

A review: a comparison of different adsorbents for removal of Cr (VI), Cd (II) and Ni (II)

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Received: 06.02.2020

Accepted/Published Online: 07.06.2020

Final Version: 18.08.2020

Abstract: A review of the studies dealing with the removal of chromium, cadmium, and nickel ions with different adsorbents published in the literature between 2014 and 2018 is given in tabular form, along with the adsorption conditions, adsorption isotherm, and kinetic models applied by the authors to model the experimental data and adsorption capacities. The review focuses on the efficiency of ion removal.

Key words: Adsorption, chromium, cadmium, nickel, adsorption comparison

1. Introduction

The evolution of civilization has led to the growth and development of all of the necessities that mankind needs for a comfortable life. Various industries have flourished (chemical, metallurgical, food, pharmaceutical, agricultural industry, etc.), which has resulted in environmental pollution.

According to the Reference Document for Common Waste Water and Waste Gas Treatment Data for Europe (EU-27 plus Iceland, Liechtenstein, Norway, and Serbia), water is contaminated annually with 18.53 tons of cadmium, 284.4 tons of chromium, and 324.9 tons of nickel [1]. These metals are problematic because of their toxicity; their emissions must therefore be kept under control.

With growing awareness of the consequences, legislation has become stricter; much effort has been invested in developing procedures for establishing and maintaining a cleaner environment.

The most common procedures for the removal of pollutants from wastewater and industry effluents are ion exchange, membrane separation processes (reverse osmosis, electrolysis), evaporation, chemical precipitation, reduction, coagulation, flocculation, solvent extraction, photo reduction, and adsorption [2,3]. Membrane separation processes and evaporation are quite expensive, as they use much energy. For optimal procedure conditions and for enhancing all of the above-stated operations, many additional reagents are used. Removal procedures usually produce secondary wastes, which are usually quite concentrated and hard to discard or recycle [4].

Many studies focus on adsorption. Commercial adsorbents are available, but most of them are expensive and difficult to regenerate and separate from the rest of the solution; furthermore, they lack selectivity and adsorption capacity. The development of adsorbents is focused now on alternative sources; researchers are focusing on utilizing biomass residue, which is abundantly available throughout the world [5,6].

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1.1. Adsorbents and adsorption

Adsorption is the process wherein components from gas or liquid phases bind to the surface of a solid substance. Binding itself can occur on a physical or chemical basis. Adsorbents are usually porous materials and usually have a large surface area due to their high porosity. Because of porosity, the internal area is generally bigger than the external area [7].

Adsorbents can be divided into 3 groups: natural inorganic, natural organic, and synthetic adsorbents. Natural inorganic adsorbents are clays, minerals (e.g., goethite, hydroxy-apatite, calcite), fly ash, zeolite, calcareous soils, slags, sludges, modified asphaltite, etc. Natural organic adsorbents include sawdust, coconut shell, corncob waste, tea waste, rice hulls, bark, hazelnut shells, wool, peat, and chitosan; synthetic adsorbents include nano-sized metal oxides, zero-valent iron, modified nano materials, etc. Nanoadsorbents, especially magnetic nanoadsorbents, have enormous industrial potential due to their high reactivity, many active sites, and consequent large surface area. Their shortcomings include instability and consequent aggregation, which diminishes their surface area; as a result, their reactivity is reduced. For prevention of aggregation and dissolvment, different additives like clays and polymers are generally used [8,9].

Due to the circular economy, natural organic and inorganic adsorbents have tremendous potential for general use. Many residues and wastes from industrial and agricultural activities are used. In order to optimize their functionality and properties, adsorbents can be modified and improved with different functional groups, which can provide better results in pollutant removal.

Many factors can influence the course of adsorption. For example, pH value has tremendous influence on adsorption's course, as it affects the chemical state of the solution as well as the chemical state of the adsorbent and its surface [10]. With a pH value of zero-point charge (pHpzc) and with a charge of adsorbate, it is possible to estimate which pH value of the solution would be appropriate for the removal of a particular adsorbate. If the pH value is below the pH value of zero-point charge, the adsorbent surface is positively charged and attracts anions; if the pH value is above pHpzc, the surface has a negative charge and attracts cations [11]. It is therefore necessary to know the chemistry of the adsorbate itself. At specific pH values, precipitation can occur, and the adsorption results may therefore be faulty.

The course of adsorption can also be altered and influenced by changing the initial concentration of adsorbate or by changing the dose of the adsorbent. Both variables can increase or decrease adsorption.

In some cases, a higher initial concentration shows a large increase in adsorption rate, because it creates the necessary driving force to overcome liquid resistance. The rate of adsorption may decrease quickly after initial adsorption, because the active sites that are easily accessible are occupied, causing a slight change in the adsorbent surface's charge. Because easily accessible places are already occupied, only places that are difficult to access remain. Occupied sites also influence the surface charge, which results in a decrease in the adsorption rate [9,12].

A higher adsorbent dose generates more active sites for binding; thus, adsorption rate usually increases to some extent. If the adsorbent dose is too high, it can diminish adsorption rate, because aggregates are formed and the number of active sites decreases [13].

2. Review of adsorbents for chromium, cadmium, and nickel removal

2.1. Chromium

Chromium is the thirteenth most common element found in the earth's crust. It is usually found in ore chromate. Chromium and its compounds are used in the manufacture of stainless steel, alloys, metal plating and finishing

solutions, leather tanning, pigment, and wood preservatives; it can be used as a corrosion inhibitor and as a catalyst. It has many oxidation states, but the most toxic form is hexavalent chromium. It causes severe health problems, especially due to its oxidating properties and its high solubility in water, which makes it available for biological uptake [14,15].

Cr (VI) likes to bond with hydroxyl groups; in most studies, the adsorption of Cr (VI) was successful when pH value was rather low, especially if pH value was below pH_{pzc} . With a pH value below pH_{pzc} , Cr (VI) is pulled toward the negatively charged surface of the adsorbent. If the pH value is above pH_{pzc} , chromium ions are repelled by the adsorbent surface and adsorption is decreased. The adsorption selectivity at high and low pH values can be explained by different forms of chromium in the aqueous environment. At pH values below 1, chromium exists as H_2CrO_4 . When the pH value is between 2 and 6.0, the dominant species HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ form; with pH values above 6.0, CrO_4^{2-} is dominant, which is harder to bind [10,15].

Most of the reviewed experiments were conducted at pH value 3. In some studies, experiments were performed at higher pH values primarily to prevent the adsorbent from dissolving. Higher pH values (above 6) will also cause chromium precipitation.

By increasing the initial Cr (VI) concentration and maintaining the adsorbent dose, the percentage of adsorbed Cr (VI) may be lower because the number of active sites is limited; when they are occupied, adsorption is complete. In addition, the reason for lower adsorption may be found in the formation of a film around the adsorbent, which prevents the adsorbate from accessing the surface. At the same time, the adsorbent capacity may be higher, because the higher initial concentration provides the necessary driving force to overcome liquid resistance [8,16].

Depending on the adsorbent, a higher adsorbent dose will increase adsorption because of the higher number of active sites. If the adsorption is slower, the main cause is the aggregation of adsorbent particles, which results in fewer active sites [8].

The overview of the adsorption studies of chromium (VI) is summarized in Table 1.

A review of studies with synthetic adsorbents showed that 100% chromium removal was achieved with the use of magnetic multiwall carbon nanotubes (MWCNT) [17] and nanomagnetite particles, which were synthesized in a low-pressure procedure [18]. The use of $\text{BaFe}_{12}\text{O}_{19}$ magnetic nano powder [19] and ionic liquid functionalized oxidized multiwall carbon nanotubes (IL-oxi-MWCNT) resulted in 99.5% removal [20]. The maximum adsorbent capacity of 293.3 mg/g was determined with the use of a magnetic composite of reduced graphene oxide, polypyrrole, and Fe_3O_4 nanoparticles (Ppy- $\text{Fe}_3\text{O}_4/\text{rGO}$) [10]. The surface area of Ppy- $\text{Fe}_3\text{O}_4/\text{rGO}$ was $80 \text{ m}^2/\text{g}$. In the same study, the comparison was made with $\text{Fe}_3\text{O}_4/\text{rGO}$. The adsorption capacity of Ppy- $\text{Fe}_3\text{O}_4/\text{rGO}$ was higher, even though the surface area of $\text{Fe}_3\text{O}_4/\text{rGO}$ was $126.42 \text{ m}^2/\text{g}$. It was established that the surface area does not represent a decisive parameter in the adsorption process. Ppy- $\text{Fe}_3\text{O}_4/\text{rGO}$ showed excellent adsorption properties. Chain-like Ppy forms a 3-dimensional network with Fe_3O_4 nanoparticles and with rGO sheets. The adsorption process happens because of electrostatic attraction, ion exchange, and chemical reduction of Cr (VI) to Cr (III) [10].

Table 1. Chromium (VI) adsorption capacities/parameters.

Adsorbent	Adsorbent characterization	Adsorption conditions	Isotherm and kinetic models with calculated constants and adsorption capacities			Adsorption capacity	Ref	
			Isotherm model	Calculated constants	Kinetic model			Calculated constants
Synthetic adsorbents								
Fe ₃ O ₄ -NH ₂ (amino functionalized magnetic nanoadsorbent)	D ₅₀ = 25 nm, pH _{pzc} = 5.8	pH = 3, T = 298 K, c ₀ = 5 mg/L, m _{ads} /V = 0.05 g/50 mL	Langmuir	q _m = 232.51 mg/g	Pseudo-second	R ² = 0.9871 q _{e,cal} = 28.25 mg/g	R% > 96 q _{e,exp} = 24.25 mg/g	[2]
Ppy-Fe ₃ O ₄ /rGO (magnetic composite of reduced graphene oxide, polypyrrole and Fe ₃ O ₄ nanoparticles)	S _M = 80.53 m ² /g	pH = 3, T = 318 K, c ₀ = 48.4 mg/L, m _{ads} /V = 0.25 g/L	Langmuir	q _m = 293.3 mg/g	/	/	/	[10]
Magnetite nanoparticles	D ₅₀ = 56 nm	pH = 3, T = 30 °C	Freundlich	R ² = 0.996 K _f = 3.81 mg/g	/	/	R% = 72 %	[13]
EDA-MPMs (ethylenediamine functionalized magnetic polymer microspheres)	S _M = 286 m ² /g, V _P = 0.512 cm ³ /g, D _P = 6.8 nm	pH = 2, T = 298 K, c ₀ = 300 mg/L, m _{ads} /V = 0.05 g/50 mL	Langmuir	R ² = 0.999 q _m = 236.9 mg/g	Pseudo-second	R ² = 0.997 q _{e,cal} = 169.205 mg/g	q _{e,exp} = 145.2 mg/g	[15]
MWCNT (magnetic multiwall carbon nanotubes)	S _M = 200 m ² /g, D ₅₀ = 20–40 nm, L = 2 μm	pH = 3, c ₀ = 2 mg/L, m _{ads} /V = 0.08 g/100 mL	Langmuir	R ² = 0.998 q _m = 16.234 mg/g	Pseudo-second	R ² = 0.9997 q _{e,cal} = 1.747 mg/g	R% = 100 % q _{e,exp} = 1.729 mg/g	[17]
Nanomagnetite particles (low pressure synthetic procedure)	/	pH = 4, c ₀ = 0.1 mg/L, m _{ads} /V = 10 mg/4 mL, t _{cont.} = 1 h	Langmuir	R ² = 0.995	/	/	R% = 100 % q _{e,exp} = 1.705 mg/g	[18]
BaFe ₁₂ O ₁₉ magnetic nanopowder (sample 4)	S _M = 13 m ² /g, D = 87 nm, pH _{pzc} = 5 ± 0.5	pH = 3, T = 25 °C, c ₀ = 133 mg/L, m _{ads} /V = 1.5 g/150mL, t _{cont.} = 1 h	/	/	Pseudo-second	R ² = 0.9706 q _{e,cal} = 14.3 mg/g	R% = 99.5 % q _{e,exp} = 13.25 mg/g	[19]

Table 1. (Continued).

Adsorbent	Adsorbent characterization	Adsorption conditions	Isotherm and kinetic models with calculated constants and adsorption capacities				Adsorption capacity	Ref
			Isotherm model	Calculated constants	Kinetic model	Calculated constants		
IL-oxi-MWCNT (ionic liquid functionalized oxidized multiwalled carbon nanotubes)	$S_M = 87.4 \text{ m}^2/\text{g}$, $V_P = 0.82 \text{ cm}^3/\text{g}$, $\text{pH}_{\text{pzc}} = 4-2$	$\text{pH} = 2.5-4$, $c_0 = 20 \text{ mg/L}$, $m_{\text{ads}}/V = 0.15 \text{ g}/20 \text{ mL}$	Langmuir	$R^2 = 0.96$ $q_m = 85.83 \text{ mg/g}$	Pseudo-second	$R^2 = 0.91$ $q_{e,\text{cal}} = 2.58 \text{ mg/g}$	$R\% = 99.5\%$ $q_{e,\text{exp}} = 2.54 \text{ mg/g}$	[20]
Fe_3O_4 nanoparticles	$S_M = 42.53 \text{ m}^2/\text{g}$, $d_{50} = 15 \text{ nm}$	$\text{pH} = 3$, $T = 55^\circ\text{C}$, $c_0 = 10 \text{ mg/L}$, $m_{\text{ads}} = 0.5 \text{ g/L}$, $t_{\text{cont.}} = 90 \text{ min}$	/	/	/	/	$R\% = 88\%$ $q_{e,\text{exp}} = 33.45 \text{ mg/g}$	[37]
$\text{Fe}_3\text{O}_4/\text{CTAB}$ (Fe_3O_4 nanoparticles capped with cetyltrimethylammonium bromide)	Fe_3O_4 crystal: $D_{50} = 16.25 \text{ nm}$	$\text{pH} = 4$, $T = 25 \pm 1^\circ\text{C}$, $c_0 = 100 \text{ mg/L}$, $m_{\text{ads}}/V = 12 \text{ mg/mL}$, $t_{\text{cont.}} = 12 \text{ h}$	Langmuir	$R^2 = 0.99$, $q_m = 18.5 \text{ mg/g}$	Pseudo-second	$R^2 = 0.99$	$R\% = 95.77\%$ $q_{e,\text{exp}} = 10.05 \text{ mg/g}$	[38]
PANISA (Polianiline nanofibers; PANI; acid treated natural silica)	PANI nanofibers: $D = 30-80 \text{ nm}$	$\text{pH} = 2$, $T = 25^\circ\text{C}$, $c_0 = 20 \text{ mg/L}$, $m_{\text{ads}}/V = 4 \text{ g/L}$, $t_{\text{cont.}} = 2 \text{ min}$	/	/	/	/	$R\% = 99.31\%$	[39]
WT (NH_3) Magnetic nanocomposite (from waste toner)	$S_M = 42.53 \text{ m}^2/\text{g}$, $D_{50} = 53.5 \text{ nm}$	$\text{pH} = 2$, $T = 25^\circ\text{C}$, $c_0 = 50 \text{ mg/L}$, $m_{\text{ads}}/V = 4 \text{ g/L}$	Langmuir	/	Pseudo-second	/	$R\% = 99\%$	[40]
Core-shelled Fe_3O_4 hybrid nanoparticle aggregate	$S_M = 238.18 \text{ m}^2/\text{g}$, $D_{50} = 700 \text{ nm}$, $D_{P50} = 7.5-9.1 \text{ nm}$	$\text{pH} = 3$, $c_0 = 10 \text{ mg/L}$, $m_{\text{ads}}/V = 20 \text{ mg}/50 \text{ mL}$	/	/	/	/	$R\% = 94.8\%$	[41]
h.mag-poly (EGDMA-VIM) microbeads	$S_M = 81.4 \text{ m}^2/\text{g}$ $D = 53-211 \mu\text{m}$	$\text{pH} = 2$, $c_0 = 50 \text{ mg/L}$, $m_{\text{ads}}/V = 50 \text{ mg}/50 \text{ mL}$	Langmuir	$R^2 = 0.995$ $q_m = 174.3 \text{ mg/g}$	/	/	$R\% = 32\%$ $q_{e,\text{exp}} = 16.2 \text{ mg/g}$	[42]
Natural organic/inorganic adsorbents								

Table 1. (Continued).

Adsorbent	Adsorbent characterization	Adsorption conditions	Isotherm and kinetic models with calculated constants and adsorption capacities				Adsorption capacity	Ref
			Isotherm model	Calculated constants	Kinetic model	Calculated constants		
Grape waste	$D_{50} = 0.2-0.5$ mm	pH = 2, T = 20 °C, $c_0 = 120$ mg/L, $m_{ads}/V = 0.05$ g/100 mL	Langmuir	$R^2 = 0.9847$ $q_m = 108.12$ mg/g	Pseudo-second	$R^2 = 0.997$ $q_{e,cal} = 104.5$	$q_{e,exp} = 104.3$ mg/g	[4]
FBA-Fe/Ni NP (Fe/Ni nanoparticles supported by a novel fly ash-based porous adsorbent)	$S_M = 20.63$ m ² /g, $D_{P50} = 2.89$ nm	pH = 1, T = 303 K, $c_0 = 1000$ mg/L, $m_{ads}/V = 0.2$ g/100 mL, $t_{cont.} = 24$ h	/	/	/	/	R% < 6 % $q_{e,exp} = 25.07$ mg/g	[8]
BCS (biochar from wheat straw)	$S_M = 26.3$ m ² /g, $V_P = 0.026$ cm ³ /g	pH = 2, T = 25 °C, $c_0 = 100$ mg/L, $m_{ads}/V = 0.2$ g/50 mL, $t_{cont.} = 21$ h	Langmuir	$R^2 = 0.990$ $q_m = 24.6$ mg/g	Pseudo-second	$R^2 = 0.983$ $q_{e,cal} = 14.36$ mg/g	$q_{e,exp} = 14.36$ mg/g	[14]
BCW (biochar from whicker)	$S_M = 11.4$ m ² /g, $V_P = 0.0061$ cm ³ /g	pH = 2, T = 25 °C, $c_0 = 100$ mg/L, $m_{ads}/V = 0.2$ g/50 mL, $t_{cont.} = 18$ h	Langmuir	$R^2 = 0.978$ $q_m = 23.6$ mg/g	Pseudo-second	$R^2 = 0.992$ $q_{e,cal} = 10.31$ mg/g	$q_{e,exp} = 10.28$ mg/g	[14]
Andisols zeolite composite	$S_M = 48.61$ m ² /g, $D_P = 95.9$ Å	pH = 4, $c_0 = 2$ mg/L, $m_{ads}/V = 0.1$ g/10 mL, $t_{cont.} = 60$ min	Freundlich	$R^2 = 0.963$ $K_f = 0.17$ mg/g	/	/	R% = 76.10 % $q_{e,exp} = 0.16$ mg/g	[16]
Microporous activated carbon from almond shell	$S_M = 1223$ m ² /g, $V_P = 0.326$ cm ³ /g, $D_{P50} = 2.39$ nm, pH _{pzc} = 5.5	pH = 2, T = 25 °C, $c_0 = 100$ mg/L, $m_{ads}/V = 2.5$ g/L, $t_{cont.} = 240$ min	Langmuir	$R^2 = 0.976$ $q_m = 195.34$ mg/g	Pseudo-second	$R^2 = 0.999$ $q_{e,cal} = 47.6$ mg/g	R% = 100 %, $q_{e,exp} = 45.12$ mg/g	[21]
FNAC (activated carbon from fox nutshell)	$S_M = 2869$ m ² /g, $V_P = 1.96$ cm ³ /g	pH = 2, T = 30 °C, $c_0 = 10$ mg/L, $m_{ads}/V = 0.05$ g/100 mL, $t_{cont.} = 3$ h	Langmuir	$R^2 = 0.971$, $q_m = 46.21$ mg/g	Pseudo-second	$R^2 = 0.999$, $q_{e,cal} = 43.99$ mg/g	R% = 99.08 %, $q_{e,exp} = 43.45$ mg/g	[22]

Table 1. (Continued).

Adsorbent	Adsorbent characterization	Adsorption conditions	Isotherm and kinetic models with calculated constants and adsorption capacities				Adsorption capacity	Ref
			Isotherm model	Calculated constants	Kinetic model	Calculated constants		
Modified activated carbon	$S_M = 1.4 \text{ m}^2/\text{g}$	pH = 3, $c_0 = 1 \text{ mg/L}$, $m_{ads} = 75 \text{ mg}$, $t_{cont.} = 4 \text{ h}$	Langmuir	$R^2 = 0.94$ $q_m = 18.519 \text{ mg/g}$	Pseudo-second	$R^2 = 0.994$ $q_{e,cal} = 1.805 \text{ mg/g}$	R% = 99 %	[23]
GSC (Graphene sand composite)	$S_M = 157 \text{ m}^2/\text{g}$	pH = 1.5, $c_0 = 20 \text{ mg/L}$	Langmuir	$R^2 = 0.99108$, $q_m = 2859.38 \text{ mg/g}$	Pseudo-second	$R^2 = 0.98003$	R% = 93 %	[24]
CMAC (Activated carbon from Cucumis melo peel)		pH = 3, $c_0 = 100 \text{ mg/L}$, $m_{ads} = 250 \text{ mg/L}$, $t_{cont.} = 180 \text{ min}$	Elovich	$R^2 = 0.978$	Pseudo-first	$R^2 = 0.996$	R% = 97.95 % $q_{e,exp} = 7.29 \text{ mg/g}$	[34]
La-RM (red mud modified by lanthanum)	$D_{50} = 25.6 \text{ nm}$	pH = 7, T = 25 °C, $c_0 = 40 \text{ mg/L}$, $m_{ads}/V = 4 \text{ g/L}$	Langmuir	$R^2 = 0.9956$, $q_m = 16.581 \text{ mg/g}$	Pseudo-second	/	$q_{e,exp} = 17.35 \text{ mg/g}$	[36]
ACLL (Activated carbon from leucaena leucocephala)	$S_M = 1131 \text{ m}^2/\text{g}$, $d_{50} = 250 \text{ }\mu\text{m}$, $\text{pH}_{pzc} = 5.42$	pH = 4, T = 30 °C, $c_0 = 100 \text{ mg/L}$, $m_{ads}/V = 300 \text{ mg/50 mL}$, $t_{cont.} = 60 \text{ min}$	Redlich-Peterson	$R^2 = 0.994$	Pseudo-second	$R^2 = 0.99$ $q_{e,cal} = 14.29 \text{ mg/g}$	R% < 80 % $q_{e,exp} = 13.85 \text{ mg/g}$	[43]
20 wt% β -FeOOH/SYBK (activated carbon supported β -FeOOH)	$S_M = 670.65 \text{ m}^2/\text{g}$, $D_{P50} = 2.66 \text{ nm}$, $V_P = 0.447 \text{ cm}^3/\text{g}$	pH = 2, $c_0 = 49.21 \text{ mg/L}$, $m_{ads}/V = 2 \text{ g/L}$, $t_{cont.} = 60 \text{ min}$	Langmuir	$R^2 = 0.9799$, $q_m = 37.036 \text{ g/kg}$	Pseudo-first	$R^2 = 0.975$	R% = 96% $q_{e,exp} = 37.04 \text{ g/kg}$	[44]
WPAC (wood based activated carbon)	$S_M > 1000 \text{ m}^2/\text{g}$	pH = 3, T = 25 °C, $c_0 = 80 \text{ mg/L}$, $m_{ads}/V = 20 \text{ mg/50 mL}$, $t_{cont.} = 24 \text{ h}$	/	/	/	/	R% = 40.04 % $q_{e,exp} = 70.95 \text{ mg/g}$	[45]

Table 1. (Continued).

Adsorbent	Adsorbent characterization	Adsorption conditions	Isotherm and kinetic models with calculated constants and adsorption capacities				Adsorption capacity	Ref
			Isotherm model	Calculated constants	Kinetic model	Calculated constants		
BCP (biochar Onopordom Heteracthion)	$S_M = 5.73 \text{ m}^2/\text{g}$ $D_P = 1-50 \text{ nm}$, $\text{pH}_{pzc} = 2$	$\text{pH} = 2$, $T = 15 \pm 1 \text{ }^\circ\text{C}$, $c_0 = 40 \text{ mg/L}$, $m_{ads}/V = 0.1 \text{ g}/100 \text{ mL}$	Langmuir	$R^2 = 0.9795$, $q_m = 37.28 \text{ mg/g}$	Pseudo-second	$R^2 = 0.994$ $q_{e,cal} = 31.08 \text{ mg/g}$	$R\% = 69 \%$	[46]
Chitosan-magnetite nanocomposite strip	$D_{50} = 15-30 \text{ nm}$	$\text{pH} = 2-3$, $t_{cont.} = 130 \text{ min}$	/	/	/	/	$R\% = 92.33 \%$	[47]
Algae biomass from C-glomerata		$\text{pH} = 2$, $T = 45 \text{ }^\circ\text{C}$, $c_0 = 20 \text{ mg/L}$, $m_{ads}/V = 1 \text{ g}/100 \text{ mL}$, $t_c = 60 \text{ min}$	Freundlich	$R^2 = 0.949$, $K_f = 0.19 \text{ mg/g}$	/	/	$R\% = 66.6 \%$	[48]
Kaolin	$S_M = 14.93 \pm 0.32 \text{ m}^2/\text{g}$, $V_P = 0.167 \pm 0.27 \text{ cm}^3/\text{g}$, $D_P = 12.59 \pm 0.49 \text{ nm}$	$\text{pH} = 4.5$, $T = 25 \pm 1 \text{ }^\circ\text{C}$, $c_0 = 200 \text{ mg/L}$, $m_{ads}/V = 0.5 \text{ g}/20 \text{ mL}$, $t_{cont.} = 120 \text{ min}$	Langmuir	$R^2 = 0.985$ $q_m = 0.878 \text{ mg/g}$	Pseudo-first	$R^2 = 0.993$ $q_{e,cal} = 0.865 \text{ mg/g}$	$q_{e,exp} = 0.853 \text{ mg/g}$	[49]
MCARM (mechanical-chemical activated red mud)	$S_M = 176 \text{ m}^2/\text{g}$ $D_{50} = 3.83 \text{ }\mu\text{m}$	$\text{pH} = 2$, $c_0 = 400 \text{ mg/L}$, $m_{ads} = 4.8 \text{ g}$	Langmuir	$R^2 = 0.9903$ $q_m = 6.7 \text{ mg/g}$	Pseudo-second	$R^2 = 0.999$	$R\% = 95 \%$ $q_{e,exp} = 5.45 \text{ mg/g}$	[50]
ARM (heat-acid active red mud)	$\text{pH}_{pzc} = 8.5$	$\text{pH} = 2$, $T = 30 \text{ }^\circ\text{C}$, $c_0 = 0.08 \text{ mg/L}$, $m_{ads}/V = 0.5 \text{ g}/100 \text{ mL}$, $t_c = 120 \text{ min}$	Langmuir	$q_m = 0.03 \text{ mg/g}$	/	/	$R\% = 97.31 \%$ $q_{e,exp} = 0.015 \text{ mg/g}$	[51]
PPH (powdered Peganum harmalo)	$S_M = 7.8 \text{ m}^2/\text{g}$ $\text{pH}_{pzc} = 6.4$	$\text{pH} = 1.5$, $c_0 = 100 \text{ mg/L}$, $m_{ads}/V = 10 \text{ g/L}$, $t_{cont.} = 80 \text{ min}$	Freundlich	$R^2 = 0.986$	Pseudo-second	$R^2 = 0.99$ $q_{e,cal} = 10.13 \text{ mg/g}$	$q_{e,exp} = 9.99 \text{ mg/g}$	[52]

Table 1. (Continued).

Adsorbent	Adsorbent characterization	Adsorption conditions	Isotherm and kinetic models with calculated constants and adsorption capacities				Adsorption capacity	Ref
			Isotherm model	Calculated constants	Kinetic model	Calculated constants		
Fungal biomass		pH = 2, T = 27 °C, $c_0 = 62.5$ mg/L, $m_{ads}/V = 2$ g/L, $t_{cont.} = 37.5$ min	Langmuir	$R^2 = 0.999$ $q_m = 71.9$ mg/g	Pseudo-second	$R > 0.99$	R% = 63.82 %	[53]
Biomass from Ceratocystis paradoxa MSR2	D = 80 μ m	pH = 2, $c_0 = 62.5$ mg/L, $m_{ads}/V = 2$ g/L, $t_{cont.} = 60$ min	Langmuir	$R^2 = 0.991$ $q_m = 72.46$ mg/g	Pseudo-second	$R^2 > 99$ %	R% = 68.72 %	[54]

D_{50} – average particle size, pH_{pzc} – point of zero charge, S_M – specific surface area in a unit of mass, V_P – pore volume, D_P – pore size, D – particle size, L – length, D_{P50} – average pore size, c_0 – initial concentration, m_{ads}/V – adsorbent dose per sample volume, $t_{cont.}$ – the time of contact of solution and adsorbent, m_{ads} – adsorbent dose, q_m – maximum adsorbent capacity (Langmuir), K_f – adsorption capacity (Freundlich), $q_{e,cal}$ – calculated adsorption capacity, $q_{e,exp}$ – experimentally determined adsorption capacity, R% – adsorption percent.

Similar adsorption capacities of 236.9 mg/g [15] and 232.51 mg/g [2] were determined with the use of ethylenediamine-functionalized magnetic polymer microspheres (EDA-MPMs) [15] and amino-functionalized magnetic nanoadsorbent ($\text{Fe}_3\text{O}_4\text{-NH}_2$) [2], respectively. By increasing the temperature to 318 K, the EDA-MPMs achieved a maximum adsorption capacity of 253.2 mg/g. Synthesis of EDA-MPM's adsorbent starts in the presence of Fe_3O_4 nanoparticles. After polymerization, the particles are modified with ethylenediamine [15]. Through synthesis of $\text{Fe}_3\text{O}_4\text{-NH}_2$, amino groups were fixed to the surface of Fe_3O_4 nuclei and a core-shell structure was created. The core-shell structure is considered to have unique properties such as stability and chemical capability, which are important properties of the adsorbent [2]. Both adsorption procedures were conducted in an acidic environment and both adsorbents had similar chemistry behind their successful adsorption capacity. Because of the acidic conditions in which both experiments were conducted, the amino groups were protonated to NH^{3+} , resulting in an even stronger electrostatic attraction between NH^{3+} and Cr (VI) [2,15]. In the natural organic and inorganic adsorbent section, Cr (VI) removal of 100% [21], 99.08% [22], and 99% [23] was achieved with the use of microporous activated carbon from almond shell [21], activated carbon from fox shell (FNAC) [22], and with modified activated carbon [23]. Among the 3 adsorbents, microporous activated carbon had the highest maximum capacity of 195.34 mg/g [21].

Astonishing results were achieved with the graphene-sand composite (GSC) [24], where the maximum adsorption capacity calculated with the Langmuir model was 2859.38 mg/g. In the study, the high adsorption capacity was attributed to the graphene sheets on the sand surface used for preparation of the composite [24].

For the adsorbents mentioned above with the highest adsorption capacities, we found that the researchers proposed a similar binding mechanism for chromium adsorption. Adsorption is more successful at low pH values, from pH 1 to 4. In this case, there are many H^+ ions in the solution that protonate the surface of the adsorbent. At low pH levels, the chromium in the solution is in the form of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ and the attraction between the ionic species and the surface of the adsorbent is large; thus, the adsorption is high. As the pH increases, the adsorption capacity drops as the charge on the surface of the adsorbent changes, and chromium species, which are more difficult to bind, form in the solution.

2.2. Cadmium

It is estimated that only 0.1 ppm of cadmium is present in Earth's crust. It is usually found near sphalerite as a mineral, greenockite. Cadmium or its compounds are mainly used in battery manufacturing, electroplating, pigments, metal finishing, fertilizers, tanneries, and plastic manufacturing [11,25].

Cadmium, which occurs in industrial effluents, usually accumulates in soil. Soil contamination is also accelerated by the use of artificial phosphate fertilizers. Due to soil contamination, the most common cadmium exposure is through food intake. Inhalation of fine cadmium powder or vapor and ingestion of its soluble compounds is hazardous. Cadmium is toxic and carcinogenic even at low concentrations [11,25].

Cadmium exists in several different states, at pH levels below 7 as Cd^{2+} , between pH 7 and 11 as $\text{Cd}(\text{OH})^+$, and above pH 11 as $\text{Cd}(\text{OH})_2$. Low pH values cause low adsorption of cadmium. If a higher adsorbent dose is added, the adsorption is enhanced because of the higher number of active sites. When the maximum dose of adsorbent is reached, the capacity starts to decrease again. Furthermore, it was observed that temperature also has an impact on adsorption; at higher temperatures, the adsorption of cadmium is reduced. Because copper has similar chemistry to cadmium, the adsorption capacity of cadmium decreased in the presence of copper [11].

Adsorption capacities of different adsorbents for cadmium removal are shown in Table 2.

Table 2. Cadmium (II) adsorption capacities/parameters.

Adsorbent	Adsorbent characterization	Adsorption conditions	Isotherm and kinetic models with calculated constants and adsorption capacities			Adsorption capacity	Ref
			Isotherm model	Calculated constants	Kinetic model		
Synthetic adsorbents							
CuO NP (copper oxide nanoparticles)	$S_M = 220 \text{ m}^2/\text{g}$, $D_{50} = 33\text{-}160 \text{ nm}$	pH = 6, T = 25 ± 0.5 °C, $c_0 = 250 \text{ mg/L}$, $m_{ads}/V = 0.4 \text{ g/L}$	Langmuir	$R^2 = 0.9945$ $q_m = 84.75 \text{ mg/g}$	Pseudo-second	$R^2 = 0.989$ $q_{e,cal} = 131.33 \text{ mg/g}$	[3]
Manganese oxide	$S_M = 84.9 \text{ m}^2/\text{g}$, $D_{P50} = 11.32 \text{ nm}$	pH = 6, T = 298 K, $c_0 = 100 \text{ mg/L}$, $m_{ads}/V = 1 \text{ g/L}$	Langmuir	$R^2 = 0.8889$ $q_m = 104.17 \text{ mg/g}$	Pseudo-second	$R^2 = 0.9991$ $q_{e,cal} = 104.2 \text{ mg/g}$	[26]
FMWCNT (functionalized multiwall carbon nanotube)	$S_M = 206.45 \text{ m}^2/\text{g}$, $V_P = 0.49 \text{ cm}^3/\text{g}$, $D_P = 96.27 \text{ Å}$	pH = 5, $c_0 = 10 \text{ mg/L}$, $m_{ads}/V = 1.0 \text{ g/100 mL}$, $t_{cont.} = 90 \text{ min}$	Langmuir Freundlich	$R^2 = 0.999$ $q_m = 83.33 \text{ mg/g}$ $R^2 = 0.999$	Pseudo-second	/	[27]
DWCNT/iron oxide composite	$S_M = 127 \text{ m}^2/\text{g}$, $D_{50} = 10\text{-}30 \text{ nm}$, $\text{pH}_{pzc} = 6$	pH = 7, $c_0 = 20 \text{ mg/L}$, $m_{ads}/V = 50 \text{ mg/50 mL}$, $t_{cont.} = 50 \text{ min}$	/	/	/	/	[55]
A2/MWCNT (multiwall carbon nano tubes with polyamidoamine dendrimers)	$S_M = 99.66 \text{ m}^2/\text{g}$, $D_{P50} = 21 \text{ nm}$, $V_P = 0.584 \text{ cm}^3/\text{g}$, $\text{pH}_{pzc} = 5.92$	pH = 6, $c_0 = 0.5 \text{ mg/L}$, $m_{ads}/V = 100 \text{ mg/L}$	Langmuir	$R^2 = 0.991$ $q_m = 44.18 \text{ mg/g}$	Pseudo-second	$R^2 = 0.993$ $q_{e,cal} = 2.338 \text{ mg/g}$	[56]
Carboxyl modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles		pH = 6, $c_0 = 50 \text{ mg/L}$, $m_{ads}/V = 40 \text{ mg/20 mL}$, $t_{cont.} = 30 \text{ min}$	Langmuir	$R^2 = 0.999$ $q_m = 81.627 \text{ mg/g}$	/	/	[57]
M-CNT (modified carbon nano tubes)	d = 10–20 nm, L = 1–10 nm	pH = 7, $c_0 = 1 \text{ mg/L}$, $m_{ads} = 50 \text{ mg}$, $t_{cont.} = 2 \text{ h}$	Langmuir	$R^2 = 0.993$ $q_m = 4.35 \text{ mg/g}$	Pseudo-second	$R^2 = 0.999$	[58]
Natural organic/inorganic adsorbents							

Table 2. (Continued).

Adsorbent	Adsorbent characterization	Adsorption conditions	Isotherm and kinetic models with calculated constants and adsorption capacities				Adsorption capacity	Ref
			Isotherm model	Calculated constants	Kinetic model	Calculated constants		
KPP (Kaniar pod powder from Bauhinia purpurea)	$S_M = 1.8 \text{ m}^2/\text{g}$, $D_{P50} = 22.6 \text{ nm}$, $V_P = 0.01 \text{ cm}^3/\text{g}$, $\text{pH}_{pzc} = 4$	pH = 5, T = 25 °C, $c_0 = 10 \text{ mg/L}$, $m_{ads}/V = 1 \text{ g/L}$	Langmuir	$q_m = 11 \text{ mg/g}$	Pseudo-second	$R^2 = 0.99$ $q_{e,cal} = 10.31 \text{ mg/g}$	R% = 96 %, $q_{e,exp} = 10.7 \text{ mg/g}$	[11]
MKPP (Magnetic Kaniar pod powder from Bauhinia purpurea)	$S_M = 52 \text{ m}^2/\text{g}$, $D_{P50} = 15.3 \text{ nm}$, $V_P = 0.2 \text{ cm}^3/\text{g}$, $\text{pH}_{pzc} = 5$	pH = 5, T = 25 °C, $c_0 = 10 \text{ mg/L}$, $m_{ads}/V = 2 \text{ g/L}$	Langmuir	$q_m = 4.8 \text{ mg/g}$	Pseudo-second	$R^2 = 0.98$ $q_{e,cal} = 3.8 \text{ mg/g}$	R% = 79 %, $q_{e,exp} = 4.47 \text{ mg/g}$	[11]
CH-FeO nanopositive (chitosan-iron oxide nanocomposite)	$D_{50} = 50 \text{ nm}$	pH = 3, T = 298 K, $c_0 = 10 \text{ mg/dm}^3$, $m_{ads}/V = 0.05 \text{ g/20 dm}^3$, $t_{cont.} = 30 \text{ min}$	Langmuir	$R^2 = 0.99$	Pseudo-second	$R^2 = 0.99$	$q_{e,exp} = 201.84 \text{ mg/g}$	[28]
NTAA-LCM (nitrotriactic acid anhydride modified ligno-cellulosic material)	$S_M = 1.8006 \text{ m}^2/\text{g}$, $D_P = 8.9278 \text{ nm}$	pH = 4, T = 298 K, $c_0 = 200 \text{ mg/L}$, $m_{ads} = 50 \text{ mg/50 mL}$	Langmuir	$R^2 = 0.998$, $q_m = 143.4 \text{ mg/g}$	Pseudo-second	$R^2 = 1$ $q_{e,cal} = 98.80 \text{ mg/g}$	$q_{e,exp} = 98.81 \text{ mg/g}$	[31]
CMAC (Activated carbon from Cucumis melo peel)		pH = 6, $c_0 = 100 \text{ mg/L}$, $m_{ads} = 250 \text{ mg/L}$, $t_{cont.} = 180 \text{ min}$	Elovich	$R^2 = 0.973$	Pseudo-first	$R^2 = 0.993$	R% = 97.96 %, $q_{e,exp} = 7.23 \text{ mg/g}$	[34]
FGCX (aminobenzoic grafted cross-linked chitosan)		pH = 6, T = 45 °C, $c_0 = 0.5 \text{ mmol/L}$, $m_{ads}/V = 6 \text{ g/L}$, $t_{cont.} = 60 \text{ min}$	Langmuir	$R^2 = 0.99$ $q_m = 1.82 \text{ mg/g}$	Pseudo-second	$R^2 = 0.99$ $q_{e,cal} = 3.52 \text{ mg/g}$	R% = 97.8 %	[35]
Dry biomass from Spirulina plantensis		pH = 8, T = 26 °C, $c_0 = 60 \text{ mg/L}$, $m_{ads}/V = 2 \text{ g/100 mL}$, $t_{cont.} = 90 \text{ min}$	Langmuir	$R^2 = 0.916$			R% = 96.77 %	[59]

Table 2. (Continued).

Adsorbent	Adsorbent characterization	Adsorption conditions	Isotherm and kinetic models with calculated constants and adsorption capacities				Adsorption capacity	Ref
			Isotherm model	Calculated constants	Kinetic model	Calculated constants		
ZFA (zeolite fly ash)	$S_M = 8.22 \text{ m}^2/\text{g}$, $D_{P50} = 29 \text{ \AA}$	pH = 5, $c_0 = 50 \text{ mg/L}$, $m_{ads} = 0,08 \text{ g/25 mL}$, $t_{cont.} = 7 \text{ h}$	Langmuir	$R^2 = 0.9919$ $q_m = 26.246 \text{ mg/g}$	Pseudo-second	$R^2 = 0.9964$ $q_{e,cal} = 16.583 \text{ mg/g}$	R% = 96 % $q_{e,exp} = 14.431 \text{ mg/g}$	[60]
Mag-ligand	$d = 30 \text{ nm}$	pH = 7, $c_0 = 10 \text{ mg/L}$, $m_{ads} = 2 \text{ g/L}$	Langmuir	$R^2 = 0.951$ $q_m = 79.365 \text{ mg/g}$	Pseudo-second	$R^2 = 1$ $q_{e,cal} = 52.549 \text{ mg/g}$	R% = 97 %	[61]
Iron oxide nanoparticles with tanerine peel extract	$D_{50} = 50 \text{ nm}$	pH = 4, $m_{ads}/V = 0.4 \text{ g/100 mL}$, $t_{cont.} = 90 \text{ min}$	Freundlich	$R^2 = 0.999$, $K_f = 1.789 \text{ mg/g}$	Pseudo-second	$R^2 = 0.999$ $q_{e,cal} = 10.9 \text{ mg/g}$	R% = 90 %	[62]
SHC (sunflower head carbon)	$S_M = 2.5577 \text{ m}^2/\text{g}$, $D = 300 \text{ \mu m}$, $pH_{pzc} = 3.8$	pH = 6, $T = 25 \pm 1 \text{ }^\circ\text{C}$, $c_0 = 100 \text{ mg/L}$, $m_{ads}/V = 20 \text{ g/L}$, $t_{cont.} = 120 \text{ min}$	Freundlich	$K_f = 1.22 \text{ mg/g}$	Pseudo-second	$R^2 = 0.9978$	R% = 84.7 % $q_{e,exp} = 4.3 \text{ mg/g}$	[63]
SSC (sunflower stem carbon)	$S_M = 2.6622 \text{ m}^2/\text{g}$, $D = 300 \text{ \mu m}$, $pH_{pzc} = 4.2$	pH = 6, $T = 25 \pm 1 \text{ }^\circ\text{C}$, $c_0 = 100 \text{ mg/L}$, $m_{ads}/V = 20 \text{ g/L}$, $t_{cont.} = 120 \text{ min}$	Freundlich	$K_f = 1.48 \text{ mg/g}$	Pseudo-second	$R^2 = 0.9981$	R% = 87.1 % $q_{e,exp} = 4.4 \text{ mg/g}$	[63]
GAC (granulated activated carbon)	$S_M = 750 \text{ m}^2/\text{g}$ $D = 0.3\text{--}2.4 \text{ nm}$, $pH_{pzc} = 5.3$	pH = 6.5, $T = 24 \pm 1 \text{ }^\circ\text{C}$, $c_0 = 0.11 \text{ mg/L}$, $t_{cont.} = 24 \text{ h}$	Langmuir	$R^2 = 0.95$ $q_m = 2 \text{ mg/g}$	/	/	$q_{e,exp} = 0.9 \text{ mg/g}$	[64]
CP (Peat moss-derived biochar)		pH = 5, $T = 20 \pm 1 \text{ }^\circ\text{C}$, $c_0 = 100 \text{ mg/L}$, $m_{ads}/V = 0.2/200 \text{ mL}$	Langmuir	$R^2 = 0.977$ $q_m = 39.8 \text{ mg/g}$	Second order	$R^2 = 0.999$ $q_{e,cal} = 29.5 \text{ mg/g}$	$q_{e,exp} = 29.4 \text{ mg/g}$	[65]
BC-MnO _x (biochar from rape straw impregnated with KMnO ₄)	$S_M = 110.68 \text{ m}^2/\text{g}$, $V_P = 0.087 \text{ cm}^3/\text{g}$	pH = 5, $c_0 = 20 \text{ mg/L}$, $m_{ads}/V = 1.25 \text{ g/L}$	Langmuir	$R^2 = 0.994$ $q_m = 81.1 \text{ mg/g}$	Pseudo-second	$R^2 = 0.998$ $q_{e,cal} = 7.288 \text{ mg/g}$	R% = 95%	[66]

The best cadmium removal was achieved with the use of manganese oxide, with 98% cadmium removal [26]. Experimental data showed that the adsorption capacity of manganese oxide was 82.7 mg/g, and the maximum adsorption capacity calculated with the Langmuir model was 104.17 mg/g [26]. Functionalized multiwall carbon nanotubes (FMWCNT) [26] and copper oxide nanoparticles (CuO NP) [3] exhibited similar adsorption capacities, which were 83.33 mg/g [27] and 84.75 mg/g [3], respectively. Both adsorbents had similar surface areas of 206.45 m²/g for FMWCNT [27] and 220 m²/g for CuO NP [3].

With natural organic and inorganic adsorbents, the best experimental results were reached with chitosan-iron oxide nanocomposite (CH-FeO nanocomposite), where the adsorption capacity of 201.84 mg/g was achieved experimentally [28]. This adsorbent was also effective in real wastewater samples, where 99.91% of cadmium was removed [28]. Chitosan consists of amino and hydroxyl groups that can bind heavy metals and form chelates. Chitosan itself is soluble under acidic conditions; with chitosan modification, a wider pH range can be obtained [29]. Furthermore, with modification procedures, adsorption properties and selectivity can be enhanced. The maximum adsorption capacity achieved with modified chitosan was 405 mg/g [30]. This value was attained with chitosan grafted with itaconic acid and crosslinked with glutaraldehyde (CS-g-IA(G)). The results are not presented in this study, as Kyzas and Bikiaris have already conducted a detailed analysis in their review [30].

A maximum adsorption capacity of 143.4 mg/g was calculated for nitrilotriacetic acid anhydride-modified lignocellulosic material (NTAA-LCM) [31]. Experimental data showed that cadmium ions reacted with the carboxyl groups of adsorbents. It was established that sodium was exchanged with cadmium after adsorption took place. The adsorption process of cadmium onto NTAA-LCM occurred through surface chelation and ion exchange [31].

In general, it can be concluded that cadmium binding is not very successful at low pH values. The reason is that there are many H⁺ ions present in the aqueous solution which compete with Cd²⁺ for binding to the surface of the adsorbent. The adsorption of cadmium increases with increasing pH (pH from 4 to 8.5) as the surface of the adsorbent deprotonates and begins to attract cadmium ions. In accelerated adsorption, a mechanism of cation exchange has been shown to occur in several cases.

2.3. Nickel

It is estimated that around 10% of the earth's core is made of nickel. Much nickel is dissolved in water and accumulates in coal and oil. It occurs in millerite with sulphur, and in niccolite with arsenic. It can also be found in ores such as pentlandite. Nickel is a good conductor of heat and electricity. It is mainly used for alloys, as an additive for increasing the hardness of stainless steel, in the production of batteries, porcelain enameling, electroplating, dyeing, and pigments. A large amount of nickel is used in galvanization procedures because of its stability when in contact with atmospheric air [32].

Nickel only occurs in nature in low concentration levels. Nickel began to accumulate in the soil due to industry. Nickel present in soil can adsorb in sediments and become immobilized. In acidic soil nickel becomes mobile, which can result in it dissolving into groundwater. If groundwater is contaminated, exposure can happen with drinking. In addition, plants are subjected to nickel accumulation, exposing animals and humans to nickel through ingestion. It is an essential element in small quantities, but in high quantities, it can cause numerous negative consequences, such as lung, nose, or larynx cancer, lung embolism, asthma, chronic bronchitis, heart disorders, etc. [32,33].

Table 3 summarizes the studies on nickel adsorption. A review of synthetic adsorbents showed that the best nickel adsorption and maximum adsorbent capacity were achieved with amino-functionalized magnetic

nanoadsorbent ($\text{Fe}_3\text{O}_4\text{-NH}_2$) [2]. The percentage of nickel removed was above 96%, and the maximum capacity was 222.12 mg/g. In the study conducted with this adsorbent, removal of Cr (VI) was examined; high capacities were reached for Cr (VI) removal as well. In both cases, amino groups played a decisive role. The study of kinetic parameters confirmed the theory which suggested that adsorption might be achieved through chemical processes such as sharing or exchange of electrons. The difference between the two ions was in the optimal adsorption pH value. Nickel adsorption was more efficient at higher pH values than Cr (VI) adsorption. By increasing the pH value from 2 to 9, nickel removal increased from 46.21% to 93.03%, although it was also observed that nickel started to precipitate at a pH around 8.5. The study compared the results with other adsorbents such as $\text{Fe}_3\text{O}_4\text{-CNTs}$, Fe_3O_4 , and $\text{Fe}_3\text{O}_4\text{-GS}$ with maximum adsorption capacities of 65.96 mg/g, 38.3 mg/g, and 158.5 mg/g, respectively. According to the comparative results, nanomagnetite functionalized with amino groups achieved the highest maximum adsorption [2].

Furthermore, natural organic and inorganic adsorbents also showed good experimental results. Removal rates of 98.78% [34] and 98.6% [35] were attained with activated carbon from *Cucumis melo* peel (CMAC) [34] and aminobenzoic grafted crosslinked chitosan (FGCX) [35], respectively.

Activated carbon (AC) is a widely used adsorbent. Its main feature is a porous structure which enables a large surface area. The surface area of AC can range from 300 to 4000 m^2/g . Additional surface functional groups can greatly improve adsorption [6]. According to the analysis of the data that was obtained for CMAC, it could be concluded that the adsorption process can be attributed to a chemical reaction with functional groups on the surface [34].

Chitosan itself is a suitable adsorbent because it contains amine and hydroxyl groups [35]. Its disadvantage is that it is soluble at low pH values. Crosslinking helps overcome this disadvantage [29]; however, some studies have noted that crosslinking can reduce the overall adsorption capacity of an adsorbent. Furthermore, grafting allows the formation of functional derivatives with more established adsorption sites, which compensates for possible diminishment in capacity on account of crosslinking. The study of Igberase indicates that the binding of metal ions can occur through chemisorption, electrostatic attraction, or ion exchange [35].

A maximum adsorption capacity of 94.86 mg/g was achieved with lignocellulose/montmorillonite nanocomposite (LNC/MMT) [12]. By analyzing the adsorption procedure, it was shown that the main mechanism of adsorption was chemical adsorption. Additional adsorbent studies showed that hydroxyl and carboxyl groups were involved in adsorption process. Furthermore, in the results of a desorption study, LNC/MMT showed stability after desorption, indicating that the adsorbent is stable and has possible applications in industry [12].

The most successful results for nickel adsorption come from binding to amino groups at pH values between 6 and 8. At lower pH levels, many H^+ ions that are present in solution are protonating $-\text{NH}_2$ to NH_3^+ . This causes a repulsive force between the positive surface and the nickel ions. When pH is increased, deprotonation of amino groups occurs, thus allowing nickel binding, which is reflected in higher adsorption.

Table 3. Nickel (II) adsorption capacities/parameters.

Adsorbent	Adsorbent characterization	Adsorption conditions	Isotherm and kinetic models with calculated constants and adsorption capacities			Adsorption capacity	Ref	
			Isotherm model	Calculated constants	Kinetic model			Calculated constants
Synthetic adsorbents								
Fe ₃ O ₄ -NH ₂ (amino functionalized magnetic nanoadsorbent)	D ₅₀ = 25 nm, pH _{pzc} = 5.8	pH = 6, T = 298 K, c ₀ = 5 mg/L, m _{ads} /V = 0.05 g/50 mL	Langmuir	q _m = 222.12 mg/g	Pseudo-second	R ² = 0.994 q _{e,cal} = 25.97 mg/g	R% > 96 % q _{e,exp} = 25.12 mg/g	[2]
Carboxyl modified Fe ₃ O ₄ @SiO ₂ nanoparticles		pH = 6, c ₀ = 50 mg/L, m _{ads} /V = 50 mg/20 mL, t _{cont.} = 30 min	Langmuir	R ² = 0.989 q _m = 63.995 mg/g			R% = 65 %	[57]
Activated carbon coated Al ₂ O ₃ nanoparticles	D ₅₀ = 50 nm	c ₀ = 300 mg/L, m _{ads} /V = 20 mg/50 mL, t _{cont.} = 180 min	/	/	/	/	R% = 82 %	[70]
GO (Graphene oxide)	W = 0.77–2.94 nm	pH = 7, c ₀ = 25 mg/L, m _{ads} /V = 20 mg/200 mL, t _{cont.} = 320 min	Langmuir	R ² = 0.9993 q _m = 35.6 mg/g	Pseudo-second	q _{e,cal} = 32.4 mg/g	q _{e,exp} = 31.7 mg/g	[71]
Fe@G (magnetic Fe@graphite nanocomposite)	S _M = 47 m ² /g, V _P = 17.7 cm ³ /g, r _p = 0.016 nm, pH _{pzc} = 7.7	pH = 8.2, T = 20 °C, c ₀ = 20 mg/L	Langmuir	R ² = 0.998 q _m = 9.2 mg/g	Pseudo-second	R ² = 0.999 q _{e,cal} = 8.95 mg/g	q _{e,exp} = 9.33 mg/g	[72]
Natural organic/inorganic adsorbents								
Fe ₃ O ₄ /talc nanocomposite	S _M = 37.079 m ² /g	pH = 7, c ₀ = 92 mg/L, m _{ads} = 0.12 g, t _{cont.} = 120 s	Langmuir	R ² = 0.9772 q _m = 33.33 mg/g	Pseudo-second	R ² = 0.9812	R% = 50.23 %	[9]
LNC/MMT (Lignocellulose/montmorillonite nanocomposite)		pH = 6.8, T = 70 °C, c ₀ = 0.0032 mol/L, m _{ads} /V = 0.1 g/50 mL, t _{cont.} = 40 min	Langmuir	R ² = 0.9989 q _m = 94.86 mg/g	Pseudo-second	R ² = 0.998 q _{e,cal} = 87.72 mg/g	q _{e,exp} = 94.86 mg/g	[12]

Table 3. (Continued).

Adsorbent	Adsorbent characterization	Adsorption conditions	Isotherm and kinetic models with calculated constants and adsorption capacities			Adsorption capacity	Ref
			Isotherm model	Calculated constants	Kinetic model		
CH-FeO nanocomposite (chitosan-iron oxide nanocomposite)	D ₅₀ = 50 nm	pH = 3, T = 298 K, c ₀ = 10 mg/dm ³ , m _{ads} /V = 0.05 g/20 dm ³ , t _{cont.} = 1800 s	Langmuir	R ² = 0.99 q _m = 3.29 mg/g	Pseudo-second	R ² = 0.99 q _{e,cal} = 3.772 mg/g	[28]
CMAC (Activated carbon from Cucumis melo peel)		pH = 6, c ₀ = 100 mg/L, m _{ads} /V = 250 mg/L, t _{cont.} = 180 min	Elovich	R ² = 0.976	Pseudo-first	R = 0.973	[34]
FGCX (aminobenzic cross-linked chitosan)		pH = 7, T = 45 °C, c ₀ = 0.5 mmol/L, m _{ads} /V = 6 g/L, t _{cont.} = 60 min	Langmuir	R ² = 0.99 q _m = 2.8 mmol/g	Pseudo-second	R ² = 1.0 q _{e,cal} = 3.12 mmol/g	[35]
GAC (granulated activated carbon)	S _M = 750 m ² /g D = 0.3-2.4 nm, pH _{pzc} = 5.3	pH = 6.5, T = 24 ± 1 °C, c ₀ = 0.12 mg/L, t _{cont.} = 24 h	Langmuir	R ² = 0.98 q _m = 1.8 mg/g	/	/	[64]
Longan hull	S _M = 1.6 m ² /g	pH = 5, c ₀ = 50 mg/L, m _{ads} /V = 1 g/30 mL	Langmuir	R ² = 0.9696 q _m = 3.96 mg/g	Pseudo-second	/	[68]
PFP (palm fibers powder)		pH = 5, c ₀ = 100 mg/L, m _{ads} /V = 1 g/100 mL, t _{contact} = 45 min	Freundlich	R ² = 0.937 K _f = 5.058 mg/g	Pseudo-second	R ² = 0.996 q _{e,cal} = 3.736 mg/g	[69]
Chitosan		pH = 5, T = 25 ± 1 °C, c ₀ = 100 mg/L, m _{ads} /V = 5 g/100 mL	Langmuir	R ² = 0.997 q _m = 52.6 mg/g	Pseudo-second	R ² = 0.997 q _{e,cal} = 10.63 mg/g	[73]
AC (activated carbon from sewage sludge)	S _M = 132.7 m ² /g, V _P = 0.23 cm ³ /g	pH = 8, T = 55 °C, c ₀ = 50 mg/L, m _{ads} /V = 4 g/L	Langmuir	R ² = 0.9655 q _m = 11.52 mg/g	Pseudo-second	R ² = 0.999 q _{e,cal} = 9.8078 mg/g	[74]

Table 3. (Continued).

Adsorbent	Adsorbent characterization	Adsorption conditions	Isotherm and kinetic models with calculated constants and adsorption capacities				Adsorption capacity	Ref
			Isotherm model	Calculated constants	Kinetic model	Calculated constants		
ONF/KOH (old newspaper fibers treated with KOH)	$D_{50} = 53.87 \mu\text{m}$	pH = 6, $T = 25^\circ\text{C}$, $c_0 = 100 \text{ mg/L}$, $m_{ads}/V = 4 \text{ g/L}$	Langmuir	$R^2 = 0.9825$ $q_m = 20.2 \text{ mg/g}$	Pseudo-second	$R^2 = 0.9998$ $q_{e,cal} = 18.31 \text{ mg/g}$	R% = 88 %	[75]
GAC (activated carbon from Gyri-cidia)	$D = 45\text{--}180 \mu\text{m}$	pH = 7, $c_0 = 50 \text{ mg/L}$, $m_{ads}/V = 0.4 \text{ g/100 mL}$	Langmuir	$R^2 = 0.879$ $q_m = 24.39 \text{ mg/g}$	/	/	R% = 97.3 % $q_{e,exp} = 12.1 \text{ mg/g}$	[76]
Sawdust)		pH = 6, $c_0 = 100 \text{ mg/L}$, $m_{ads}/V = 1.75 \text{ g/100 mL}$	Langmuir	$R^2 = 0.982$ $q_m = 12.5 \text{ mg/g}$	Pseudo-second	$R^2 = 0.942$ $q_{e,cal} = 5.62 \text{ mg/g}$	R% = 94.6 % $q_{e,exp} = 5.41 \text{ mg/g}$	[77]
Chitosan/kenaf fiber bio-composite		pH = 5, $c_0 = 200 \text{ mg/L}$, $m_{ads}/V = 1 \text{ g/100 mL}$	Langmuir	$R^2 = 0.8916$ $q_m = 70.55 \text{ mg/g}$	Pseudo-second	$R^2 = 0.999$ $q_{e,cal} = 10.67 \text{ mg/g}$	R% = 89 %	[78]

D_{50} – average particle size, pH_{pzc} – point of zero charge, W – thickness, S_M – specific surface area in a unit of mass, V_P – pore volume, D – particle size, r_p – radius, c_0

– initial concentration, m_{ads}/V – adsorbent dose per sample volume, $t_{cont.}$ – the time of contact of solution and adsorbent, q_m – maximum adsorbent capacity (Langmuir),

K_f – adsorption capacity (Freundlich), $q_{e,cal}$ – calculated adsorption capacity, $q_{e,exp}$ – experimentally determined adsorption capacity, R% – adsorption percent.

3. Discussion

Generally good results for chromium removal were obtained in an acidic environment that extended from pH value 1 to pH value 4. Low pH values can protonate the adsorbent surface. A positively charged surface is optimal for the removal of Cr species present in solution at this pH. The binding expires with electrostatic attraction. Experiments were conducted at pH value 7 in only one study out of all of the studies that we reviewed regarding chromium removal. The adsorbent used at these higher pH values was red mud modified by lanthanum (La-RM) [36]; the experimentally achieved adsorption capacity was 17.35 mg/g. The optimal pH value for Cr (VI) adsorption was adsorbent-dependent. Furthermore, a review of various studies has shown that specific surface area is not a determining factor for the adsorption process. It has also been shown that amino and hydroxyl groups can be strongly involved in the adsorption process and are usually responsible for enhancing chromium adsorption. Furthermore, the results of natural organic and inorganic adsorbents showed the great potential of adsorbents functionalized with amino and hydroxyl groups, and of graphene sand composite.

Cadmium adsorption was achieved with acidic and neutral solutions. The pH values of the various experiments ranged from 3 to 8, although the best results were obtained at slightly higher pH values, e.g., 6. The reason for the better adsorption at higher pHs lies in the deprotonation of the surface of the adsorbent, which in turn allows electrostatic attraction of cadmium. In addition, cadmium removal studies have shown that there is no correlation between specific surface area and adsorption. More accurate information about surface properties (e.g., micropore volume, total pore volume, macropore volume, pore diameter) would be required to properly evaluate the effect of a given surface area on adsorption.

Due to similar properties of heavy metals and similar removal mechanisms, nickel removal studies have shown similar results to those of chromium and cadmium removal. Amino and hydroxyl groups show potential for nickel adsorption. Moreover, chitosan and graphene showed high potential for removal of all examined ions. It was also seen that nickel binding performed more successfully in a less acidic environment between pH values 6 and 8, as the deprotonated surface of the adsorbent is important for electrostatic attraction. As the pH of the solution increased, nickel adsorption increased.

Comparing metal removal, natural adsorbents performed better in all 3 cases.

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