zinc was chemisorbed, a higher  $\text{pH}_{\text{IEP}}$  (isoelectric point) should be observed, according to the next equation:



The electrokinetic measurements of this system, presented in Fig. 3B, showed that the  $\text{pH}_{\text{IEP}}$  of akaganéite shifted from  $\text{pH} \sim 7.3$  to 7.9, when zinc ion was sorbed. Therefore, chemisorption rather than physical sorption of zinc ion onto the adsorbent material may be concluded.

$\text{N}_2$  adsorption-desorption isotherms of the hybrid akaganéite nanocrystals are shown in Fig. 4. The isotherms are of classical type IV, characteristic of mesoporous materials according to the IUPAC. The sample showed well-defined hysteresis loops with a steep desorption branch and a less steep adsorption branch, belonging to the H2 type, characteristic of mesoporous materials. A narrow pore size distribution was determined by Barrett, Joyner, and Halenda (BJH) method from the desorption branch of the isotherm, centered at 4.6 nm (figure inset). The decrease of surface area presented by the surfactant-modified adsorbent was attributed to the presence of the cationic surfactant [32]. Although there is no universal agreement on how sorption of surfactants occurs to the surfaces, it was speculated that at low concentrations, on polar surfaces cationic surfactants adsorb with their polar moiety in contact with the surface, due to interaction between the surfactant head group and the surface—according to the equation:



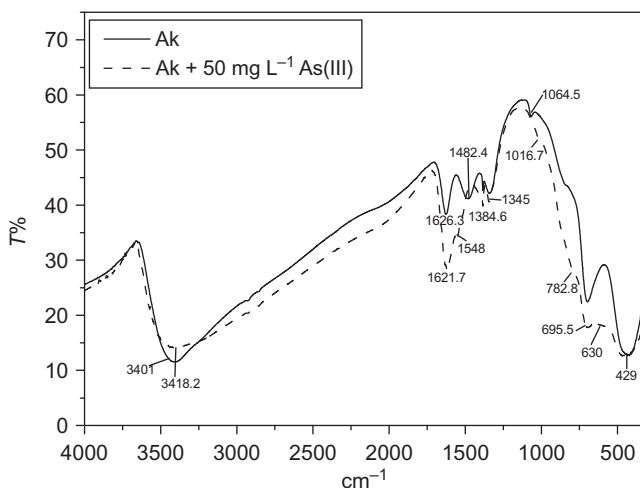
**FIG. 4** Nitrogen adsorption-desorption isotherm of surfactant-modified akaganéite; the inset displays the desorption (DV)log  $d$  graph of the sorbent. Reprinted with permission, copyright Taylor & Francis, E.A. Deliyanni, E.N. Peleka, K.A. Matis, Effect of cationic surfactant on the adsorption of arsenites onto akaganéite nanocrystals, *Sep. Sci. Technol.* 42 (2007) 993–1012.

The arsenites were found to react with hydroxyls of the material and during this sorption, electron transfer from adsorbate to substrate occurred [24]. It was observed also that, in the process, the oxygen atoms act as a Lewis acid and the iron atom acts as a Lewis base. Finally, the potential energy of the complexes formed was high; hence this was an effective removal. It is also mentioned that desorption experiments were carried out, showing that neither measurable amount of surfactant nor arsenite ions released to the solution in all pH range.

From XPS measurements and FTIR spectra, it was concluded that the surfactant was sorbed on the surface of akaganéite. In addition, arsenite ions reacted with surface OH<sup>-</sup> functional groups suggesting that there is a specific adsorption between the arsenite ions and the surfactant-modified akaganéite. A comparison of experimental uptake data with theoretical predictions (curves) was also conducted, based on Elovich, Lagergren, and Ritchie kinetic equations. The best fit for the experimental series of this study was achieved by the application of the latter—see also Karapantsios et al. [23].

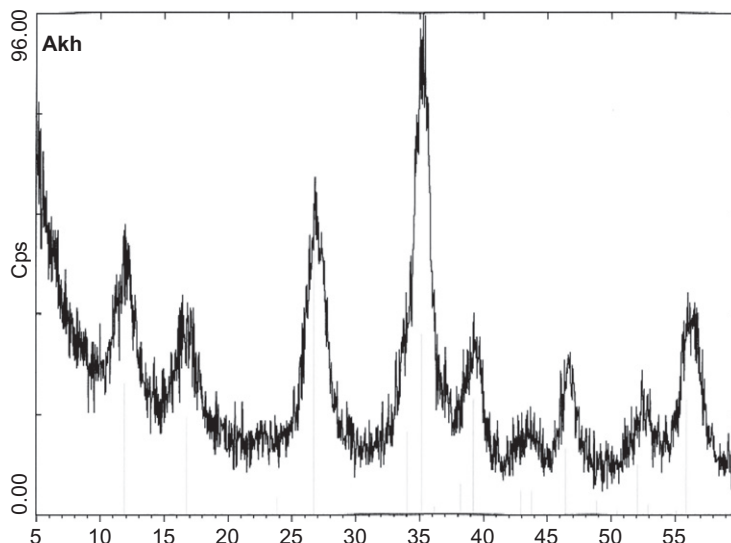
The infrared spectra measurements of pure akaganéite and of samples after sorbed As(III) ions, were performed with the KBr pressed disk technique (Fig. 5). The bands of the OH stretching, OH bending (librational) and the translational modes were presented and compared for the different samples. There were two sets of librations, due to hydrogen bonds [33]. In the nanocrystalline sample (prepared in the laboratory), the bands at 847 and 820 cm<sup>-1</sup> were diminished and mostly disappeared, due to the washing of the chlorine ions. In the case of arsenite sorption on iron oxides, the As(III) species was clearly identified by the bands at 783 cm<sup>-1</sup> that correspond to the As—O vibration.

Thermodynamic parameters were also estimated [34] for arsenites sorption onto akaganéite; the negative values found of  $\Delta G^0$  (obtained according to the van't Hoff equation)



**FIG. 5** Fourier transform infrared (FTIR) spectra of akaganéite before and after As(III) sorption (with the KBr pressed disk technique). Reprinted with permission, copyright Inderscience Enterprises, E.A. Deliyanni, E.N. Peleka, K.A. Matis, Removal of arsenites onto akaganéite-type adsorbents, *Int. J. Environ. Waste Manag.* 2(3) (2008) 279–291.





**FIG. 6** X-ray diffraction (XRD) pattern of nanohybrid anionic surfactant-akaganéite. Reprinted with permission, copyright Inderscience Enterprises, E.A. Deliyanni, E.N. Peleka, Nanohybrid anionic surfactant-akaganéite: preparation, structural analysis and cations sorption, *Intl J. Environ. Manag.* 12 (2/3/4) (2010) 369–380.

suggested that the process was spontaneous with high preference of As(III) for akaganéite. The positive values of  $\Delta H^0$  (calculated by means of the integrated form of the Clausius-Clapeyron equation) suggested the endothermic nature of the process, while the positive values of  $\Delta S^0$  are indicated an increased randomness (see also Table 1).

A representative X-ray diffraction (XRD) pattern of nanohybrid anionic surfactant-akaganéite (using sodium dodecyl sulfate) is presented in Fig. 6. Wide-angle diffraction pattern showed the characteristic of akaganéite structure (JCPDS card no. 34–1266). The weak and broad diffraction peaks indicated that the sample was composed of small crystals with a crystalline size in nanometer scale. The intensity of 211 peak was higher than that of 310 peak, implying that the sorbent was mainly present in the shape of rod-like crystals. Calculating the full width at half maximum (FWHM) showed that the crystalline size of nanohybrid surfactant-akaganéite was 4.2 nm, while the average crystallite size of the pure nanocrystalline akaganéite was 2.6 nm, estimated by TEM [20]. Moreover, from equilibrium experiments with this new mesoporous form of crystalline  $\beta$ -FeOOH, it was concluded that this nanocrystalline hybrid surfactant-akaganéite had about three times higher sorption capacity on Zn(II) and Cd(II) ions removal from aqueous solution compared with pure akaganéite.

### 3 Selected Recent Literature

There are a few limitations to using nanosized metal oxides as adsorbents; reducing metal oxides to nanoscale sizes can increase surface area, but this increase can also cause

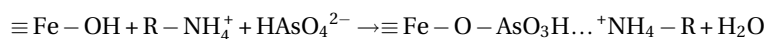
instability [35]. As a result of being unstable, they become more prone to agglomeration due to the presence of van der Waals forces and other interactions. Once these interactions occur, they lose high capacity, selectivity, and develop poor mechanical strength. To circumvent these limitations, metal oxides are typically incorporated into supports or other bulk adsorbents [7]. Bare nanoparticles, prone to oxidation by atmospheric oxygen are easily aggregated in aqueous systems which have necessitated the surface modification of these nanoparticles for their stabilization and subsequent applications as adsorbents [36].

The interactions of chloride anion with the iron oxyhydroxide precursors occurring during the hydrolysis process, as well as its mechanistic role during the formation of a solid phase have been debated [37]. The effect of the capping agent polyethylenimine in the synthesis (two-step approach) of intermediate  $\beta$ -FeOOH nanorods was studied [38].

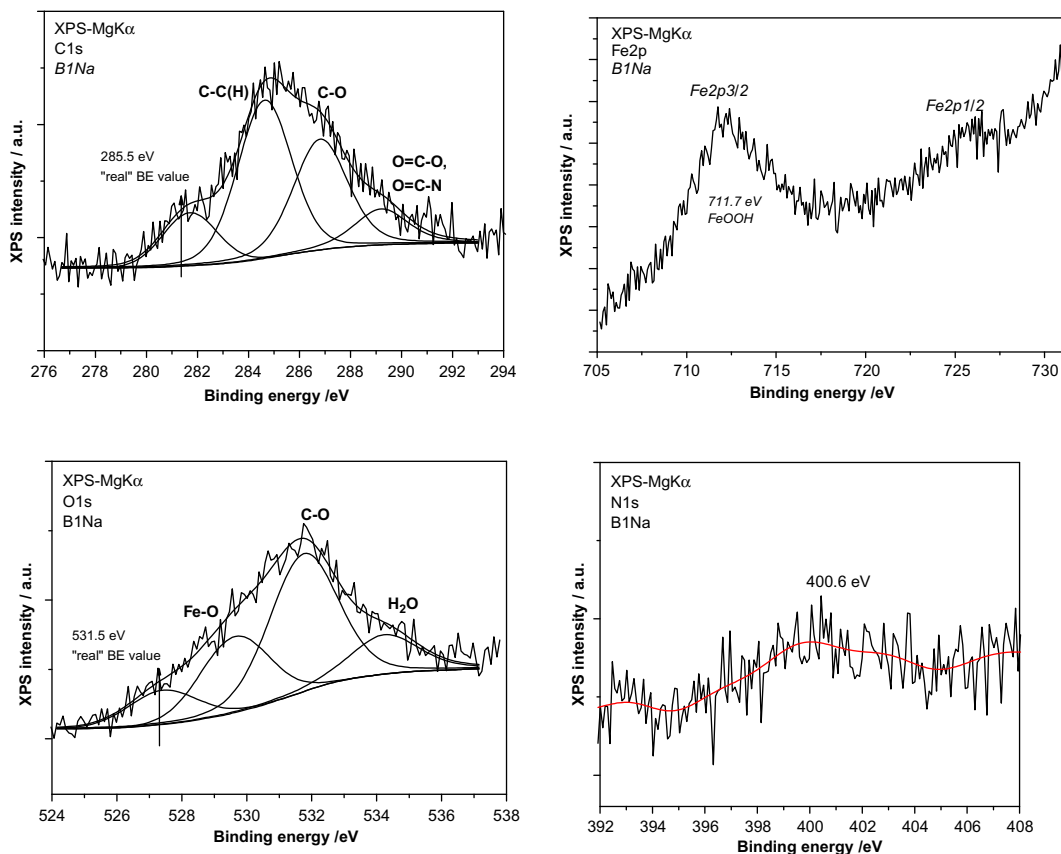
Controlled synthesis of anisotropic iron oxide nanoparticles was stated to be a challenge in the field of nanomaterial research that requires an extreme attention to detail. As it was above described, iron(III) hydrolysis in the presence of chloride ions yields akaganéite, an iron oxyhydroxide mineral with a tunnel structure stabilized by the inclusion of chloride. A method for the synthesis of iron oxide-based sorbents from bauxite residue (red mud) was developed, by way of a sequential digestion and selective precipitation; this process allowed the production of a relatively pure crystalline akaganéite, and its performance was then tested as a fluoride sorbent material [39].

### 3.1 Activated Carbon

There are certainly various techniques for activated carbon modification, in order to become suitable for certain applications and among them, different inorganic materials have been used. For instance, impregnation (doping) of activated carbon or oxidized activated carbon was carried out using iron(III) nitrate as starting solution (in order to introduce it in the form of iron oxyhydroxide) and ammonia as the precipitating agent, intending the removal from aqueous solution of arsenates [40]; it was suggested that the *meso*/microporous carbon surface (wood-based industrial product) contributed to changes of arsenic, via reduction of As(V) to As(III) (see Fig. 7). In the XPS spectra, the binding energy for the main Fe 2p<sub>3/2</sub> peak for the carbon sample fell within the range of binding energy representing the reported values for goethite ( $\alpha$ -FeOOH). The binding energy at 400.6 eV could be assigned to the N in the ( $-\text{NH}_2^+$ ) groups on the surface of the sample, which verified that ammonia groups were responsible for the enhanced nitrogen content. The ammonium moieties were perhaps capable to attract arsenate anionic species by electrostatic forces, facilitating the arsenate adsorption via the following reaction:

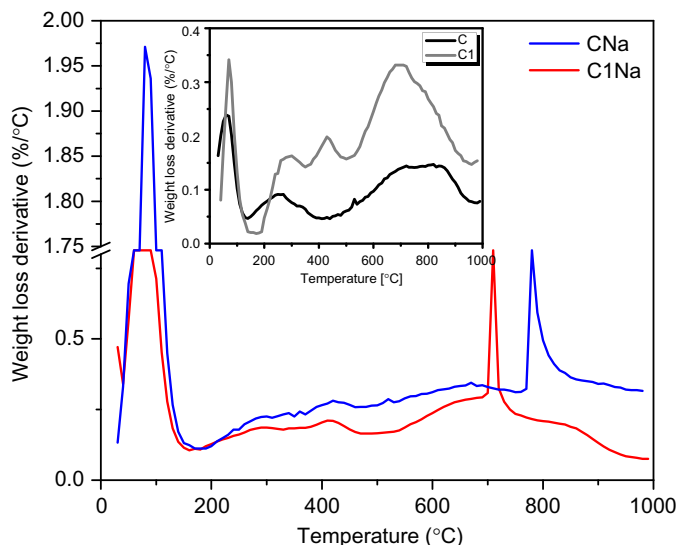


which may further explain the promising removal behavior of the prepared carbon adsorbent, as aforementioned, toward the arsenates.



**FIG. 7** X-ray photoelectron spectroscopy (XPS) spectra for the oxidized activated carbon, prepared after iron impregnation from ammonia solution. Reprinted with permission, copyright Soc. Chem. Ind., E. Deliyanni, T.J. Bandoz, K.A. Matis, *Impregnation of activated carbon by iron-hydroxide and its effect on arsenate removal*, *J. Chem. Technol. Biotechnol.* 88 (2013) 1058–1066.

The effect on the final chemistry of the activated carbons (microporous, spherical) modified with iron species and on arsenate removal was also evaluated using thermal analysis. The differential thermogravimetric (DTG) curves were obtained in nitrogen, where the weight loss is associated with the removal/decomposition of species present on the carbons surface (Fig. 8). The DTG curve of the initial C sample reveals three peaks at 80°C, ~200°C, and ~700–800°C. The first peak (at about 80°C) is common for all carbon samples and is related to the removal of water. Peaks at about 700°C and 800°C could correspond to the evolution of CO attributed to the decomposition of phenol, ether, carbonyl, and quinone functional groups. An appearance of the new peaks in a 200–500°C temperature range for the C1 carbon corresponds to the decomposition of carboxylic groups, carboxylic anhydrides, and/or lactone groups formed by oxidation of carbon surface with HNO<sub>3</sub> [41]. However, a reduction was noticed this time in the capacity, to



**FIG. 8** Comparison of the differential thermogravimetric (DTG) curves, in nitrogen for the initial and exhausted iron oxyhydroxide impregnated activated carbon. Reprinted with permission, copyright Bentham, G.Z. Kyzas, E.A. Deliyanni, S.I. Bele, K.A. Matis, Nano-adsorbent for arsenates: iron oxyhydroxide impregnated microporous activated carbon, *Current Environ. Eng.* 1(1) (2014) 51–58.

around 8 from the  $\sim 32$  mg arsenic per g carbon that we obtained previously for the *meso*/microporous sample, with exactly similar experimental conditions.

Volatile organic compounds, that is, formaldehyde, could pollute the indoor and outdoor air, and activated carbon is the widely used adsorbent for removal of this pollutant. An adsorbent made of silver nanoparticles attached onto activated carbon was prepared, deposited on the pore structures, and examined; the adsorption experiments were conducted in a continuous fixed-bed column [42]. Nano-Cu<sub>2</sub>O/Cu modified activated carbon composite was also synthesized by a hydrothermal method and used to adsorb iodide ion (I<sup>−</sup>) from simulated radioactive wastewater [43]. In another paper, MgO-impregnated porous biochar composites were prepared using an integrated adsorption-pyrolysis method for pollutants removal from swine wastewater; results revealed that the MgO-biochar was composed of nano-sized MgO flakes and nanotube-like porous carbon [44].

Two synthetic mesoporous carbons, a highly ordered (CMK-3) sample with hexagonal structure and a disordered mesoporous carbon were investigated for the sorption of a dye (Remazol Red 3BS), in comparison with three commercial activated carbons and a hexagonal molecular silica (HMS) mesoporous silica with a wormhole pore structure [11]. A surfactant-enhanced carbon regeneration technique was used to regenerate the dye-loaded carbon sorbents. Further, the nitrogen adsorption-desorption isotherms of HMS showed a relatively broader uptake step at lower  $P/P_0$  due to framework mesopores with wormhole-like structure, as well as a more pronounced step at  $P/P_0 \sim 0.95$  due to the

presence of high external area and/or textural porosity (interparticle voids between primary nanoparticles that constitute larger particles). The sorption of organic pollutants from aqueous solutions by activated carbons depends on the nature of the adsorbate and the surface characteristics of the adsorbent. The adsorbent-adsorbate interactions in the case of organic compounds involve a more complex interplay between electrostatic and dispersive interactions. Both the synthetic mesoporous carbons show high surface area and pore sizes larger than ca. 3 nm, which makes them ideal for the sorption of the Reactive Red 3BS dye. The molecular size (mean kinetic diameter) of the dye was estimated to be 1.2 nm (using the WINMOPAC program). It is a large molecule with high molecular weight (1085.84 g/mol).

### 3.2 Graphene Oxide

Graphene oxide (GO), particularly as magnetic particles, was reviewed as an adsorbent for wastewater treatment applications, such as heavy metals and organics (antibiotics, dyes, etc.) separation [45]. The two-dimensional (2D) layer structure, large surface area, pore volume, and the presence of surface functional groups in the modified graphene materials. Fe<sub>3</sub>O<sub>4</sub>/grapheme oxides nanocomposites were prepared by different routes (impregnation or coprecipitation). Nanocomposites possessing magnetic properties are especially useful since they can be easily eliminated from the solutions after the treatment procedures (i.e., of radionuclides). Various kinds of magnetic GO-based composites were used for treatment of contaminated solutions [46].

Nanoparticle goethite anchored onto GO and rice spike-like akaganéite anchored onto GO were synthesized, using acetate as novel crystal modifier for metal oxides and examined for fluoride removal elsewhere [47]. A composite of reduced GO and akaganéite was synthesized by a coprecipitation and reduction process; the degradation of 2-chlorophenol was evaluated in a heterogeneous Fenton reaction [48].

### 3.3 Other Sorbents

The HMS mesoporous silica was synthesized following the procedure reported by Pauly et al. [49]. Adsorption characteristics of nano-functionalized HMS-type mesoporous silica with amine groups, for the removal of Pb(II) ions from aqueous solutions, were investigated; the adsorbent was previously characterized [50]. Nanoporous carbons with extremely high mesopore volumes and surface areas were also produced using silica nanoparticles as templates, and exhibiting excellent adsorption capacities for bulky dyes [51].

A series of composites based on nano-hydroxyapatite and natural polysaccharides was synthesized by liquid-phase two-step method and characterized; adsorption of Sr(II) on the composites from the aqueous solutions was then studied [52]. Nano-birnessite was prepared, characterized, and used for removal of cobalt and strontium ions from aqueous solutions [53]; birnessite is a common name for manganese oxide with metal ions,



sodium, or potassium cations, in the interlayer together with water molecules. A stable nanoscale zero-valent iron composite also was obtained (via modification by organics), showing high Cr(VI) removal capacity, as well as the magnetic recovery property to facilitate separation [54].

Synthetic layered double hydroxides (LDHs) (being hydrotalcite-like materials), known for their ability to sorb anions from aqueous solutions, were in-depth reviewed [55]. These materials usually exist in powder form, thereby exhibiting high surface area, especially their calcined compounds and so, rapid kinetics for adsorption. Magnetic nanoparticles supported calcined layered double oxide were prepared and applied to remove As(V) and Sb(V) in water [56]. Hypersensitive and highly selective nanomaterials for the measurement of heavy metal ions hold a key to electroanalysis—that is, with the application of ternary LDHs [57]. Co—Ni layered double nanohydroxides were synthesized by the coprecipitation method and characterized; phenol and its derivatives in wastewater were treated by catalytic wet peroxide oxidation [58]. LDH-containing hybrids (with other materials such as carbon nanotubes, graphene, carbon nanofibers, etc.) are finally emerging as potential nano-sized adsorbents for water treatment [59]. The efficiency of nanocrystalline materials is mainly dependent on their particle size and geometry, specific surface area and porosity, crystal structure, and morphology. These properties apparently should be strictly controlled in order to increase their effect in multipurpose uses.

## 4 Conclusions

The impact of nanostructures on the properties of high surface area materials is a field of increasing importance to understand, create, and improve inorganic materials for diverse technological applications. Inorganic sorbents have received far less attention for the treatment of wastewaters. Heavy metals cations and also oxyanions (such as arsenic) removal from dilute aqueous streams, being often of great significance, was the main focus in the present review for the adsorbents application. The adsorptive capacity of akaganéite (also modified, even as composite) was found, among other sorbents, to be effective; batch and column experiments were conducted. Advantage of the sorbent, which was found to be nanostructured, was its high surface area and narrow pore size distribution. Various instruments and equipment are generally used in the studies of this area, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), usually equipped with an energy dispersive X-ray (EDX) micro-analytical system, TEM, XPS, thermogravimetric analyzer (TGA), FTIR spectroscopy, nitrogen adsorption-desorption isotherm measurement, potentiometric and Boehm titration, surface pH measurement, atomic absorption or UV-vis spectrophotometer, elemental analyzer, electrokinetic measurement apparatus, etc. Selected figures, originating from experimental data, were presented. As has been shown, being apparent even from the introduction, sorption is not an “easy” process to deal with. The application of fundamental chemistry (including sorption isotherms, thermodynamic, and kinetic studies) usually assists to investigate and explain the

corresponding process mechanism. Over the last years, considerable research on the use of inorganic nanoadsorbents for adsorption of pollutants (i.e., heavy metals) has shown great progress.

## Acknowledgments

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## References

- [1] T. Erwe, V. Mavrov†, E.N. Peleka, K.A. Matis, Bonding of toxic metal ions, in: J. Lehr (Ed.), *Water Encyclopedia—Domestic, Municipal and Industrial Water Supply and Waste Disposal*, vol. 1, Wiley, Hoboken, NJ, 2005, pp. 586–591.
- [2] S. Mandjiny, A.I. Zouboulis, K.A. Matis, Removal of cadmium from dilute solutions by hydroxyapatite. Part I. Sorption studies, *Sep. Sci. Technol.* 30 (1995) 2963–2978.
- [3] A.I. Zouboulis, K.A. Kydros, K.A. Matis, Removal of hexavalent chromium anions from solutions by pyrite fines, *Water Res.* 29 (1995) 1755–1760.
- [4] S. de Gisi, G. Lofrano, M. Grassi, M. Notarnicola, Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: a review, *Sustainable Mater. Tech.* 9 (2016) 10–40.
- [5] G.Z. Kyzas, E.A. Deliyanni, K.A. Matis, Activated carbons produced by pyrolysis of waste peels: Cobalt ions removal by adsorption, *Colloids Surf. A Physicochem. Eng. Asp.* 490 (2016) 74–83.
- [6] G. McKay, *Use of Adsorbents for the Removal of Pollutants From Wastewater*, CRC Press, Boca Raton, Florida, 1996.
- [7] P.Z. Ray, H.J. Shipley, Inorganic nano-adsorbents for the removal of heavy metals and arsenic: a review, *RSC Adv.* 5 (2015) 29885–29907.
- [8] D. Zamboulis, E.N. Peleka, N.K. Lazaridis, K.A. Matis, Metal ion separation and recovery from environmental sources using various flotation and sorption techniques, *J. Chem. Technol. Biotechnol.* 86 (2011) 335–344.
- [9] E.A. Deliyanni, N.K. Lazaridis, E.N. Peleka, K.A. Matis, Metals removal from aqueous solution by iron-based bonding agents, *Environ. Sci. Pollut. Res.* 11 (2004) 18–21.
- [10] E.N. Peleka, K.A. Matis, Water separation processes and sustainability, *Ind. Eng. Chem. Res.* 50 (2011) 421–430.
- [11] D.D. Asouhidou, K.S. Triantafyllidis, N.K. Lazaridis, K.A. Matis, S.-S. Kim, T.J. Pinnavaia, Sorption of reactive dyes from aqueous solutions by ordered hexagonal and disordered mesoporous carbons, *Microporous Mesoporous Mater.* 117 (2009) 257–267.
- [12] G.Z. Kyzas, K.A. Matis, Nanoadsorbents for pollutants removal: a review, *J. Mol. Liq.* 203 (2015) 159–168.
- [13] S.A. Shelley, Nanotechnology: turning basic science into reality, in: L. Theodore, R.G. Kunz (Eds.), *Nanotechnology: Environmental Implications and Solutions*, Wiley & Sons, New York, 2005, pp. 61–107.
- [14] M. Khajeh, S. Laurent, K. Dastafkan, Nanoadsorbents: classification, preparation, and applications (with emphasis on aqueous media), *Chem. Rev.* 113 (2013) 7728–7768.
- [15] V.N. Thekkudan, V.K. Vaidyanathan, S.K. Ponnusamy, C. Charles, S. Sundar, D. Vishnu, S. Anbalagan, V.K. Vaithyanathan, V.K. Subramanian, Review on nanoadsorbents: a solution for heavy metal removal from wastewater, *IET Nanobiotechnol.* (2016), <https://doi.org/10.1049/iet-nbt.2015.0114>.

- [16] E.A. Deliyanni, G.Z. Kyzas, K.S. Triantafyllidis, K.A. Matis, Activated carbons for heavy metal ions removal: a systematic review of recent literature focused on lead and arsenic ions, *Open Chem.* 13 (2015) 1–7.
- [17] K.J. Gallagher, The atomic structure of tubular subcrystals of  $\beta$ -iron(III) oxide hydroxide, *Nature* 226 (1970) 1225–1228.
- [18] H. Naono, R. Fujiwara, H. Sugioka, K. Sumiya, H. Yanazawa, Micropore formation due to thermal decomposition of acicular microcrystals of  $\beta$ -FeOOH, *J. Colloid Interface Sci.* 87 (1982) 317–332.
- [19] E.A. Deliyanni, D.N. Bakoyannakis, A.I. Zouboulis, K.A. Matis, L. Nalbandian, Akaganéite-type  $\beta$ -FeO(OH) nanocrystals: preparation and characterization, *Microporous Mesoporous Mater.* 42 (2001) 49–57.
- [20] D.N. Bakoyannakis, E.A. Deliyanni, A.I. Zouboulis, K.A. Matis, L. Nalbandian, T. Kehagias, Akaganéite and goethite-type nanocrystals: synthesis and characterization, *Microporous Mesoporous Mater.* 59 (2003) 35–42.
- [21] E.A. Deliyanni, D.N. Bakoyannakis, A.I. Zouboulis, K.A. Matis, Sorption of as(V) ions by akaganéite-type nanocrystals, *Chemosphere* 50 (2003) 155–163.
- [22] E.A. Deliyanni, N.K. Lazaridis, K.A. Matis, Arsenates sorption by nanocrystalline hybrid surfactant-akaganéite, *Sep. Sci. Technol.* 47 (2012) 2331–2339.
- [23] T.D. Karapantsios, M.X. Loukidou, K.A. Matis, Sorption kinetics, in: J. Lehr (Ed.), *Water Encyclopedia—Ceanography; Meteorology; Physics and Chemistry; Water Law; and Water History, Art and Culture*, vol. 4, Wiley, Hoboken, NJ, 2005, pp. 564–569.
- [24] E.A. Deliyanni, L. Nalbandian, K.A. Matis, Adsorptive removal of arsenites by a nanocrystalline hybrid surfactant-akaganéite sorbent, *J. Colloid Interface Sci.* 302 (2006) 458–466.
- [25] Y.S. Ho, J.C.Y. Ng, G. McKay, Kinetics of pollutant sorption by biosorbents: review, *Sep. Purif. Rev.* 29 (2000) 189–232.
- [26] E.A. Deliyanni, K.A. Matis, Sorption of cd ions onto akaganéite-type nanocrystals, *Sep. Purif. Technol.* 45 (2) (2005) 96–102.
- [27] E.A. Deliyanni, E.N. Peleka, K.A. Matis, Removal of zinc ion from water by sorption onto iron-based nanoadsorbent, *J. Hazard. Mater.* 141 (2007) 176–184.
- [28] E.A. Deliyanni, E.N. Peleka, K.A. Matis, Modeling the sorption of metal ions from aqueous solution by iron-based adsorbents, *J. Hazard. Mater.* 172 (2009) 550–558.
- [29] E.A. Deliyanni, D.N. Bakoyannakis, A.I. Zouboulis, E.N. Peleka, Removal of arsenic and cadmium by akaganéite fixed-beds, *Sep. Sci. Technol.* 38 (2003) 3967–3981.
- [30] M. Lehmann, A.I. Zouboulis, K.A. Matis, A. Grohmann, Sorption of arsenic oxyanions from aqueous solution on goethite: a study of process modeling, *Microchim. Acta* 151 (2005) 269–275.
- [31] D.A. Dzombak, F.M.M. Morel, *Surface Complexation Modelling: Hydrous Ferric Oxide*, Wiley, New York, 1990. 416 p.
- [32] E.A. Deliyanni, E.N. Peleka, K.A. Matis, Effect of cationic surfactant on the adsorption of arsenites onto akaganéite nanocrystals, *Sep. Sci. Technol.* 42 (2007) 993–1012.
- [33] E.A. Deliyanni, E.N. Peleka, Nanohybrid anionic surfactant-akaganéite: preparation, structural analysis and cations sorption, *Intl J. Environ. Manag.* 12 (2/3/4) (2010) 369–380.
- [34] E.A. Deliyanni, E.N. Peleka, K.A. Matis, Removal of arsenites onto akaganéite-type adsorbents, *Int. J. Environ. Waste Manag.* 2 (3) (2008) 279–291.
- [35] M. Hua, S. Zhang, B. Pan, W. Zhang, L. Lv, Q. Zhang, Heavy metal removal from water/wastewater by nanosized metal oxides: a review, *J. Hazard. Mater.* 211–212 (2012) 317–331.
- [36] D. Maity, D.C. Agrawal, Synthesis of iron oxide nanoparticles under oxidizing environment and their stabilization in aqueous and non-aqueous media, *J. Magn. Magn. Mater.* 308 (2007) 46–55.

- [37] J. Scheck, T. Lemke, D. Gebauer, The role of chloride ions during the formation of akaganéite revisited, *Fortschr. Mineral.* 5 (2015) 778–787.
- [38] S.L. Mozo, E. Zuddas, A. Casu, A. Falqui, Synthesizing iron oxide nanostructures: the polyethylene-nemine (PEI) role, *Crystals* 7 (2017) 22–33.
- [39] R.A. Pepper, S.J. Couperthwaite, G.J. Millar, Value adding red mud waste: high performance iron oxide adsorbent for removal of fluoride. *J. Environ. Chem. Eng.* (2017), <https://doi.org/10.1016/j.jece.2017.04.031>.
- [40] E. Deliyanni, T.J. Bandosz, K.A. Matis, Impregnation of activated carbon by iron-hydroxide and its effect on arsenate removal, *J. Chem. Technol. Biotechnol.* 88 (2013) 1058–1066.
- [41] G.Z. Kyzas, E.A. Deliyanni, S.I. Bele, K.A. Matis, Nano-adsorbent for arsenates: iron oxyhydroxide impregnated microporous activated carbon, *Current Environ. Eng.* 1 (1) (2014) 51–58.
- [42] W.D.P. Rengga, A. Chafidz, M. Sudibandriyo, M. Nasikin, A.E. Abasaeed, Silver nano-particles deposited on bamboo-based activated carbon for removal of formaldehyde, *J. Environ. Chem. Eng.* 5 (2017) 1657–1665.
- [43] X. Zhang, P. Gu, X. Li, G. Zhang, Efficient adsorption of radioactive iodide ion from simulated wastewater by nano Cu<sub>2</sub>O/Cu modified activated carbon, *Chem. Eng. J.* 322 (2017) 129–139.
- [44] R. Li, J.J. Wang, B. Zhou, Z. Zhang, S. Liu, Simultaneous capture removal of phosphate, ammonium and organic substances by MgO impregnated biochar and its potential use in swine wastewater treatment, *J. Clean. Prod.* 147 (2017) 96–107.
- [45] G.Z. Kyzas, E.A. Deliyanni, K.A. Matis, Graphene oxide and its application as adsorbent to wastewater treatment, *J. Chem. Technol. Biotechnol.* 89 (2013) 196–205.
- [46] G. Lujanienė, S. Šemčuk, A. Lečinskytė, I. Kulakauskaitė, K. Mažeika, D. Valiulis, V. Pakštas, Magnetic graphene oxide based nano-composites for removal of radionuclides and metals from contaminated solutions, *J. Environ. Radioact.* 166 (2017) 166–174.
- [47] L. Kuang, Y. Liu, D. Fu, Y. Zhao, FeOOH-graphene oxide nanocomposites for fluoride removal from water: acetate mediated nano FeOOH growth and adsorption, *J. Colloid Interface Sci.* 490 (2017) 259–269.
- [48] F. Xiao, W. Li, L. Fang, D. Wang, Synthesis of akaganéite (beta-FeOOH)/reduced graphene oxide nanocomposites for oxidative decomposition of 2-chlorophenol by Fenton-like reaction, *J. Hazard. Mater.* 308 (2016) 11–20.
- [49] T.R. Pauly, Y. Liu, T.J. Pinnavaia, S.J.L. Billinge, T.P. Rieker, Textural mesoporosity and the catalytic activity of mesoporous molecular sieves with wormhole framework structures, *J. Am. Chem. Soc.* 121 (1999) 8835–8842.
- [50] H. Javadian, B.B. Koutenai, E. Shekarian, F.Z. Sorkhrodi, R. Khatti, M. Toosi, Application of functionalized nano HMS type mesoporous silica with N-(2-aminoethyl)-3-aminopropyl methyldimethoxysilane as a suitable adsorbent for removal of Pb(II) from aqueous media and industrial wastewater, *J. Saudi Chem. Soc.* 21 (2017) S219–S230.
- [51] S. Han, K. Sohn, T. Hyeon, Fabrication of new nanoporous carbons through silica templates and their application to the adsorption of bulky dyes, *Chem. Mater.* 12 (2000) 3337–3341.
- [52] E. Skwarek, O. Goncharuk, D. Sternik, W. Janusz, K. Gdula, V.M. Gun'Ko, Synthesis, structural, adsorption properties and thermal stability of nanohydroxyapatite/polysaccharide composites, *Nanoscale Res. Lett.* 12 (2017) 155–167.
- [53] S.S. Metwally, M. Ghaly, E.A. El-Sherief, Physicochemical properties of synthetic nano-birnessite and its enhanced scavenging of Co<sup>2+</sup> and Sr<sup>2+</sup> ions from aqueous solutions, *Mater. Chem. Phys.* 193 (2017) 63–72.
- [54] Z. Peng, C. Xiong, W. Wang, F. Tan, Y. Xu, X. Wang, X. Qiao, Facile modification of nanoscale zero-valent iron with high stability for Cr(VI) remediation, *Sci. Total Environ.* 596–597 (2017) 266–273.

- [55] G.Z. Kyzas, K.A. Matis, Layered double hydroxides and certain environmental applications (the Contribution of LGICT), in: I.T. Sherman (Ed.), *Layered Double Hydroxides (LDHs): Synthesis, Characterization and Applications*, Nova Science Publishers, New York, 2015, pp. 121–132.
- [56] S.-H. Lee, H. Choi, K.-W. Kim, Removal of As(V) and Sb(V) in water using magnetic nanoparticle-supported layered double hydroxide nanocomposites. *J. Geochem. Explor.* (2016), <https://doi.org/10.1016/j.gexplo.2016.11.015>.
- [57] S.-S. Li, M. Jiang, T.-J. Jiang, J.-H. Liu, Z. Guo, X.-J. Huang, Competitive adsorption behavior toward metal ions on nano-Fe/Mg/Ni ternary layered double hydroxide proved by XPS: Evidence of selective and sensitive detection of Pb(II), *J. Hazard. Mater.* 338 (2017) 1–10.
- [58] S.A. Hosseini, M. Davodian, A.R. Abbasian, Remediation of phenol and phenolic derivatives by catalytic wet peroxide oxidation over co-Ni layered double nano hydroxides, *J. Taiwan Inst. Chem. Eng.* 75 (2017) 97–104.
- [59] M. Zubair, M. Daud, G. McKay, F. Shehzad, M.A. Al-Harthi, Recent progress in layered double hydroxides (LDH)-containing hybrids as adsorbents for water remediation, *Appl. Clay Sci.* 143 (2017) 279–292.

## Further Reading

- [60] M.X. Loukidou, K.A. Matis, A.I. Zouboulis, M. Liakopoulou-Kyriakidou, Removal of as(V) from wastewaters by chemically modified fungal biomass, *Water Res.* 37 (2003) 4544–4552.



*Demonstrates the synthesis, modifications, and applications of nanotechnology in the adsorption process*

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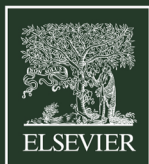
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Edited by a prolific expert in the field, *Composite Nanoadsorbents* will be a valuable resource for researchers, postgraduate students, and professionals in the field of nanotechnology, adsorption, and materials synthesis.

**About the Editors**

*Dr. George Z. Kyzas* was born in Drama (Greece) and has obtained his BSc in Chemistry. His research interests are in environmental engineering, materials science, chemical technology, nanotechnology, and adsorption. He has published significant scientific papers (more than 90), books (as author and/or editor), chapters in books, and teaching notes and reports. He also acted as Guest Editor in special issues for journals and presented many works in International Conferences. He has been awarded with honors, grants, and fellowships for his research career/profile by the Research Committee of Aristotle University of Thessaloniki, National State Scholarships Foundation of Greece, and Stavros Niarchos Foundation. He is now based in Hephaestus Advanced Laboratory, Eastern Macedonia, and Thrace Institute of Technology, Kavala, Greece.

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