Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.26148

201 (2020) 228–239
October

The 2019 year review on chromium(III) adsorption from aqueous solutions

Francisco Jose Alguacil

Centro Nacional de Investigaciones Metalurgicas (CSIC), Avda. Gregorio del Amo 8, 2804 Madrid, Spain,
email: fjalgua@cenim.csic.es (F.J. Alguacil)

Received 5 February 2020; Accepted 16 May 2020

ABSTRACT

Regardless of its toxicity, chromium is an element that lives with humans due to its various uses, and while the toxic character of Cr(VI) is of wide knowledge, this element in its (III) oxidation state is also harmful, and this harmfulness increased by the risk of its potential oxidation to the (VI) oxidation state. Thus, there is a constant effort to find technologies that eliminated this Cr(III) from the different effluents in which it is present. In liquid solutions, it seems that adsorption is one of the most popular methods, and also the finding of adsorbents which eliminated Cr(III) most easily, most selectively and with better yields. The recovery of this element from the loaded adsorbent and the recycle of the adsorbent, are also two points that always, but this is not the real situation, must be taking into account. This manuscript reviewed the most recent advances (papers published in the 2019 year) about the use of adsorption, and adsorbents aimed at the recovery of Cr(III) from liquid solutions.

Keywords: Chromium(III); Adsorption; Desorption; Recovery; Aqueous solutions

1. Introduction

Chromium is a metal which finds applications in various industries, thus, the generation of waste streams (solid or liquid), containing chromium, during the production line or at the end of service life becomes a practical problem, being their direct discharge to the environment a non-desirable option. In the case of liquid effluents, the most common (and stable) oxidation states for the element are (VI) and (III), and while a lot of information has been written about Cr(VI), this information is more scarce in the case of Cr(III). The toxicity of Cr(III) is not as evident as that of Cr(VI) [1,2], however, the presence of this oxidation state in liquid effluents is a human risk, and this risk augmented due to the real possibility of oxidation from the (III) to the (VI) state, which multiplies the harmfulness of a given effluent. Decontamination of liquid effluents by hydrometallurgical procedures is an option, and between the different possibilities, adsorption appears to be one of the most popular ones [3]. Logically the development of adsorption processes cannot be understood without the development of adsorbents suitable for a given task. Also, it cannot be forgotten that the adsorption process has a second part, the desorption step, though in many cases, as it can be seen later in this review, this step is not considered. This manuscript review the advances presented, in the form of published papers during 2019, of the adsorbents derived to remove Cr(III) from solutions, however, only a few of them applied the adsorbent on real Cr(III)-bearing solution.

2. Adsorption of chromium(III) from aqueous solutions

Ti-based metal-organic frameworks (NH_2-MIL-125) were post-synthetic modified through a strategy using bis-quinoline Mannich bases, which yielded MIL-125-HQ [4]. In the case of Cr(III), the maximum adsorption capacity was determined to be 54 mg/g. Elution was carried out

1944-3994/1944-3986

with EDTA, and after four cycles of adsorption–desorption, the adsorption capacity decreased by 25% of its original.

The removal of chromium(III) from aqueous solutions by the adsorption process using abundant vesicular basalt available around Abbay River in Ethiopia was investigated [5]. Batch adsorption experiments had been used to investigate the influence of different variables (pH, ionic strength, initial concentration, and contact time) on Cr(III) adsorption. The adsorption process was highly dependent on pH, with a maximum adsorption capacity of 0.98 mg/g at pH 6, metal initial concentration of 100 mg/L, and adsorbent dosage of 50 g/L. Experimental data fitted well with the pseudo-second-order model and the Langmuir model, whereas the adsorption mechanism of Cr(III) uptake onto the surface of the vesicular basalt involved film diffusion and/or intraparticle diffusion. No data about the elution step was included in the work.

Phosphorus oxychloride was grafted onto the surface of raw sawdust (RSD) particles to get effective adsorbent for the removal of Cr(III) (also Cd(II), and Pb(II)) from aqueous medium [6]. At 25°C, maximum adsorption capacity was 325 mg/g according to monolayer Langmuir adsorption, and the data fitted to the pseudo-second-order kinetic model in an exothermic and was a spontaneous process. Metal adsorption was attributed to the electrostatic interaction between electron-rich oxygen onto the surface of the adsorbent and Cr^{3+}. Metal elution was better with 0.1 M HCl (90%) against 74% of 0.1 M nitric acid.

The removal of chromium(III) from solutions by chemically modified pine bark was investigated [7]. The xanthate pine bark (XPB) derivative, produced with its reaction with CS_2, was screened as the best adsorbent. The equilibrium data were well described by the Langmuir isotherm with a maximum adsorption capacity of 57 mg/g, with data fitted to the pseudo-second-order model. It was proposed, that metal uptake occurred via an ion-exchange mechanism between Cr^{3+} and Na^+:

$$2\left(-OCS_2^{-}Na^{+}\right)+Cr\left(OH\right)2^{+}\Leftrightarrow\left(-OCS^{-}\right)_2Cr\left(OH\right)^{2+}+2Na^{+}\quad(1)$$

and thus, Na^+ was released to the aqueous solution. Among the desorbing agents investigated, the best results were achieved with 2 M H_2SO_4 (67% desorption). In column experiments, a reduction on the breakthrough time (36.5%) and the stoichiometric time (22.8%) were observed, if the Cr(III) concentration feeding the column, increased from 230 to 500 mg/L. The desorption efficiency on the column was 67% and 86% for the above aqueous feeds, respectively. The breakthrough curves were well modeled by Bohard–Adams, Thomas, or Yoon–Nelson equations.

Graphene oxide/alginate hydrogel membranes (GAHMs) were prepared by cross-linking a casting solution (blending graphene oxide, sodium alginate, and urea) with a calcium chloride solution, and used to remove Cr(III) (and Pb(II)) from solutions [8]. Results indicated that the optimal pH for Cr(III) removal from the solution was 6 and its adsorption was consistent with the pseudo-second-order kinetic model and the Langmuir isotherm, with an increment of the maximum adsorption capacity with the increase of the temperature (Fig. 1), thus the adsorption for Cr(III) by GAHMs was endothermic. 1 M HCl solution was used as desorbent, and after five adsorption–desorption cycles, high adsorption efficiency for both metal ions was maintained.

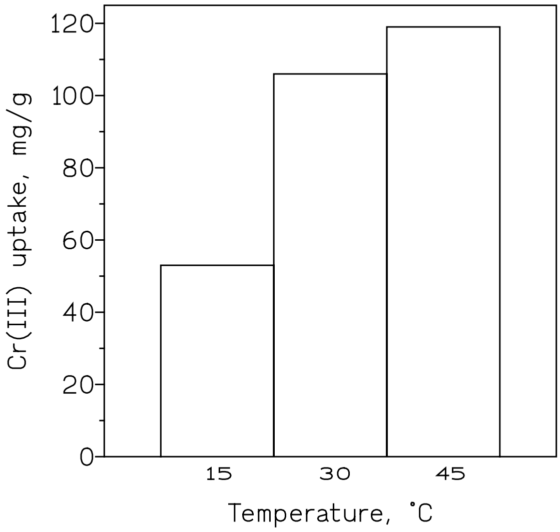

Fig. 1. Maximum adsorption capacities with temperatures.

In this Batool et al. [9], farmyard and poultry manure were converted to biochars. The sorption kinetics of Cr(III) was well-fitted to the pseudo-second-order equation, which confirmed a chemisorption process, whereas experimental data fitted to the Freundlich model due to the unfolding of multilayer adsorption. Cr(III) adsorption capacities were estimated as 38 and 34 mg/g for farmyard manure and poultry manure-derived biochars, respectively, in spontaneous and exothermic adsorption processes. After six cycles of continuous use, and using 0.1 M HCl solution as desorbent, there was a 10% loss of the initial adsorption capacity.

Removal of Cr(III) by adsorption on *Cymbopogon flexuosus* waste material entrapped within sodium alginate beads was investigated [10]. Cr(III) adsorption onto the biosorbent material followed the pseudo-first-order kinetic model, being the process of an endothermic nature. Equilibrium data followed the Freundlich model, which confirmed a multilayer chemisorption process, which showed a maximum adsorption capacity of 122 mg/g. Optimum conditions for such adsorption were: 0.05 g/L initial Cr(III) concentration in the aqueous phase of pH 4.5, agitation speed of 150 rpm, and 25°C. The above adsorption mechanism was well-supported by the intraparticle diffusion model. The saturated adsorbent was used as the catalyst for *p*-nitrophenol reduction.

An adsorbent material based on passion-fruit shell biomass (PFSB) for chromium(III) removal from contaminated aqueous mediums, was investigated [11]. Removal levels of 85%, 80%, and 53% for solutions containing 0.02, 0.05, and 0.2 g/L of Cr(III), respectively, were yielded. Experimental data showed a good fit to Langmuir and Freundlich models, with a maximum uptake of 28 mg/g. All the above data were derived using an adsorbent dosage of 5 g/L. The elution step was not considered in the work.

Column and batch experiments were carried out in order to determine the removal efficiency, competitive adsorption mechanism, and influencing factors on Cr^{3+} (and Zn^{2+}) solutions by steel slag [12]. A single column experiment showed that the removal yield of Cr^{3+} was 86%, however, in solutions containing both elements, the presence of Cr^{3+} enhanced slag hydrolysis and produced more active adsorption sites, but decreasing Cr^{3+} adsorption in favor of Zn^{2+} removal. The process runs well at pH values under 4.5 in the case of Cr^{3+} (6.8 in the case of Zn^{2+}), due to the apparition of precipitates in the system. The results of the investigation concluded that there were a number of factors affecting Cr(III) (and Zn(II)) adsorption and desorption that needed further studies and analysis.

An amidoxime-functionalized chelating resin (PAO-g-PS) was prepared through a two-step method and used in the removal of various metals from aqueous solutions [13]. The synthesis process consisted in a first reaction in which poly(acrylonitrile) was grafted onto chloromethylated polystyrene beads via surface-initiated atom transfer radical polymerization, in a second step, the nitrile group was converted to the amidoxime group by reaction with hydroxylamine. The adsorption properties were evaluated against Cr(III) (also Fe(III), Cd(II), and Pb(II)). It was found experimentally, that the maximum adsorption capacity was 130 mg/g in the case of Cr(III), with metal adsorbed onto the resin *via* a chelation interaction, and the process fitted well to the pseudo-second-order kinetic equation. Cr(III) removal process had an endothermic character. The adsorptive properties of PAO-g-PS toward the above heavy metals ions were selective, is not affected by common coexisting ions such as Na(I), K(I), Ca(II), and Mg(II). Elution was performed with 1 M HCl solution. After 10 cycles, a loss on the adsorption capacity was observed.

An adsorbent (Si-CPTS-HBAP) was produced first, when (3-Chloropropyl)triethoxysilane (CPTS) was immobilized on modified SiO_2 surface, then 2-(2-Hydroxybenzylidinoamino) pyridin-3-ol (HBAP) was covalently immobilized on the modified silica gel compound (Si-CPTS). Optimum Cr(III) adsorption was yielded under the next experimental conditions: pH 6, reaction time 120 min, adsorbent dosage 0.05 g, and 30°C [14].

The alginate extraction residue (RES) from the Brazilian *Sargassum filipendula* was employed as biosorbent on binary solutions, revealing a greater affinity and selectivity for Cr(III) over Zn(II) [15]. Experimental results revealed that the process was of endothermic nature and well fitted by the Langmuir–Freundlich binary model. Apparently, Cr(III) uptake responded to its coordination with hydroxyl groups of RES followed by carboxyl-metal and sulfate complexation. The manuscript did not show elution data.

This Cui et al. [16], investigated Cr(III) adsorption onto synthetic boehmite nanoplates in sodium hydroxide solutions up to 3 M. Adsorption isotherms and kinetics were fit to Langmuir and pseudo-second-order kinetic models, respectively, which was consistent with monotonic uptake of $Cr(OH)_4^-$ monomer species until saturation coverage of approximately half the aluminum surface site density. Maximum capacity was 20 mg/g at pH 13. Elution data were not included in the work.

Magnetic alkaline lignin−dopamine nanoparticles (AL−DA/Fe_3O_4NPs) were used to adsorb Cr(III) from solutions [17], being the metals effectively removed by physisorption and chemisorption processing. The maximum Cr(III) adsorption capacity was found to be 45 mg/g. Sensitive magnetic responsiveness (24.6 emu/g) of the adsorbent material can be more helpful in recycling (over 90% recycled within 2 min) and multiple reusing. The elution step used 0.1 M HCl solution as desorbent, with a decrease in the adsorption capacity up of five cycles of continuous use.

The biosorption mechanism of Cr(III) (and methylene blue) onto pomelo peel collected from local fruits was investigated by combining experimental analysis with ab initio simulations [18]. At 30°C, maximum biosorption capacity, calculated from the Langmuir model, was 11 mg/g. The adsorption mechanisms for Cr(III) were attributed to electrostatic attraction and *n–d* interactions. The manuscript was written without elution investigations.

Sugarcane bagasse chemically modified with citric acid was prepared and evaluated as adsorbent of Cr(III) (Cu(II) and Pb(II) from aqueous solutions [19]. The adsorption process was exothermic, and according to Langmuir isotherm linear model, this modification had little effect on Cr(III) adsorption capacity, about 22 mg/g for the pristine and modified adsorbent, but it was more significant in the case of Cu(II) (9–32 mg/g) and Pb(II) (12–53 mg/g).

The interaction between Cr(III) and chitosan/montmorillonite nanocomposites had been evaluated [20]. Using various percentages of montmorillonite added on solid chitosan, MMTCTf2% nanocomposite exhibited the best adsorption capacity of Cr(III) as compared to MMTCTf1% and MMTCTf3%. From a real tannery-waste solution (Marrakech, Morocco), MMCTf2% can adsorb 45% of the chromium(III) presented in the effluent, which presented a pH of 6 and 300 mg/L Cr(III). Other variables used were: adsorbent dosage of 0.2 g/L, and 24 h of reaction time. The results, being lower than that obtained with synthetic Cr(III) solutions, were explained by the presence of competitive metals (Cu, Cd, Ni, etc.) in the tannery wastewater. Elution experiments were no included in the work.

Nano-magnetic adsorbent $MnFe_2O_4$ was prepared by the co-precipitation method and used for Cr(III) (and Cr(VI)) elimination from aqueous phases [21]. The optimum pH, for the adsorption of Cr(III), was determined as 5, with the kinetics experiments fitted to the pseudo-second-order kinetics model; in the case of adsorption equilibrium studies, the experimental data fitted to the Langmuir isotherm model. Maximum Cr(III) adsorption capacity was 40 mg/g, value slightly higher than that of 35 mg/g of Cr(VI). Cr(III) adsorption was an endothermic and spontaneous process. The external mass transfer of Cr(III) on synthesized nanoparticles was the important and controlling step in the adsorption process. The elution step was not considered in this manuscript.

The efficiency, selectivity, and the role of surface groups of hydroxyapatite in Cr(III) removal as single species, or in the presence of Ni(II) and Pb(II), had been investigated [22]. Different mechanisms of metal uptake were active depending on the nature of the metal species and pH value of solutions: surface complexation, precipitation, ion-exchange, or dissolution–precipitation. Eluant was nitric acid, with an efficiency of 65%.

Porous biochars obtained from coniferous woods (CB) and magnetic biochars (MB) based on them were used to remove Cr(III) from aqueous solutions, which presented metal concentrations in the 260–650 mg/L range [23]. Results derived from this investigation showed that near quantitative Cr(III) adsorption occurred using both CB and MB adsorbents, this was explained to the presence of OH groups, on the surface of the biochars, which promoted the metal adsorption. This work did not include an elution investigation.

Biochars derived from the co-gasification of blends of rice husk plus corn cob (biochar 50CC) and rice husk plus eucalyptus stumps (biochar 50ES), as potential renewable low-cost adsorbents for Cr(III) recovery from wastewaters were investigated [24]. The two gasification biochars presented a weak porous structure (ABET = 63–144 m^2/g), but a strong alkaline character, promoted by a high content of mineral matter (59.8% w/w of ashes for 50CC biochar and 81.9% w/w for 50ES biochar). High Cr(III) removal percentages (around 100%) were obtained for both biochars, due to chromium precipitation, at low L/S ratios (100 and 200 mL/g), for initial pH of 5 and initial chromium(III) concentration of 50 mg/L (Fig. 2). Under the experimental conditions in which other removal mechanisms rather than precipitation occurred, that is, at more acidic pH values, a higher removal percentage (50%) and the highest uptake capacity (6.9 mg/g) were yielded for 50CC biochar. In the equilibrium, 50ES biochar presented a removal percentage of 27% with a maximum uptake capacity of 2.6 mg/g The better performance on Cr(III) recovery for the biochar 50CC was attributed to its better textural properties, as well as its higher cation exchange capacity. Elution was investigated with alkaline (pH 9–10) solutions.

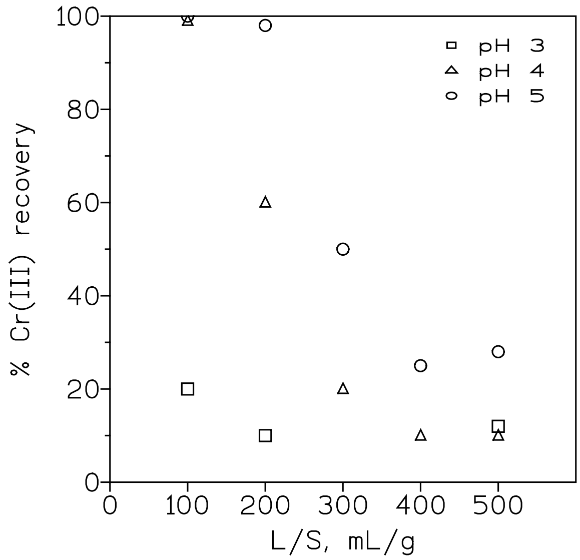

Fig. 2. Influence of the L/S variation and the pH of the solution on the Cr(III) recovery of the biochar 50CC. Cr(III): 50 mg/L and time: 24 h.

Bioregeneration experiments for brewery spent diatomite with the ammonifying bacteria *Lysinibacillus fusiformis* were conducted [25]. The resulted product, after 14 d incubation, was examined for Cr(III) (and methylene blue) removal from aqueous solutions. In the case of Cr(III), this removal reached 72% which is higher than the value obtained with the thermal regeneration method. It was confirmed, that physical adsorption, related to the porous structure of diatomite, was responsible for Cr(III) adsorption. In addition, chemical adsorption associated with the ion exchange process might be an important sorption mechanism of Cr(III). The recovery of Cr(III) from the metal-loaded adsorbent was not considered in the work.

Chromium and nickel(II) adsorption on *Durvillaea antarctica* surface were investigated under various experimental variables [26]. In the case of Cr(III), best adsorption results were obtained at a pH value of 5, with contact times of 7 h, and maximum adsorption capacity of 103 mg/g. It was suggested that the interaction of Cr(III) with the surface and the changes in the chemical behavior of the solid were responsible for metal uptake. Equilibrium data fitted well to the Sips model, which simultaneously involved the Freundlich and Langmuir isotherms:

$$\left[\mathrm{Cr}\right]_{a,e} = \frac{\left[\mathrm{Cr}\right]_{a,m}\left(K_s\left[\mathrm{Cr}\right]_{\mathrm{aq},e}\right)^{\frac{1}{m_s}}}{1+\left(K_s\left[\mathrm{Cr}\right]_{\mathrm{aq},e}\right)} \quad (2)$$

In the above equation, $[\mathrm{Cr}]_{a,e}$ and $[\mathrm{Cr}]_{\mathrm{aq},e}$ were the chromium concentrations in the adsorbent and in the aqueous solutions at the equilibrium, respectively, K_s was the equilibrium Sips constant, and m_s was the heterogeneity factor, a value of m_s near or equal to 1 occurred in biosorbents with homogeneous active sites; if the values were close to zero, the adsorbent had heterogeneous active sites. In binary solutions, Ni(II) was adsorbed in preference to Cr(III). Elution investigations were not included in the work.

Silica extracted from rice husk (SRH) was synthesized through calcination at 650°C in an oxidant atmosphere, yielding mesoporous silica (BET area of 297 m^2/g) with an average pore diameter of 2.3 nm. The surface of this silica was modified through a post-synthesis route with amine and polyamine groups obtained at 16% and 47% of modified surface with amine or polyamine groups (SRH-NH_2 and SRH-triamine). These materials were used to adsorb Cr(III) from aqueous solutions [27]. With all of them, equilibrium was reached after 20 min of reaction, with adsorption capacities of 6.7 mg/g (SRH), 22 mg/g (SRH-NH_2), and 34 mg/g (SRH-triamine). SRH and SRH-amine materials were used to adsorb Cr(III) from a sample taken from a tannery waste effluent from the city of Leon (Mexico), with adsorptions of 70% and 90%, respectively.

Hybrid phosphonate-functionalized silica adsorbents were synthesized through a modified route of sol–gel processing (SPMF), and used in the removal of Cr(III) from solutions [28]. At equilibrium (80 min reaction time), maximum uptake was of 79 mg/g at pH 3.6 on adsorbent SPMF, and the equilibrium data fitted with Langmuir isotherm (maximum Cr(III) adsorption capacity of 34 mg/g at pH 3), whereas kinetics experiments fitted to the pseudo-second-order model. At pH value around 3.6, the selectivity order with SPMF04 (containing 2.9 mmol P/g) was Zn > Cr > Pb > Cu > Cd > Ni. Apparently, chromium(III) interacted not only with phosphonate surface groups but also with a large of amount of geminal OH surface groups. The desorption step investigation was not included in the manuscript.

C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarene were synthesized and it was used to adsorb Cr(III) (also Cu(II) and Pb(II)) [29]. The optimum pH value for Cr(III) adsorption was 4.5, and the adsorption followed the next order: Pb(II) > Cu(II) > Cr(III). The competitive adsorption of these heavy metal ions was also investigated. The manuscript did not include the elution step.

Taking into account the proven efficiency of multifunctional TiO_2/Alg/FeNPs magnetic beads for the removal of organic pollutants, this adsorbent was used the removal of mixed heavy metals (MHM), specifically Cr(III), Cu(II), and Pb(II), under ultraviolet irradiation at a wavelength of 254 nm [30]. From a solution containing 44 mg/L of each of the above elements, the removal of all of these from the aqueous solution was almost complete (>98%) after 72 min of irradiation at pH 6.8. The active sites of the beads presented a great stability.

Polymer/Fe_3O_4 composite was synthesized via radical polymerization. Acrylamide was used as monomer and copolymerized with 1,3,5-triacryloylhexahydro-1,3,5-triazine in the presence of the iron oxide particles. The as-obtained polymer was hydrolyzed by N,N,N′,N′-tetramethylethylenediamine to increase ionized groups amount; after drying, the powdered composite was used for the removal of Cr^{3+}, Pb^{2+}, and Cd^{2+} [31]. Also, the synthesized composite was trapped in a cellulose acetate membrane filter. The effect of shaking speed had little influence on Cr(III) adsorption, 98% (50 1/min) against >99% (100 1/min) Cr(III) removal occurred in 3–5 s by using a syringe filter system, with a yield of 96% in the case of the Cr(III)-bearing aqueous solution of pH 6. Elution step used 1 M NaOH as eluent solution.

Cobalt–ferrite nano-composite (CFNC) was used to adsorb chromium(III) and cadmium(II) from synthetic wastewater [32]. The results showed that the maximum recovery of and Cr(III) (also Cd(II)) were determined as 20 mg/L (CO), 50 min (reaction time), 25°C (temperature), 20 g/L (adsorbent dosage), and pH 7 (pH 6 in the case of cadmium(II)). The adsorption process followed the Langmuir isotherm, and the maximum adsorption capacity for Cr(III) was 217 mg/g (303 mg/g for Cd(II)). The experimental data fitted to the pseudo-first-order kinetic model, in a spontaneous and endothermic process.

Biogenic magnetite nanoparticles (BMNs), produced by metal-reducing bacteria, were used in the removal of Cr(III) from solutions [33]. The BMNs that were coated with organic matter were more effective than chemically synthesized magnetite nanoparticles in the adsorption of Cr(III) with electrostatic interactions (82% against 13%, after 2 weeks of reaction time) and in preventing Fe(II) oxidation within the magnetite structure.

Copper(II) oxide (CuO) with dendrite, leaf, and feather morphologies were synthesized and used as adsorbents of Cr(III) [34]. The results demonstrate that CuO feather, at 24 h contact time and 0.1 g adsorbent, and with an adsorption efficiency of 57% had the highest efficiency if compared with the other CuO morphologies. The elution step was not considered here.

It was reported [35], the uses of industrial waste/by-products-based composites as adsorbents for the removal of heavy metals from wastewater. Detailed investigations onto the adsorption mechanism and the role of the different adsorption parameters had also been discussed, however, there was not included any information about the elution step.

A pseudo-surface imprinting technique was applied on carboxylated macadamia activated carbon (MAC) by grafting MAC with triethylenetetramine, N,N′-diisopropylcarbodiimide and $CrCl_3 \cdot 6H_2O$ (template ion) to produce MAC-pseudo-ion imprinted adsorbents (MAC-PIIA) [36]. MAC-pseudo-non-imprinted adsorbent (MAC-PNIA) counterparts were prepared by the same procedure, but Cr^{3+} was excluded in the synthesis. The adsorption performance, over Cr(III), of the MAC-PIIA under pH 5, contact time of 120 min, and 3.3 g/L adsorbent dosage was 80% (70 mg/g adsorption capacity). Application of the MAC-PIIA or MAC-PNIA on spiked acid mine drainage artificial sample led to a decrease the removal efficiency (72% and 56%, respectively). Freundlich isotherm fitted the experimental data. There were not desorption data included in the work.

An adsorbent was prepared by laccase-catalyzed self-polymerization of GAL and cross-linking with PEI [37]. When the mass ratio of GAL and PEI was 2:1, the self-polymerization temperature, pH and time are 50°C, 4.5, and 24 h, respectively, and the cross-linking temperature, pH and time are 70°C, 8–9, and 24 h, respectively. GAL-PEI had a Cr(III) adsorption capacity of 175 mg/g, being the adsorption order: Cu(II) > Cr(III) > Pb(II) = Zn(II) > Cd(II) > Fe(III) (Table 1). The stability experiment showed that PGAL-PEI has good stability under acidic conditions, but elution investigations were absent in the work.

Magnetic resin microspheres (MPMDG2) were prepared by suspension polymerization combined with basic and acidic hydrolysis, and the adsorption property of the material to heavy metals was investigated [38]. Structural and morphological analysis revealed that the resin had a high specific surface area and mesoporous structure. Adsorption experiments showed that the resin preferably adsorbed Cr(III) (and Pb(II)) over Cu(II) and Cd(II). The adsorption process was well described by the pseudo-second-order kinetic model, whereas the equilibrium adsorption data fitted the Langmuir isotherm model. Ion exchange and chemistry chelating was the most probable mechanisms for Cr(III) uptake onto the resin. In this investigation, elution was done using a 0.1 M HCl solution. With mixed solutions of the three elements and up to six

Table 1
Adsorption capacity of PGAL-PGI

Element	Element uptake, mmol/g
Zn(II)	2.4
Fe(III)	1.6
Cu(II)	5.1
Pb(II)	2.5
Cr(III)	3.4
Cd(II)	2.1

Initial concentration: 0.2 g/L each, pH: 5, temperature: 25°C, and time: 18 h.

cycles, there was a slight but continuous decrease in Cr(III) adsorption capacity.

A three-dimensional (3D) porous graphene-based hydrogel with good mechanical strength and large surface area was fabricated by self-assembly of graphene oxide (GO) sheets reduced and modified by gallic acid (GA) through π–π interactions [39]. As an adsorbent, this hydrogel (GA-GH) adsorbed Cr(III), at pH 4, by coordination complexation between the metal and deprotonated carboxylic groups of GA modified on graphene sheets. At pH 3, the adsorption capacity (305 mg/g) of GA-GH adsorbent was greater than that showed by GH adsorbent (112 mg/g). Cr(III) was desorbed at pH 2, and with the two adsorbents, there was a slight decrease in the adsorption capacity up to 10 cycles.

Corn cob immobilized, onto calcium alginate beads, biomass was used as adsorbent of chromium(III) and (VI) [40]. Cr(III) was adsorbed up to 278 mg/g (209 mg/g in the case of Cr(VI)), following Langmuir isotherm and the pseudo-second-order kinetic model. The immobilized corn cob biomass was run up to five repeated adsorption–desorption cycles and 0.98% and 1.51% adsorption efficiencies were reduced at the end of 5 adsorption–desorption cycles of Cr(III) and Cr(VI), respectively. NaOH (0.1 M) desorbed (80%) Cr(III) loaded onto the adsorbent (86% of Cr(VI)). Optimized conditions were employed for chromium adsorption from a tannery effluent (Kasur, Pakistan) and after near 7 h, up to 65% Cr(III) (56% Cr(VI)) were removed from the effluent.

An adsorbent in the form of a CLCh/MWCNT/Fe film was prepared using multiple walled carbon nanotubes (MWCNT) doped with magnetic iron oxide and deposited in crosslinked chitosan (CLCh) [41]. The CLCh/MWCNT/Fe film presented a maximum adsorption capacity for Cr(III) of 66 mg/g (150 min) and for Cr(VI) of 449 mg/g (60 min) at 25°C. The CLCh/MWCNT/Fe was removed from the aqueous solution by a mechanical separation or by magnetization due to its magnetic properties. Elution was performed using 0.1 M NaOH solution. After 10 consecutive adsorption–desorption cycles, the CLCh/MWCNT/Fe film presented efficiency losses from 26 to 14 mg/g.

Amine-terminated hyperbranched PAMAM (polyamidoamine) polymer (AT-HBP) was synthesized as a multifunctional chelating agent to remove Cr(III) (and Cu(II)) from simulated wastewater solutions [42]. The removal process was carried out in two different methods, centrifuged process, and ultrafiltration. The overall results indicated that removal percentages higher than 98% for Cr(III) (86% for Cu(II)) were achieved for initial metal concentrations of 100 mg/L, and using both removal process methods. Furthermore, the function of the second generation of polypropylenimine (PPI) was compared to AT-HBP, the results revealed that the removal of Cr(III) (and Cu(II)) by AT-HBP were approximately 20% and 10% higher compared to PPI, respectively. The performance of the polymer was not significantly influenced by the presence of NaCl in the aqueous solution. The manuscript did not present desorption results.

Polystyrene-poly(N-isopropylmethacrylamide-acrylic acid) [PSt@p(NIPMAM-Aac] core/shell gel particles were prepared by two-step precipitation polymerization method and used as an adsorbent for removal of heavy metal ions such as Cr(III) (also Pb(II), Cu(II), and Cd(II)) (III) from aqueous medium [43]. The adsorption capacity of gel particles for Cr(III) was found as 435 mg/g, with equilibrium data fitted to the Langmuir model. Kinetic study showed the adsorption process followed pseudo-second-order equation. Elution was investigated with 0.5 M HCl solutions, after three cycles, there was a slight decrease in the adsorption capacity.

Cotton fiber functionalized with tetraethylenepentamine and chitosan (CTPC) was prepared and used as absorbents for the removal of Cr(III), Cu(II), and Pb(II) from aqueous solution [44]. Experimental results showed that the maximum adsorption capacity was 73 mg/g for Cr(III), based on the Langmuir isotherm model at optimal pH of 5. Adsorption kinetics of CTPC fibers for Cr(III) ions fitted the pseudo-second-order model. The presence of Mg^{2+} in the aqueous solution slightly reduced the adsorption capacity. The manuscript did not include elution data.

Clays are cost-effective, high abundance, and most importantly, and they have high sorption capacities, thus, an Iranian clay was used to remove Cr(III) from aqueous solutions [45]. The maximum adsorption capacity was obtained at pH 4 and at initial concentration of the metal of 140 mg/L. Langmuir isotherm was the best fit for the equilibrium data., and the pseudo-first-order kinetic model described the dynamic data, which resulted to be an exothermic and spontaneous process. A comparison done among Cr(III) adsorption processes by natural adsorbents showed that this adsorbent provides the highest adsorption capacity. Data about the elution step were not included in the work.

The adsorption process of Cr(III) (also Cd(II), Cu(II), Hg(II), Pb(II), and Zn(II)) onto the methacrylate monomer derived of vanillin (VMA), using the density functional theory, was investigated [46]. By means of the molecular electrostatic potential and frontier molecular orbital (FMOs), the best region for adsorption was found, thus, each element was placed close to the nitrogen and oxygen atoms of the imine and carboxyl groups of vanillin monomer, respectively. The bond of the metal ions with the nitrogen atom was shown to be stronger than with oxygen atoms, because the charge density of the nitrogen was increased in the formation of the Schiff base with the proximity of the aromatic ring. Adsorption of Cr(III) (also Cu(II), and Pb(II) was best because of the high energy values involved in the process. Moreover, it was determined that the interaction between vanillin monomer and these metallic elements was covalent partial. The elution step was not considered here.

Tannins are renewable materials, coming from multiple vegetable sources. A variety of biosorbents had been developed from tannins, including tannin resins, rigid foams, composites with mesoporous silica, cellulose, collagen, and magnetic adsorbents [47]. These materials showed an excellent ability to uptake heavy metal cations, that is, Cr(III), Cd(II), Cu(II), Pb(II), and Ni(II), due to the chelating ability provided by the plentiful adjacent hydroxyl groups. Desorption investigations were not included in the manuscript.

The silylant agent 3-aminopropyl trimethoxysilane (APTES) was anchored on expanded glass aggregate (GA) to prepare an adsorbent. N-Benzoyl-N′-(4-methylphenyl) thiourea (TTU) bonded to amino-functionalized GA adsorbent with reflux. Developed adsorbent (GA-APTES-TTU) was used for the removal of Cr(III) from aqueous solutions [48]. The increase of the aqueous pH increased Cr(III) adsorption (Table 2), but this uptake was not solely due to the adsorption of Cr^{3+}, since as the authors literary said "the higher adsorption of Cr(III) from solutions of pH higher than 4 is mainly due to precipitation of $Cr(OH)_3$ onto the adsorbent surface". The adsorption followed the Langmuir isotherm model, with a maximum capacity of 22 mg/g. Thermodynamic data showed that Cr(III) adsorption was spontaneous, endothermic, and a physisorption reaction; the experimental data fitted to the pseudo-second order model. Elution investigations were not contemplated in the work.

Three dimensional chitinous microcages from ephippial eggs of a microcrustacean, *Daphnia longispina* (water flea) by keeping the original shape of its chitinous structure were prepared and iron-based magnetic particles were loaded into the chitinous microcages to enhance its heavy metal adsorption capacity [49]. The adsorbent was evaluated in the adsorption of Cr(III), Cd(II), Cu(II), Ni(II), and Zn(II) from aqueous solutions. Magnetic particles loaded microcages exhibited a better performance in removal of Cd(II), Cu(II), and Ni(II) ions; while unloaded microcages showed a higher affinity for Cr(III) and Zn(II). Chitinous microcages showed a Cr(III) adsorption capacity of 58 mg/g, whereas in the iron-based magnetic particles loaded chitinous microcages this was of 68 mg/g. Elution was not considered here.

The adsorption performance of native and magnetic oxide (Fe_3O_4) impregnated bentonite clays for the adsorption of Cr(III) from aqueous solutions was investigated [50]. The results showed that magnetized bentonite with high specific surface area provides high affinity and fast kinetics for Cr(III) uptake. Using low Cr(III) concentrations, the adsorption efficiency of the impregnated material was better than the native form. Maximum adsorption capacity for Cr(III) uptake was estimated as 65 and 67 mg/g for native and impregnated bentonite, respectively, and followed the Langmuir model, whereas with the two adsorbents Cr(III) adsorption was physisorption in nature. With both adsorbents, there was an increase in the percentage of chromium(III) removal with the pH, in the range of 2–7, and then remained constant up to pH 10; also in the two cases, the experimental data followed the pseudo-second-order equation at 10°C and 40°C. There was not included elution step investigation in the work.

Triamine-functionalized SiO_2 hollow microspheres (TAS-HMSs) with shell-in-shell morphology and micro-mesoporous walls were used to remove some heavy metals as Cr(III) (also Pb(II), Cu(II), and Cd(II)) from aqueous solution [51]. Adsorption kinetics fitted by both pseudo-first-order and pseudo-second-order models, with the equilibrium data fitted to the Langmuir isotherm. Adsorption increased from pH 2 to 5 and then decreased until pH 7. The sequence of maximum adsorption under optimal conditions of pH: 5, adsorbent dosage 5 mg and contact time 120 min) was: 295 mg/g Pb(II), 276 mg/g Cu(II), 252 mg/g Cd(II), and 193 mg/g Cr(III). Experimental data indicated that the adsorption of all the above elements onto TAS-HMSs was spontaneous, endothermic, in a physicochemical adsorption process. 0.2 M HCl solution appeared to be the best eluent (up to 85% desorption efficiency). After four cycles of continuous use, there was not a notable change in the amount of metals uptake.

Table 2
Effect of pH on adsorption of Cr(III)

pH	% adsorption[a]
2	25
3	75
4	80
5	95
6	99

[a]Approximate values. Cr(III): 150 mg/L, time: 2 h, temperature: 25°C, and adsorbent dosage: 0.3 g.

A biomass-derived hierarchically porous carbon (HPC) with oxygen- and nitrogen-containing functional groups had been used to investigate the adsorption equilibrium and mechanism toward heavy metals Cr(III), Cu(II), Zn(II), Pb(II), and Cd(II) [52]. Data obtained from experimentation indicated that the adsorption of all the above onto HPC fitted well with the Langmuir isotherm. Experimental data showed that there was a continuous increment of the adsorption capacity with the increase (2–6) of the pH of the solution. At pH 5, maximum Cr(III) uptake was 52 mg/g. The work did not present desorption data.

A CaO/Fe_3O_4 nanocomposite was modified by sodium dodecyl sulfate (SDS) and used for Cr(III) removal from aqueous solution [53]. The results of equilibrium and kinetic studies indicate that the adsorption process follows the Langmuir isotherm and the pseudo-second-order kinetic model, respectively. The thermodynamic results demonstrated that the adsorption process was spontaneous and exothermic. Maximum adsorption occurred at pH 5, with a maximum capacity of 6 mg/g. The elution step was not considered in the investigation.

Natural marne clay (NMC) is a material that was used for the adsorption of heavy metals Cr(III), Co(II), and Ni(II) from aqueous solutions [54]. The Langmuir isotherm fitted the equilibrium data, with the maximum adsorption capacities of 77, 48, and 21 mg/g for Cr(III), Co(II), and Ni(II), respectively. The thermodynamic data indicated the endothermic nature of the adsorption process of the three metals onto the adsorbent. The selectivity sequence of the adsorption was found as Co(II) > Cr(III) > Ni(II) from single and binary components.

Several adsorbents featuring mercapto or amine-mercapto groups were used in the removal of several heavy metals, including Cr(III) [55]. Metals uptake ranged from 84 to 140 mg/g. Using the best adsorbent, adsorption capacities followed the order Cu(II) > Pb(II) > Zn(II) > Cr(III) > Cd(II) > Ni(II), being the adsorption related to both surface complexation and surface precipitation. Using the amine-mercapto adsorbent, and from ternary elements solutions, Cr(III) was adsorbed preferably to Cu(II), Zn(II), and Ni(II). The elution step was not included in the work.

The isothermal adsorption properties of ettringite toward Cr(III) and Cr(VI) were investigated [56]. The results showed that the adsorption of Cr(III) onto ettringite at 20°C agreed with the Langmuirs isotherm, while the adsorption of Cr(VI) onto ettringite followed the Freundlich isotherm. It can be concluded that the adsorption of Cr(III) onto ettringite is mainly by chemical adsorption and that the adsorption of Cr (VI) onto ettringite is mainly by physical adsorption. The adsorption of Cr(III) onto ettringite agreed with the pseudo-second-order kinetic equation. The manuscript did not include any information about the elution step.

A chemically modified magnetic Amberlite XAD-7HP was synthesized using Fe(II) and Fe(III) ions (iron oxide coated Amberlite XAD-7HP) and used for the removal of Cr(III) ions from aqueous solutions [57]. The optimum adsorption parameters were investigated in a batch system and evaluated as pH of 6, 60 min of contact time, 10 mg of adsorbent, and 25°C. It was found that the best kinetic fit of the adsorption data was the pseudo-second-order model, while the Langmuir isotherm model was found to be more appropriate for the description of metal uptake. Ninety Percent of the adsorbed Cr(III) can be removed from the loaded adsorbent by the use of 0.1 M nitric acid solution. The adsorption, though with a slight decrease, was over 90% of its original adsorption value after five cycles. The applicability of the material was tested using real water samples and the results demonstrated the efficiency of the method.

A series of silica-gel/polyamidoamine (PAMAM) dendrimer hybrid materials (SG-G0–SG-G4.0) were used for the removal of Cr(III) from aqueous solution [58]. The sequence G0–G4.0 was characterized by a decrease of the surface area (G0 the greater one). Experimental results demonstrated that the adsorption capacity of ester-terminated silica-gel/PAMAM dendrimers followed the sequence of SG-G2.5 > SG-G3.5 > SG-G1.5 > SG-G0.5, while that of amino-terminated materials decreased in the order of SG-G2.0 > SG-G 4.0 > SG-G3.0 > SG-G1.0 > SG-G0. The highest adsorption results were achieved at pH 4 for both ester- and amino-terminated materials, and that the adsorption equilibrium can be reached at about 240 and 180 min for amino- and ester-terminated hybrids, respectively. Adsorption kinetic can be well fitted by pseudo-second-order kinetic model with film diffusion process as the rate-limiting step, and the adsorption isotherm followed Langmuir model with monolayer adsorption behavior. The adsorption of Cr(III) by PAMAM dendrimer mainly involved the participation of N–H and C=O groups. The uptake of Cr(III) onto the ester-terminated adsorbents involved carbonyl oxygen and secondary amine nitrogen atoms to form tetra-coordinated chelates, while that of amino-terminated one tended to form hexa-coordinated chelates by carbonyl oxygen, primary, and secondary amine nitrogen atoms. The increase of the aqueous ionic strength decreased the adsorption capacity, and the elution step was investigated using 4 M HCl as eluent. Table 3 compares the performance of some of these derivatives with other Cr(III) adsorbents.

The biosorption of Cr(III) and Cr(VI), from aqueous solutions, on dry *Spirulina platensis* biomass was investigated under laboratory conditions as a function of pH, initial metal ion concentration, biomass dosage, time and temperature [59]. Optimum adsorption pH values for Cr(III) and Cr(VI) were estimated as 3 and 2, respectively. The Langmuir adsorption isotherm model fit well the sorption equilibrium of the experimental data obtained for Cr(III), while Freundlich isotherm fit better data obtained for the (VI) oxidation state. The kinetic data were best described using the pseudo-second-order kinetic model, and the adsorption process was exothermic in nature. The manuscript did not include the desorption step study.

Carbon microspheres were synthesized under nitrogen flow from walnut shells (WS) and then used as an adsorbent for the removal of Cr(III), Pb(II), Cu(II), and Cd(II) [60]. These materials presented the highest adsorption capacity at pH of 5, which in the case of Cr(III) was 345 mg/g. The results were explained to that Cr(III) had stronger binding ability to the OH and/or COOH functional groups followed by Pb, Cu, and Cd. The elution step was not considered here.

N-[4-morpholinecarboximidamidoyl]carboximidamidoylmethylated polyphenylene sulfide (MCMPPS) was synthesized by grafting moroxydine on cholomethylated polyphenylene sulfide (CMPPS) resin for the removal of some heavy metals, including Cr(III), from water [61]. The resin MCMPPS exhibited excellent chemical stability under strong acid, basic, and oxidative conditions. In the case of Cr(III), the maximum adsorption capacity of the adsorbent was found to be 120 mg/g Cr(III), with the equilibrium reached about at 30 min. It was suggested that Cr(III) (and the other metals investigated in the work) were adsorbed onto the surface of the adsorbent by coordination reaction of the element with amino and imino groups. Information about the elution step was not included in the work.

Four common waste keratin biofibers (human hair, dog hair, chicken feathers, and degreased wool) had been used as biosorbents for the removal Cr(III) and others heavy metals from aqueous solutions [62]. Using multielemental solutions of eight metals: Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II), the total metal biosorption increased in the order: degreased wool > chicken

Table 3
Comparison of SG derivatives with other Cr(III) adsorbents

Adsorbent	Cr(III) uptake, mg/g	Reference
SG-G2.0	98	58
SG-G2.5	102	58
Sawdust	325	6
Pomelo fruit peel	11	18
[PSt@p(NIPMAM-Aac]	435	43
modified CaO/Fe_3O_4 nanocomposite	6	53

feathers > human hair > dog hair. The pseudo-second-order equation fitted well to the experimental results, and there were not results about the elution step.

A modified attapulgite had been developed [63]. The procedure was based on the modification of attapulgite with humic acid, the material was used for the removal of Cr(III) under different conditions (pH, contact time, temperature, metal concentration, and adsorbent dosage). Experimental data showed Cr(III) adsorption on modified attapulgite was better than that of natural attapulgite, with the temperature markedly influenced the metal adsorption, which resulted to be an exothermic and spontaneous process. The Langmuir isotherm was used to describe these experimental data, which fitted to the pseudo-first-order and pseudo-second-order equations. The elution step was not considered in the work.

Biochars derived from wood and water caltrop shell waste, and a third biochar consisted in the blend of the above two, were used for the adsorption of Cr(III) and Cu(II) in solutions [64]. Whereas from monoelemental and binary solutions, and in the pH range 2–4, Cr(III) uptake was greater than that of Cu(II), in the case of binary solutions, blended biochars (1+1 mixture) showed a greater Cu(II) uptake. Each biochar adsorption equilibrium data fitted well with the Freundlich model. The effectiveness of the adsorption of Cr(III) and Cu(II) solutions utilizing biochar is proven to be effective in continuous adsorption columns.

Three different types of feedstocks and their biochars were used to remove Cr(III), Cd(II), Cu(II), and Pb(II) from multielemental solutions [65]. The results showed that the adsorption capacity is dependent on the type of feedstock and on the pyrolysis conditions. The adsorption capacity of the various biomasses followed the sequence: FO (from sewage sludge) >> LO > ZO (both from agriculture biomass waste) >> CO (from wood biomass waste), which in the case of Cr(III) varies from 0.83 to 5.9 mg/g (Fig. 3). In the case of wood and agricultural biomasses materials, the corresponding biochars clearly improved the adsorption efficiency. Formation of complexes and cation exchange had been found to be the two main adsorption mechanisms in these multielemental systems, with cation exchange being the most significant, though the contribution of the pore structure of biomass/biochar cannot be neglected.

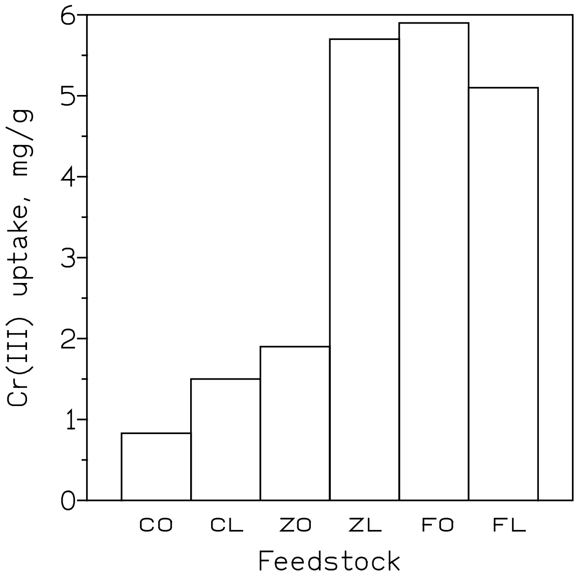

Fig. 3. Chromium(III) adsorption using various types of feedstock. CO: wood, CL: biochar of CO, ZO: may, ZL: biochar of ZO, FO: sludge, FL: biochar of FO. Aqueous phase: multielemental (Cr(III), Cu(II), Cd(II), and Pb(II)) solution of pH 4.

Zhu et al. [66], as it was shown by the title, indicated the non-usability of this adsorbent to remove Cr(III) from solutions, at least in the experimental conditions used in the work.

3. Conclusions

This review demonstrated that there was a real interest in the investigation of how to remove chromium(III) from contaminated solutions, and a number of new adsorbents (more than 63) were developed, with a great disparity in Cr(III) uptakes (Table 3), though just a small fraction (6%) of the reviewed manuscript showed their applications on real wastewaters. Most of these investigations come from China (24%), followed by Iran (10%), Turkey (8%), Brazil (6%), and Pakistan (5%), though institutions from other countries were also represented: Algerie, Colombia, Egypt, Ethyopia, India, Italy, Korea, Malaysia, Mexico, Morocco, Peru, Portugal, Russia, Saudi Arabia, South Africa, Spain, Taiwan, Ukranie, USA, and Vietnam.

However, as it was said in the Abstract and in the Introduction sections of this work, in many of these investigations, about 68% which represented a very important amount, their authors did not take into account, that equally important to the adsorption step, was the desorption step. Thus, in all these investigations it can not be known the real usefulness of the adsorbent(s) considered.

Another point to consider here, and only mentioned in a couple of works, was the role of the aqueous pH in Cr(III) adsorption step. It was a common consideration that chromium(III), as many other elements, were present in the aqueous solution as cation, that is, Cr^{3+}, and the given adsorbent was developed to adsorb the cation, however, it was regularly considered that many of the adsorption results, that is, Cr(III) removal from the solution, at pH near 4 were due

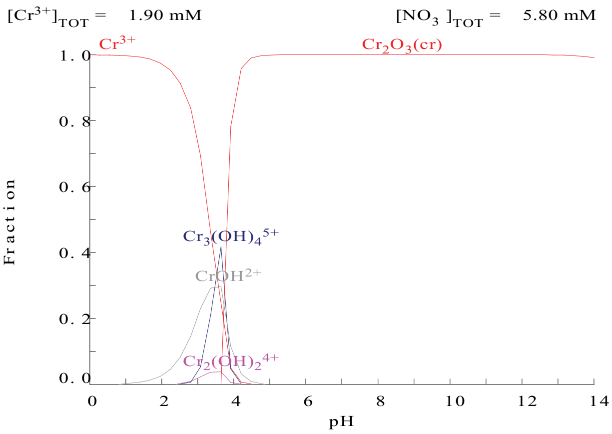

Fig. 4. Cr(III) speciation vs. the pH of the aqueous solution.

to the adsorption process and NOT to the precipitation of chromium(III) species, which evidently it was not a cation–adsorption process. Thus, it was also a fault of the reviewers of the manuscripts, which must indicated it in their respective reviews. As an example, in Fig. 4, this author generated, via the MEDUSA program [67], a Cr(III) – speciation vs. pH diagram to show the situation; in this case, the non-soluble Cr(III) species had been represented as Cr_2O_3.

All the above reviewed manuscripts but one lacked the stirring speed, applied to the system, as a variable to consider in batch mode investigations, when this variable can have the same importance that others, that is, the pH of the solution, the temperature, etc., to achieve the best adsorption results [68]. The explanation from the above is that, with the correct stirring speed, the mixing of the adsorbent and the bulk of the metal-bearing aqueous solution reached a maximum in effectiveness, and the thickness of the aqueous diffusion layer reached a minimum which maximizes the adsorption. The question is then, must we put all this quantitative results into quarantine? This author can provide examples of the above.

In conclusion, only one [10], of the reviewed manuscripts, finds a final application to their system, in all the other cases, authors limited their investigation to move Cr(III) from the feed solution to the adsorbent or to the eluate, thus, they translated the contamination problem from one side to another without considering what to do with the new Cr(III)-bearing material or solution, that is, dumping?, any kind of further treatment?, etc.

In any case, the use of chromium in the various industries is far to be finish, and the topic of using adsorbents for chromium(III) (or (VI)) removal from solutions is far to end.

Acknowledgment

To the CSIC (Spain) for support.

References

[1] R.T. Achmad, Budiawan, E.I. Auerkari, Effects of chromium on human body, Ann. Res. Rev. Biol., 13 (2017), doi: 10.9734/ARRB/2017/33462.

[2] A.L. Luz, X. Wu, E.J. Tokar, Toxicology of inorganic carcinogens, Adv. Mol. Toxicol., 12 (2018) 1–46.

[3] F.J. Alguacil, F.A. Lopez, On the active adsorption of chromium(III) from alkaline solutions using multiwalled carbon nanotubes, Appl. Sci., 10 (2020), doi: 10.3390/app10010036.

[4] R.M. Abdelhameed, R.A. Ismail, M. El-Naggar, E.S. Zarie, R. Abdelaziz, M.T. El Sayed, Post-synthetic modification of MIL-125 with bis-quinoline Mannich bases for removal of heavy metals from wastewater, Microporous Mesoporous Mater., 279 (2019) 26–36.

[5] A. Alemu, B. Lemma, N. Gabbiye, Adsorption of chromium(III) from aqueous solution using vesicular basalt rock, Cogent Environ. Sci., 5 (2019), doi: 10.1080/23311843.2019.1650416.

[6] M.S. Alhumaimess, I.H. Alsohaimi, A.A. Alqadami, M.M. Kamel, M. Naushad, T. Ahamad, H. Alshammari, Synthesis of phosphorylated raw sawdust for the removal of toxic metal ions from aqueous medium: adsorption mechanism for clean approach, J. Sol-Gel Sci. Technol., 89 (2019) 602–615.

[7] A.L. Arim, M.J. Quina, L.M. Gando-Ferreira, Uptake of trivalent chromium from aqueous solutions by xanthate pine bark: characterization, batch and column studies, Proc. Saf. Environ. Prot., 121 (2019) 374–386.

[8] C. Bai, L. Wang, Z. Zhuab, Adsorption of Cr(III) and Pb(II) by graphene oxide/alginate hydrogel membrane: characterization, adsorption kinetics, isotherm and thermodynamics studies, Int. J. Biol. Macromol., 147 (2020) 898–919.

[9] S. Batool, M. Idrees, M.I. Al-Wabel, M. Ahmad, K. Hina, H. Ullah, L. Cui, Q. Hussain, Sorption of Cr(III) from aqueous media via naturally functionalized microporous biochar: mechanistic study, Microchem. J., 144 (2019) 242–253.

[10] A. Basu, S.S. Behera, S. Dash, S. Banerjee, S. Sarkar, C.K. Mohanty, N.K. Dhal, P.K. Parhi, S.K. Tripathy, A study on removal of Cr(III) from aqueous solution using biomass of *Cymbopogon flexuosus* immobilized in sodium alginate beads and its use as hydrogenation catalyst, J. Taiwan Inst. Chem. Eng., 102 (2019) 118–132.

[11] G. Campos-Flores, J. Gurreonero-Fernández, R. Vejarano, Passion-fruit shell biomass as adsorbent material to remove chromium III from contaminated aqueous mediums, IOP Conf. Ser.: Mater. Sci. Eng., 620 (2019), doi: 10.1088/1757–899X/620/1/012110.

[12] G. Chen, L. Yang, J. Chen, T. Miki, S. Li, H. Bai, T. Nagasaka, Competitive mechanism and influencing factors for the simultaneous removal of Cr(III) and Zn(II) in acidic aqueous solutions using steel slag: batch and column experiments, J. Cleaner Prod., 230 (2019) 69–79.

[13] Y. Chen, H. Zhao, Y. Li, W. Zhao, X. Yang, X. Meng, H. Wang, Two-step preparation of an amidoxime-functionalized chelating resin for removal of heavy metal ions from aqueous solution, J. Chem. Eng. Data, 64 (2019) 4037–4045.

[14] A. Çimen, A. Bilgiç, Immobilization of 2-(2-hydroxybenzylidinoamino) pyridin-3-ol on silica gel and application to ındustrial wastewater, Desal. Water Treat., 147 (2019) 116–124.

[15] C.S.D. Costa, B.G.M. Queiroz, R. Landers, M.G.C. da Silva, M.G.A. Vieira, Equilibrium study of binary mixture biosorption of Cr(III) and Zn(II) by dealginated seaweed waste: investigation of adsorption mechanisms using X-ray photoelectron spectroscopy analysis, Environ. Sci. Pollut. Res., 26 (2019) 28470–28480.

[16] W. Cui, X. Zhang, C. Pearce, Y. Chen, S. Zhang, W. Liu, M.H. Engelhard, L. Kovarik, M. Zong, H. Zhang, E.D. Walter, Z. Zhu, S. Heald, M.P. Prange, J.J. De Yoreo, S. Zheng, Y. Zhang, S.B. Clark, P. Li, Z. Wang, K.M. Rosso, Cr(III) adsorption by cluster formation on boehmite nanoplates in highly alkaline solution Environ. Sci. Technol., 53 (2019) 11043–11055.

[17] L. Dai, Y. Li, R. Liu, C. Si, Y. Ni, Green mussel-inspired lignin magnetic nanoparticles with high adsorptive capacity and environmental friendliness for chromium(III) removal, Int. J. Biol. Macromol., 132 (2019) 478–486.

[18] V.P. Dinh, T.D.T. Huynh, H.M. Le, V.D. Nguyen, V.A. Dao, N.Q. Hung, L.A. Tuyen, S. Lee, J. Yi, T.D. Nguyen, L.V. Tan, Insight into the adsorption mechanisms of methylene blue and chromium(III) from aqueous solution onto pomelo fruit peel, RSC Adv., 9 (2019) 25847–25860.

[19] V.C.G. Dos Santos, C.A.T. Gomes, D.C. Dragunski, L.A.D. Koslowski, K. Lunelli, Removal of metals ions from aqueous solution using modified sugarcane bagasse, Rev. Virtual Quim., 11 (2019) 1289–1301.

[20] N. Eladlani, E. Dahmane, E. Ablouh, A. Ouahrouch, M. Rhazi, M. Taourirte, M. Neffa, Chitosan/montmorillonite nanocomposites: adsorption of Cr(III), J. Water Chem. Technol., 41 (2019) 175–181.

[21] B. Eyvazi, A. Jamshidi-Zanjani, A. Khodadadi Darbanb, Synthesis of nano-magnetic $MnFe_2O_4$ to remove Cr(III) and Cr(VI) from aqueous solution: a comprehensive study, Environ. Pollut., (2019), doi: 10.1016/j.envpol.2019.113685.

[22] M. Ferri, M. Campisi, C. Scavini, P. Evangelisti, P. Carniti, A. Gervasini, In-depth study of the mechanism of heavy metal trapping on the surface of hydroxyapatite, Appl. Surf. Sci., 475 (2019) 397–409.

[23] L. Frolova, M. Kharytonov, Synthesis of magnetic biochar for efficient removal of Cr(III) cations from the aqueous medium, Adv. Mater. Sci. Eng., 2019 (2019), doi: 10.1155/2019/2187132.

[24] D. Godinho, M. Nogueira, M. Bernardo, D. Dias, N. Lapa, I. Fonseca, F. Pinto, F. Recovery of Cr(III) by using chars from

the co-gasification of agriculture and forestry wastes, Environ. Sci. Pollut. Res., 26 (2019) 22723–22735.

[25] X. Gong, W. Tian, L. Wang, J. Bai, K. Qiao, J. Zhao, Biological regeneration of brewery spent diatomite and its reuse in basic dye and chromium(III) ions removal, Proc. Saf. Environ. Prot., 128 (2019) 353–361.

[26] J.R. Guarín-Romero, P. Rodríguez-Estupiñán, L. Giraldo, J.C. Moreno-Piraján, Simple and competitive adsorption study of nickel(II) and chromium(III) on the surface of the brown algae *Durvillaea antarctica b*iomass, ACS Omega, 4 (2019) 18147–18158.

[27] M. Gutiérrez-Valtierra, C. Salazar-Hernández, J.M. Mendoza-Miranda, E. Elorza-Rodríguez, M.J. Puy-Alquiza, M. Caudillo-González, M.M. Salazar-Hernández, Cr(III) removal from tannery effluents using silica obtained from rice husk and modified silica, Desal. Water Treat., 158 (2019) 152–163.

[28] P.I. Hernández-Velázquez, J.A. Gutiérrez-Ortega, G.G. Carbajal-Arizaga, R. Manríquez-González, W.D.L. Cruz-Hernández, S. Gómez-Salazar, Hybrid functionalized phosphonate silica: insight into chromium removal chemistry from aqueous solutions, J. Mex. Chem. Soc., 63 (2019) 130–153.

[29] Jumin, D. Siswanta, K. Nofiati, A.C. Imawan, Y. Priastomo, K. Ohto, Synthesis of C-4-hydroxy-3-methoxyphenylcalix[4] resorcinarene and its application as adsorbent for lead(II), copper(II) and chromium(III), Bull. Chem. Soc. Japan, 92 (2019) 825–831.

[30] D. Kanakaraju, N.R.b.M. Shahdad, Y.-C. Lim, A. Pace, Concurrent removal of Cr(III), Cu(II), and Pb(II) ions from water by multifunctional TiO_2/Alg/FeNPs beads, Sustainable Chem. Pharm., 14 (2019), doi: 10.1016/j.scp.2019.100176.

[31] C.S. Keskin, Rapid removal of Cd^{2+}, Pb^{2+} and Cr^{3+} by polymer/Fe_3O_4 composite, J. Water Chem. Technol., 41 (2019) 299–306.

[32] I. Khoshkerdar, H. Esmaeili, Adsorption of Cr(III) and Cd(II) ions using mesoporous cobalt-ferrite nanocomposite from synthetic wastewater, Acta Chim. Slov., 66 (2019) 208–216.

[33] Y. Kim, Y. Roh, Environmental application of biogenic magnetite nanoparticles to remediate chromium(III/VI)-contaminated water, Minerals, 9 (2019), doi: 10.3390/min9050260.

[34] J. Kondabey, H. Aghaie, M.H. Ghorbani, Study of the adsorption and photocatalytic properties of copper oxide with different morphologies in removal of Cr(III) ion from aqueous media, Water Sci. Technol., 80 (2019) 827–835.

[35] R. Kumar, M.A. Laskar, I.F. Hewaidy, M.A. Barakat, Modified adsorbents for removal of heavy metals from aqueous environment: a review, Earth Syst. Environ., 3 (2019) 83–93.

[36] M. Lesaoana, V.E. Pakade, L. Chimuka, Crosslinker-less surface-imprinted macadamia derived activated carbons for trace Cr(III) removal from aqueous solution, Environ. Technol. Innovation, 14 (2019), doi: 10.1016/j.eti.2019.100336.

[37] C. Li, T. Wang, Y. Luo, F. Wang, H. Zhu, Y. Guo, Preparation of a novel polyfunctional and high adsorption capacity adsorbent by laccase-catalyzed self-polymerization of GAL and cross-linking with PEI, New J. Chem., 43 (2019) 111–114.

[38] Z. Li, Z. Wang, C. Wang, S. Ding, F. Li, H. Lin, Preparation of magnetic resin microspheres M-P(MMA-DVB-GMA) and the adsorption property to heavy metal ions, Appl. Surf. Sci., 496 (2019), doi: 10.1016/j.apsusc.2019.143708.

[39] G. Liu, R. Yu, T. Lan, Z. Liu, P. Zhang, R. Liang, Gallic acid-functionalized graphene hydrogel as adsorbent for removal of chromium(III) and organic dye pollutants from tannery wastewater, RSC Adv., 9 (2019) 27060–27068.

[40] Q. Manzoor, A. Sajid, T. Hussain, M. Iqbal, M. Abbas, J. Nisar, Efficiency of immobilized *Zea mays* biomass for the adsorption of chromium from simulated media and tannery wastewater, J. Mater. Res. Technol., 8 (2019) 75–86.

[41] J.D.O. Marques Neto, C.R. Bellato, D.D.C. Silva, Iron oxide/carbon nanotubes/chitosan magnetic composite film for chromium species removal, Chemosphere, 218 (2019) 391–401.

[42] M. Mohseni, S. Akbari, E. Pajootan, F. Mazaheri, Amine-terminated dendritic polymers as a multifunctional chelating agent for heavy metal ion removals, Environ. Sci. Pollut. Res., 26 (2019) 12689–12697.

[43] K. Naseem, R. Begum, W. Wu, M. Usman, A. Irfan, A.G. Al-Sehemi, Z.H. Farooqi, Adsorptive removal of heavy metal ions using polystyrene-poly(N-isopropylmethacrylamide-acrylic acid) core/shell gel particles: adsorption isotherms and kinetic study, J. Mol. Liq., 277 (2019) 522–531.

[44] Y. Niu, W. Hu, M. Guo, Y. Wang, J. Jia, Z. Hu, Preparation of cotton-based fibrous adsorbents for the removal of heavy metal ions, Carbohydr. Polym., 225 (2019), doi: 10.1016/j.carbpol.2019.115218.

[45] F.N. Oskui, H. Aghdasinia, M.G. Sorkhabi, Adsorption of Cr(III) using an Iranian natural nanoclay: applicable to tannery wastewater: equilibrium, kinetic, and thermodynamic, Environ. Earth Sci., 78 (2109), doi: 10.1007/s12665–019–8104–8.

[46] I.H.S. Ribeiro, D.T. Reis, D.H. Pereira, A DFT-based analysis of adsorption of Cd^{2+}, Cr^{3+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, and Zn^{2+}, on vanillin monomer: a study of the removal of metal ions from effluents, J. Mol. Model., 25 (2019), doi: 10.1007/s00894–019–4151-z.

[47] S.C.R. Santos, H.A.M. Bacelo, R.A.R. Boaventura, C.M.S. Botelho, Tannin-adsorbents for water decontamination and for the recovery of critical metals: current state and future perspectives, Biotechnol. J., 14 (2019), doi: 10.1002/biot.201900060.

[48] T. Sardohan-Koseoglu, U.B. Ogul, E. Kır, F. Karipcin, Chemical modification of expanded glass aggregate with N-Benzoyl-N′-(4-methylphenyl) thiourea (TTU) for the adsorptive removal of Cr(III) ion, Arabian J. Chem., 12 (2019) 772–779.

[49] I. Sargin, G. Arslan, M. Kaya, Production of magnetic chitinous microcages from ephippia of zooplankton *Daphnia longispina* and heavy metal removal studies, Carbohydr. Polym., 207 (2019) 200–210.

[50] K.H. Shah, S. Ali, M. Waseem, F. Shah, M. Fahad, S. Shahida, A.M. Khan, A.R. Khan, Native and magnetic oxide nanoparticles (Fe_3O_4) impregnated bentonite clays as economic adsorbents for Cr(III) removal, J. Solution Chem., 48 (2019) 1640–1656.

[51] R. Soltani, A. Marjani, S. Shirazian, Shell-in-shell monodispersed triamine-functionalized SiO_2 hollow microspheres with micro-mesostructured shells for highly efficient removal of heavy metals from aqueous solutions, J. Environ. Chem. Eng., 7 (2019), doi: 10.1016/j.jece.2018.102832.

[52] J. Sun, M. Li, Z. Zhang, J. Guo, Unravelling the adsorption disparity mechanism of heavy-metal ions on the biomass-derived hierarchically porous carbon, Appl. Surf. Sci., 471 (2019) 615–620.

[53] S. Tamjidi, H. Esmaeili, Chemically modified CaO/Fe_3O_4 nanocomposite by sodium dodecyl sulfate for Cr(III) removal from water, Chem. Eng. Technol., 42 (2019) 607–616.

[54] K. Tizaoui, B. Benguella, B. Makhoukhi, Selective adsorption of heavy metals (Co^{2+}, Ni^{2+}, and Cr^{3+}) from aqueous solutions onto natural marne clay, Desal. Water Treat., 142 (2019) 252–259.

[55] J.P. Vareda, L. Durães, Efficient adsorption of multiple heavy metals with tailored silica aerogel-like materials, Environ. Technol., 40 (2019) 529–541.

[56] X. Wang, S. Cui, B. Yan, L. Wang, Y. Chen, J. Zhang, Isothermal adsorption characteristics and kinetics of Cr ions onto ettringite, J. Wuhan Univ. Technol. Mater. Sci. Ed., 34 (2019) 587–595.

[57] E. Yayayürük, O. Yayayürük, Facile synthesis of magnetic iron oxide coated Amberlite XAD-7HP particles for the removal of Cr(III) from aqueous solutions: sorption, equilibrium, kinetics and thermodynamic studies, J. Environ. Chem. Eng., 7 (2019), doi: 10.1016/j.jece.2019.103145.

[58] R. Yin, Y. Niu, B. Zhang, H. Chen, Z. Yang, L. Yang, Y. Cu, Removal of Cr(III) from aqueous solution by silica-gel/PAMAM dendrimer hybrid materials, Environ. Sci. Pollut. Res., 26 (2019) 18098–18112.

[59] N. Yushin, I. Zinicovscaia, L. Cepoi, T. Chiriac, T. Mitina, Study of chemistry of Cr(VI)/Cr(III) biosorption from batch solutions and electroplating industrial effluent using cyanobacteria *Spirulina platensis*, Rev. Roum. Chim., 64 (2019) 173–181.

[60] M. Zbair, H. Ait Ahsaine, Z. Anfar, A. Slassi, Carbon microspheres derived from walnut shell: rapid and remarkable uptake of heavy metal ions, molecular computational study and surface modeling, Chemosphere, 231 (2019) 140–150.

[61] C.-Z. Zhang, H. Sheng, Y.-X. Su, J.-Q. Xu, An efficient and health-friendly adsorbent N-[4-morpholinecarboximidamidoyl] carboximidamidoylmethylated polyphenylene sulfide for

removing heavy metal ions from water, J. Mol. Liq., 296 (2019), doi: 10.1016/j.molliq.2019.111860.

[62] H. Zhang, F. Carrillo, M. López-Mesas, C. Palet, Valorization of keratin biofibers for removing heavy metals from aqueous solutions, Text. Res. J., 89 (2019) 1153–1165.

[63] X. Zhang, Q. Lei, X. Wang, J. Liang, C. Chen, H. Luo, H. Mou, Q. Deng, T. Zhang, J. Jiang, Removal of Cr(III) using humic acid-modified attapulgite, J. Environ. Eng., 145 (2019), doi: 10.1061/(ASCE)EE.1943–7870.0001541.

[64] Y.P. Zhang, V.S.K. Adi, H.-L. Huang, H.-P. Lin, Z.-H. Huang, Adsorption of metal ions with biochars derived from biomass wastes in a fixed column: adsorption isotherm and process simulation, J. Ind. Eng. Chem., 76 (2019) 240–244.

[65] J.J. Zhao, X.-J. Shen, X. Domene, J.-M. Alcañiz, X. Liao, C. Palet, Comparison of biochars derived from different types of feedstock and their potential for heavy metal removal in multiple-metal solutions, Sci. Rep., 9 (2019), doi: 10.1038/s41598–019–46234–4.

[66] G.-j. Zhu, H.-y. Tang, H.-l. Zhang, L.-l. Pei, P. Zhou, Y.-l. Shi, Z.-h. Cai, H.-b. Xu, Y. Zhang, A novel ion-imprinted polymer for selective removal of trace Fe(III) from Cr(III)-containing solutions, Hydrometallurgy, 186 (2019) 105–114.

[67] Available at: www.kth.se/che/medusa

[68] F.J. Alguacil, I. Garcia-Diaz, F. Lopez, O. Rodriguez, Removal of Cr(VI) and Au(III) from aqueous streams by the use of carbon nanoadsorption technology, Desal. Water Treat., 63 (2017) 351–356.