Cr(VI) Sorption from Aqueous Solution: A Review

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Abstract: Hexavalent chromium (Cr(VI)) in water systems is a major hazard for living organisms, including humans. The most popular technology currently used to remove Cr(VI) from polluted water is sorption for its effectiveness, ease of use, low cost and environmental friendliness. The electrostatic interactions between chromium species and the sorbent matrix are the main determinants of Cr(VI) sorption. The pH plays a central role in the process by affecting chromium speciation and the net charge on sorbent surface. In most cases, Cr(VI) sorption is an endothermic process whose kinetics is satisfactorily described by the pseudo second-order model. A critical survey of the recent literature, however, reveals that the thermodynamic and kinetic parameters reported for Cr(VI) sorption are often incorrect and/or erroneously interpreted.

Keywords: hexavalent chromium; sorption; sorption isotherm; sorption kinetics; pseudo first order model; pseudo second order model; sorption thermodynamics

1. Introduction

Environmental pollution is currently a cause of serious concern worldwide. Anthropogenic activities produce increasing amounts of processing waste and effluents that contain a diversity of pollutants, including harmful heavy metals [1]. Among these, chromium is well known for its mutagenic and carcinogenic effects [2]. Chromium naturally occurs in the earth’s crust and water bodies but its level in the environment tends to increase in association with anthropogenic activities such as metallurgy, wood processing, and production of inorganic chemicals, printed circuit boards and dyes [3,4].

Chromium predominantly occurs in the +3 (Cr(III)) and +6 (Cr(VI)) oxidation states. Cr(VI) is highly soluble in aqueous systems and exhibits higher soil mobility and higher toxicity than Cr(III) [5]. In fact, the hexavalent form of chromium is highly toxic and carcinogenic, while the trivalent form is innocuous and may even be used as a micronutrient in certain organisms [6]. Cr(VI) has a high diffusion and dissolution capacity in the tissues [7]. Its compounds can be absorbed by humans through the skin and respiratory system and rapidly diffuse in the body due to their ability to enter the erythrocytes and bind to hemoglobin. Documented harmful effects of Cr(VI) in humans include lung cancer, respiratory problems, renal failure, weakening of the immune system, skin lesions, genetic damage and infertility [8]. Cr(VI) species enter the cells across non-specific anionic channels, thanks to structural analogy with sulphate and phosphate ions. Cr⁵⁺ complexes, produced by reduction of Cr(VI) within the cells, may react with endogenous H₂O₂ to generate potentially mutagenic OH radicals [9].
Recognizing the multi-faceted harmful effects of Cr(VI) on living organisms, the US Environmental Protection Agency (US-EPA) has established a maximum level in drinking and surface water of 0.015 and 0.1 mg L\(^{-1}\), respectively [10].

The removal of Cr(VI) from water is an issue that is drawing increasing attention within the scientific community. Among a diversity of methods tested so far, sorption is the most popular because it is fast, relatively inexpensive and easy to use. Not surprisingly, therefore, a considerable effort has been done for the development of novel sorbents for Cr(VI) removal since the last century [11–16]. Here we present a critical review of the experimental work performed on Cr(VI) sorption in the last decade, with emphasis on proposed mechanisms and thermodynamic and kinetic aspects.

2. Cr(VI) Behavior in Solution and Proposed Sorption Mechanisms: Effect of pH

Sorption is a general term encompassing a diversity of processes such as adsorption, absorption, ion exchange and surface precipitation, as well as a diversity of mechanisms depending on the physicochemical properties of sorbate and sorbent. Being a surface phenomenon, sorption usually increases with an increase of the surface area of the sorbent [17–19]. Other factors, notably the pH and the surface charge of the sorbent, may play a leading role in the process [8,20].

Cr(VI) is present in water in different oxyanionic forms (e.g., HCrO\(_4\)^−, CrO\(_4\)^{2−} and Cr\(_2\)O\(_7\)^{2−}) or as undissociated chromic acid, H\(_2\)CrO\(_4\), the relative abundance of each species being strongly related to the pH. The equilibria that contribute most significantly to Cr(VI) speciation in water are reported below [21–23]:

\[
\begin{align*}
    & \text{H}_2\text{CrO}_4 \rightleftharpoons H^+ + \text{HCrO}_4^- & K_1 = 0.37 \\
    & \text{HCrO}_4^- \rightleftharpoons H^+ + \text{CrO}_4^{2-} & K_2 = 3.2 \times 10^{-7} \\
    & 2\text{HCrO}_4^- \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} & K_3 = 35.5
\end{align*}
\]

where \(K_1\), \(K_2\) and \(K_3\) are the equilibrium constants of the three reactions. The first two equilibria are pH-dependent whereas the third only depends on total Cr(VI) concentration. The effect of pH and total Cr(VI) concentration (based on Equations (1)–(3)) on Cr(VI) species distribution, is shown in Figure 1 in a range of concentrations commonly found in contaminated water systems [24].

As can be seen from Figure 1, HCrO\(_4\)^− and CrO\(_4\)^{2−} are the most abundant species at acid and basic pH, respectively. Due to the negative net charge of Cr(VI) oxyanions, Cr(VI) sorption is expected to involve electrostatic interactions or anion exchange with positively-charged sorbent sites [6,24,25]. The uptake of Cr(VI) should be favored by a pH below the point of zero charge, which would impart the sorbent a net positive charge [20]. Chromium sorption should be less efficient under alkaline conditions than in acidic medium, not only because of electrostatic repulsion between chromium oxyanions and negatively-charged sites on sorbent surface but also because of competition with OH^− for sorbent sites.

In line with the analysis above, most papers on Cr(VI) report a decreasing sorption capacity with increasing pH. A typical trend of sorption capacity vs. pH is shown in Figure 2 [20,25,26].
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Shi et al. [20], for example, investigated the sorption performance of the anion-exchange resins D301, D314 and D354 for Cr(VI). The authors ascribed the observed sorption behavior with varying pH (similar to that shown in Figure 2), to an anion exchange process between Cr species and OH$^-\text{anions associated to }$-N(CH$_3$)$_2$ functional groups of the resins, according to the following reactions:

$$\text{R} - \text{OH} + \text{HCrO}_4^- \rightleftharpoons \text{R} - \text{HCrO}_4 + \text{OH}^-$$

(4)

$$2\text{R} - \text{OH} + \text{CrO}_4^{2-} \rightleftharpoons \text{R}_2 - \text{CrO}_4 + 2\text{OH}^-$$

(5)
where R is the resins’ matrix.

The authors reported that the amount of Cr(VI) sorbed in acidic condition was double than in alkali condition. An obvious explanation is that in acidic condition the exchanged OH- reacts with H+, thus promoting the forward reactions in Equations (4)–(7). At alkaline pH values, the sorption of Cr(VI) is hampered by competition between CrO$_4^{2-}$ and OH$^-$ for binding sites. At high pH (i.e., in excess of OH$^-$), this competitive effect leads to a drastic reduction of Cr(VI) uptake (Figure 2).

Kyzas et al. [25] investigated the sorption of Cr(VI) on chitosan derivatives cross-linked and grafted with amino and carboxyl groups. The authors observed a sorption trend with increasing pH similar to that observed by Shi et al. [20]. The researchers ascribed the higher uptake of Cr(VI) in acidic conditions to the protonation of amino groups in the chitosan sorbents, which would induce an electrostatic attraction to oxyanion Cr(VI) species. The same study [25] also reported a slightly lower Cr(VI) removal efficiency at pH 2 relatively to pH 4, which was attributed to chitosan instability at this pH.

An alternative mechanism for water purification from Cr(VI) involves reduction to Cr(III), a process in which pH also plays a central role [6,27,28]. Janos et al. [6] studied the reduction and immobilization of Cr(VI) with oxyhumolite and iron humate. The authors found that the amount of Cr(VI) removed from the solution in the presence of oxyhumolite decreased with increasing pH (Figure 3A).

\[
2R - OH + 2HCrO_4^- \rightleftharpoons R_2 - Cr_2O_7 + 2OH^- + H_2O \quad (6)
\]

\[
2R - OH + Cr_2O_7^{2-} \rightleftharpoons R_2 - Cr_2O_7 + 2OH^- \quad (7)
\]
Two mechanisms were proposed to account for that, involving direct and indirect reduction of Cr(VI). In the former mechanism, Cr(VI) is directly reduced to Cr(III) in the aqueous phase by contact with electron-donor groups of the sorbent; Cr(III) thus formed may be sorbed by cation-exchange or remain in solution. The indirect reduction pathway proposed postulates that Cr(VI) in the oxyanionic form initially binds via electrostatic interaction to the positively charged sorbent surface, then undergoes reduction by adsorbent electron-donor groups and is finally released in solution or remains bound to the sorbent. The study by Janos et al. [6] clearly identified two processes: Cr(VI) reduction to Cr(III) favored at lower pH, and Cr(III) retention by the sorbent favored at higher pH. Interestingly, a somewhat different trend was observed when using iron humate as sorbent (Figure 3B). The authors related this trend to the presence of iron compounds in the sorbent material that might be able to reduce Cr(VI) over a wide pH range. The resulting Cr$^{3+}$ cations might be retained on the sorbent by several mechanisms, such as ion-exchange, covalent binding or surface precipitation and co-precipitation of Fe$^{3+}$/Cr$^{3+}$ hydroxides. It is worth mention that the pH used by Janos et al. [6] is below 5, hence their results are not strictly comparable with those shown in Figures 2 and 4.

![Figure 4](image-url)  
**Figure 4.** Typical bell-shaped trend of sorption capacity as a function of pH.

Campos [28] examined the performance of powder carbon steel for Cr(VI) removal from water. This author found a higher Cr removal efficiency with decreasing pH, probably due to Cr(VI) reduction to Cr(III) coupled with oxidation of Fe to Fe$^{3+}$. Fe$^{3+}$ and Cr$^{3+}$ thus produced could react forming mixed oxide with low solubility and consuming H$^+$. On the other hand, chromate and Fe$^{2+}$ ions may react and form mixed Cr and Fe oxides generating H$^+$ release. The following Equations (8) and (9) illustrate some of the reactions discussed above:

$$\text{Fe} + \text{CrO}_4^{2-} + 0.5\text{H}_2\text{O} + 2\text{H}^+ \rightarrow \text{Fe(OH)}_3 + 0.5\text{Cr}_2\text{O}_3$$  \hspace{1cm} (8)

$$6\text{Fe}^{2+} + 2\text{CrO}_4^{2-} + 13\text{H}_2\text{O} \rightarrow 6\text{Fe(OH)}_3 + \text{Cr}_2\text{O}_3 + 8\text{H}^+$$  \hspace{1cm} (9)

A similar reduction in the sorption capacity with the increasing pH was observed by Kantar et al. [22], who investigated the sorption and reduction of Cr(VI) to Cr(III) using pyrite (FeS$_2$). The mechanism proposed by the authors was quite complex, involving a number of simultaneous or sequential steps, including pyrite dissolution, precipitation of oxidation products, protonation/deprotonation of chromium and of oxidized surfaces. A decrease in Cr(VI) removal efficiency associated with increasing pH was ascribed, at least in part, to pyrite surface passivation due to the accumulation of oxidation products. Under acidic conditions, pyrite releases Fe$^{2+}$ which may
reduce Cr(VI) to Cr(III) in the solution phase. Interestingly, the authors also suggested that Fe$^{2+}$ ions could also be sorbed onto pyrite, thus activating a cyclic redox mechanism that would further favors Cr(VI) reduction. The overall reaction pathway proposed is:

$$3\text{FeS}_2 + 14\text{HCrO}_4^- + 50\text{H}^+ \rightarrow 3\text{Fe}^{2+} + 6\text{SO}_4^{2-} + 14\text{Cr}^{3+} + 32\text{H}_2\text{O} \quad (10)$$

Di Natale et al. [29] used an additive-competitive Langmuir model to describe the effects of both pH and temperature on the chromium adsorption capacity of a commercial granular activated carbon, accounting for the chromium ion speciation. They highlighted that the optimal pH conditions were derived from the compensation between higher Cr(VI) ionization, favored at higher pH, and lower competition with OH$^-$ ions, favored at lower pH.

Ozer et al. [26] investigated the sorption of Cr(VI) by free and immobilized biomass (*Pediastrum boryanum*) and observed the typical decreasing sorption trend with increasing pH (Figure 2). This result was related by the authors to deprotonation of amino groups at the sorbent surface, which would hamper the electrostatic binding of chromium oxyanions.

A distinctive effect of pH on the sorption of Cr(VI) was observed by Koujalagi and co-workers [30] using Tulsion A-27(MP) resin (Figure 4). The sorption capacity vs. pH followed a bell-shaped curve with a maximum in the pH range 5–6 (Figure 4). The authors ascribed the fall of sorption capacity at high pH to sorbent surface passivation of the adsorbent surface by precipitation of hydroxides. In contrast, the decrease at low pH was ascribed to competition of H$^+$ with Cr(VI) for sorption sites.

In the study carried out by Chakrava et al. [31], husk of *Lathyrus sativus* was used as a sorbent for Cr(VI). It was found that the presence of functional groups such as $\text{–NH}_2$, $\text{–OH}$ and $\text{PO}_4^{3–}$ on the biomass surface markedly affected Cr(VI) uptake. More in detail, the authors suggested that the binding of Cr(VI) involved hydrogen bonds with amino and hydroxyl groups, or electrostatic interactions with protonated phosphate groups.

A pH effect similar to that displayed in Figure 4 was also found by Wu and co-workers [32] using chitosan-xylan-TiO$_2$ adsorbent. The authors attributed the low sorption of Cr(VI) in acidic solution (pH 4) to electrostatic repulsion between the protonated functional groups of the sorbent and positively charged chromium ions. This explanation is not convincing because, as discussed above, at pH 4 Cr(VI) is prevalently present as oxyanion. An alternative explanation might be the structural alteration of the sorbent surface in acidic environment and consequent loss of sorption capacity [33–35]. A third mechanism possibly contributing to reduce Cr(VI) sorption at low pH (<2) might be the formation of oligomers of chromium species such as Cr$_3$O$_{10}^{2–}$ and Cr$_4$O$_{13}^{2–}$ [36,37].

Gheju and coworkers studied the sorption of Cr(VI) onto MnO$_2$ [24]. A pH rise from 5.9 to 8.1 remarkably reduced Cr(VI) removal. The pH dependence of the process was ascribed to: (i) an increase in the negative net charge of the sorbent with increasing pH (being the point of zero charge $\text{pH}_{\text{PZC}} = 5.8$) and consequent increase of electrostatic repulsion between the sorbent surface and chromium oxyanions; (ii) higher competition between chromium oxyanions and OH$^-$ for positive sorption sites with increasing pH.

A bell shape curve such as that shown in Figure 4 was also reported by Hans et al. [38] for the sorption of Cr(VI) onto MIEX®, a magnetic ion exchange resin. A maximum sorption capacity was observed in the pH range 4–6. The authors ascribed the reduction in sorption capacity at lower and higher pH to competition between Cr(VI) and H$^+$ and between Cr(VI) and OH$^-$, respectively.

Cr(VI) sorption capacity by siderite (FeCO$_3$) in anoxic aqueous solution was lower at pH 4 than at pH 5 and 6 [39]. This phenomenon was ascribed by the authors to reduction of Cr(VI) to Cr(III) by Fe$^{2+}$ on the mineral surface or in solution.

Cr(VI) sorption capacity of schwertmannite attained a maximum at pH 6.0 [40]. Cr(VI) sorption by schwertmannite was mainly attributed to ion exchange between Cr(VI) and structural SO$_4^{2–}$, a process possible because the Cr(VI) species and SO$_4^{2–}$ have the same charge and similar sizes.

A novel biochar-supported zero-valent iron stabilized by carbomethyl cellulose was recently developed and used for Cr(VI) sorption experiments [41]. These experiments revealed that the
uptake/removal of Cr(VI) occurred via a complex mechanism involving electrostatic attraction, reduction and surface complexation. The main reactions of the proposed mechanism are reported below:

\[
3\text{Fe}^0 + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \rightarrow 3\text{Fe}^{2+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \tag{11}
\]

\[
\text{HCrO}_4^- + 7\text{H}^+ + 3e^- \leftrightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O} \tag{12}
\]

\[
3\text{Fe}^{2+} + \text{HCrO}_4^- + 7\text{H}^+ \rightarrow 3\text{Fe}^{3+} + \text{Cr}^{3+} + 4\text{H}_2\text{O} \tag{13}
\]

\[
\text{Fe}^{2+} + \text{Cr}_2\text{O}_4^{2-} \leftrightarrow \text{FeCr}_2\text{O}_4(s) \tag{14}
\]

\[
2\text{Cr}^{3+} + 6\text{OH}^- \leftrightarrow 2\text{Cr(OH)}_3(s) \leftrightarrow \text{Cr}_2\text{O}_3(s) + 3\text{H}_2\text{O} \tag{15}
\]

\[
x\text{Cr}^{3+} + (1-x)\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow (\text{Cr}_x\text{Fe}_{1-x})(\text{OH})_3(s) + 3\text{H}^+ \tag{16}
\]

\[
x\text{Cr}^{3+} + (1-x)\text{Fe}^{3+} + 3\text{OH}^- \rightarrow (\text{Cr}_x\text{Fe}_{1-x})(\text{OH})_3(s) \tag{17}
\]

3. Equilibrium and Thermodynamic Aspects of Cr(VI) Sorption

3.1. Sorption Isotherms

The sorption equilibrium of Cr(VI), as for any other sorbate, is generally investigated using the sorption isotherms [42]. These are obtained by plotting the sorbed amount of Cr(VI) per unit mass of sorbent \((q_e)\) at equilibrium against the initial Cr(VI) concentration \((C_e)\).

The isotherm models most frequently applied for describing Cr(VI) sorption are the Langmuir model and the Freundlich model [43].

The Langmuir model [44] (Equation (18)) is a simplistic model applicable under the assumptions that (i) the sorbate encompasses a finite number of energetically equivalent sites arranged in a superficial monolayer, and (ii) the solution behaves ideally (i.e., the solution is diluted enough for solute activity being approximated by concentration), and there are no intermolecular interactions among the free solute and/or sorbate molecules [45,46]:

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{18}
\]

where \(q_m\) and \(K_L\) are the maximum sorption capacity and the Langmuir equilibrium constant, respectively.

The Freundlich model [47] (Equation (19)) is a power function empirical model especially useful for the practical purpose of describing sorption equilibrium data not including a sorption saturation level as the Langmuir model demands:

\[
q_e = K_F C_e^N \tag{19}
\]

where \(K_F\) and \(N\) are empirical constants. It has been suggested that the value of the \(N\) parameter gives information on the heterogeneity of sorbent sites: values of \(N\) significantly lower than 1 (concave downward isotherms) would reflect high heterogeneity, whereas values of \(N \approx 1\) (linear isotherms) would be indicative of a homogeneous energetic distribution of sorption sites. It is important to note that \(N\) is a dimensionless parameter. This notwithstanding, \(N\) is sometimes erroneously reported with units of \(\text{L mg}^{-1}\) [48,49].

With few exceptions [18,50–52], if compared to, the Langmuir model fits better than the Freundlich model the experimental data for Cr(VI) sorption. Liu et al. [53] obtained a higher correlation coefficient using the Langmuir model for modelling the sorption isotherms of Cr(VI) sorption by poly(N\(^1\),N\(^3\),N\(^3\),N\(^3\)-tetraallylpropane-1,3-diaminium chloride) (PTAPDAC). A better performance of the Langmuir model was confirmed by Anandaraj et al. [54] using native and chemically modified green macroalgae Codium tomentosum biomass as a sorbent. Similar results were obtained by Mikhaylov et al. [8] using Al/Fe oxyhydroxide composite powders, Sutkowy and Klosowsky [55] using the
green alga *Pseudopediastrum boryanum* and many other authors using minerals [40,56], synthetized materials [1,7,10,20,57,58] or biosorbents [26,27,48,59].

In some cases [6,25,60], a semi-empirical hybrid Langmuir-Freundlich model, also known as Sips model [61], has been used for modelling isotherm equilibrium data:

\[
q_e = \frac{q_m K_{LF} C_e^N}{1 + K_{LF} C_e^N}
\]  

(20)

where \(K_{LF}\) is a constant.

The Sips model generally gives better fitting results than either the Langmuir or the Freundlich model. This is not surprising, because the Sips model is a more general (and therefore adaptable) equation that, for \(N = 1\) or for high Cr(VI) initial concentration, reduces to the Langmuir model whereas for sufficient low Cr(VI) concentration (i.e., \(1 \gg K_{LF} C_e^N\)) reduces to the Freundlich model (with \(K_F = q_m K_{LF}\)).

In rare cases, the equilibrium sorption data exhibited unusual trends not amenable to modelling by any of the isotherm equations described above. For example, Gheju and coworkers [24] reported a bell-shaped isotherm curve for the sorption of Cr(VI) onto MnO\(_2\). Normally, sorption capacity increases with increasing sorbate initial concentration and eventually reaches a plateau that corresponds to the saturation level of the sorbent. In contrast, the sorption capacity of the sorbent was higher at low chromium concentration and declined at higher concentration. The authors attributed this unusual behavior to HCrO\(_4^-\) dimerization to Cr\(_2\)O\(_7^{2-}\). Because of its larger volume, Cr\(_2\)O\(_7^{2-}\) has more difficulty access to sorption sites, thus reducing the sorption capacity of MnO\(_2\).

### 3.2. Maximum Sorption Capacity

A most important parameter for evaluating sorbent efficiency is the maximum (saturation) sorption capacity, \(q_m\), as determined from the plateau level of the experimental isotherm. A list of values of \(q_m\) for different sorbents is given in Table 1. It is important to note that the \(q_m\) values reported here may not be strictly comparable because, as discussed above, the Cr(VI) sorption capacity may vary with operative conditions such as pH and temperature. The highest maximum sorption capacity for Cr(VI), 12.0 mmol g\(^{-1}\), was reported by Setshedi et al. [62] for a polypyrrole graphene oxide nanocomposite. High values of \(q_m\) were also found for nanosilica immobilized-fungi (\(q_m = 10.1\) mmol g\(^{-1}\)) [36], grafted aerobic granular sludge (\(q_m = 7.7\) mmol g\(^{-1}\)) [60], and chitosan/poly(vinyl amine) cryogel (\(q_m = 6.1\) mmol g\(^{-1}\)) [63].
Table 1. Thermodynamic data for Cr(VI) sorption.

| Sorbent Type                                      | \( q_m \) (mmol g\(^{-1}\)) | \( K_L \) (L mmol\(^{-1}\)) | \( q_m^o \) K(L g\(^{-1}\)) | \( \Delta H^o \) (kJ mol\(^{-1}\)) | \( \Delta S^o \) (J K\(^{-1}\) mol\(^{-1}\)) | \( \Delta G^o \) (kJ mol\(^{-1}\)) | pH | Ref. |
|--------------------------------------------------|-------------------------------|-------------------------------|--------------------------------|-------------------------------------|-------------------------------------|---------------------------------|-----|------|
| Magnetic ion exchange resin                       | 1.781                         | 181                           | 322.4                         | /                                   | /                                   | /                               | /   | [38] |
| Zero-valent iron-carboxymethyl cellulose          | 2.163                         | 16.59                         | 35.88                         | 1.856                               | 0.230                               | /                               | /   | [41] |
| Siderite                                          | /                             | /                             | 1.408                         | 0.130                               | 20                                  | /                               | /   | [39] |
| Zirconium oxide-alginate beads                    | 0.200                         | 1.633                         | 0.327                         | 0.109                               | 0.466                               | 25                              | 21.224 | 163 | −27.430 | 5 | [58] |
| Mg-Al hydrotalcite                                | 1.383                         | 22.26                         | 30.79                         | 1.722                               | 0.40                                | Room                           | /   | 25   | / | 6 | [35] |
| Anion exchanger chitosan/poly(vinyl amine)       | 6.114                         | 0.974                         | 5.955                         | 2.673                               | 0.345                               | 25                              | 61.11 | 219 | −4.18 | 5.5 | [63] |
| Cross linked-chitosan-polyaniline                 | 3.446                         | 5.928                         | 20.43                         | 2.943                               | 0.227                               | 30                              | 13.46 | 10  | −9.18 | 4.2 | [64] |
| Mg-Zn-Al hydrotalcite-derived oxides             | 0.961 *                       | /                             | /                             | 30                                  | /                                   | /                               | /   | 5.5  | / | 6 | [65] |
| Anion-exchange resins                             | 3.005                         | 81.19                         | 244.0                         | 3.084                               | 0.151                               | 27                              | 0.016 | 39.88 | −4.498 | 5 | [20] |
| MnO\(_2\)                                        | 0.016 *                       | /                             | /                             | 20                                  | −22.32                              | −50.40                          | −8.08 | 6.9 | [24] |
| Schwert- mannite                                  | 1.890                         | 3.04                           | 5.746                         | 0.97                                | 0.313                               | 25                              | /   | /   | / | 6 | [40] |
| Iron/carbon Fe/C. composites                     | 0.981                         | 5.782                         | 5.672                         | 0.998                               | 0.483                               | Room                           | /   | /   | / | 5 | [27] |
| Cereal by-product carbon                          | 2.380 *                       | /                             | /                             | 20                                  | 0.7142                              | −94.8                           | 28.479 | 6 | / | [4] |
| Calcinated Al/Fe oxide-oxhydroxide               | 0.074                         | 123.4                         | 9.132                         | 0.0837                              | 0.104                               | Room                           | /   | /   | / | 6.7 | [67] |
| Polymethylplienean graftsed sludge               | 7.721                         | 4.16                           | 32.12                         | 2.241                               | 0.48                                | 25                              | /   | /   | / | 5.5 | [60] |
| Nannochloris oculata                              | 0.725                         | 0.530                         | 0.384                         | 0.215                               | 0.67                                | /                               | /   | /   | / | 2 | [50] |
| Amine-functionalized corn stalk                   | 4.370                         | 10.92                         | 47.72                         | 3.474                               | 0.128                               | 45                              | 96.79 | 30  | −7.16 | 3 | [68] |
| Dolomite                                         | 0.192                         | 14.14                         | 2.715                         | 0.203                               | 0.304                               | 20                              | −13.23 | −22.47 | −6.617 | 2 | [51] |
| Acinetobacter junii VITSUKMW2                    | 0.436                         | 115.5                         | 50.36                         | 0.0506                              | 0.389                               | 27                              | −3.764 | 0.018 | −1.989 | 2 | [48] |
| Polypropylene graphene oxide                     | 12.030                        | 104                           | 1251                          | 11.68                               | 0.029                               | 25                              | 78.417 | 282.67 | −7.287 | 2 | [62] |
| Al/Fe oxide-oxhydroxide                          | 0.070                         | 54.6                          | 3.82                          | 0.103                               | 0.26                                | /                               | /   | /   | / | 5.4 | [8] |
| Sargassum brennori                                | 0.763                         | 1558.8                        | 884.2                         | 0.484                               | 0.342                               | 20                              | 28.656 | 115 | −5.256 | 3 | [19] |
| Iron oxide-activated carbon                      | 0.155                         | 8.84                          | 1.370                         | 0.119                               | 0.37                                | 25                              | 49.906 | 168.3 | −0.293.3 | 2 | [49] |
| Ash gourd (Rhamnaceae hispida) waste              | 0.360 *                       | /                             | /                             | 0.472                               | 0.25                                | 28                              | /   | /   | / | 1 | [69] |
| Chitosan-xylan-TiO\(_2\)                        | 1.867                         | 1.217                         | 2.272                         | 0.904                               | 0.50                                | 45                              | 4.44 | 35.98 | −7.00 | 7 | [52] |
| Teff straw                                       | 1.656                         | 86.30                         | 142.9                         | 2.166                               | 0.277                               | 45                              | 34.25 | 150.07 | −13.468 | 2 | [70] |
| Sawdust                                          | 0.870                         | 47.32                         | 41.17                         | 12.24                               | 0.813                               | 40                              | 34.67 | 124.1 | −4.2140 | 3 | [52] |
| Sodium benzoate                                  | 0.105                         | 11.44                         | 1.201                         | 0.228                               | 0.622                               | 20                              | /   | /   | / | 2 | [54] |
| Vinylypyridine divinylbenzene                    | 4.130                         | 2.777                         | 11.47                         | /                                   | 25                                  | /                               | /   | /   | / | 2 | [71] |
| β-Cyclodextrin-polyurethane                      | 0.045                         | 2.34                          | 9.739                         | 0.25                                | 25                                  | /                               | /   | /   | / | 3 | [72] |
| Husk of Lathyrus sativus                         | 0.940                         | 4.493                         | 4.223                         | 0.214                               | 0.073                               | 30                              | /   | /   | / | 2 | [31] |
Table 1. Cont.

| Sorbent Type                        | $q_m$ (mmol g\(^{-1}\)) | $K_L$ (L mmol\(^{-1}\)) | $q_m$ $K_L$ (L g\(^{-1}\)) | $K_F$ (mmol L N\(^{-1}\)) | $T$ (°C) | $\Delta H^\circ$ (kJ mol\(^{-1}\)) | $\Delta S^\circ$ (J K\(^{-1}\) mol\(^{-1}\)) | $\Delta G^\circ$ (kJ mol\(^{-1}\)) | pH | Ref. |
|-------------------------------------|---------------------------|---------------------------|-----------------------------|-----------------------------|----------|------------------------------------|------------------------------------|-------------------------------------|----|------|
| Organoclay                           | 0.045                      | 38.06                     | 1.713                       | 0.698                       | 25       | /                                 | /                                  | /                                  | /  | 2    |
| Resin Tulsion A-27                   | 1.620                      | 0.370                     | 0.599                       | 2.64                        | 50       | /                                 | /                                  | /                                  | /  | 30   |
| Nanosilica-immobilized fungi         | 10.120                     | 0.0267                    | 0.270                       | 0.804                       | 25       | /                                 | /                                  | /                                  | /  | 2    |
| Solid biodiesel waste residue        | 2.530                      | 0.936                     | 2.368                       | 1.119                       | 30       | −9.34                             | −23.27                            | −2.040                             | 2  | 75   |
| Fe-modified peanut husk              | 0.637                      | 0.52                      | 0.331                       | 0.199                       | 30       | −9.027                            | −32.488                           | 753.94                             | 2  | 74   |
| Pedietrum berihamum                  | 0.585                      | 11.08                     | 6.482                       | 0.456                       | 25       | 44.5                              | 251                               | −17.4                              | 2  | 26   |
| Tresia nudiflora                    | 5.656                      | 11.08                     | 62.67                       | 4.917                       | 30       | 20.11                             | 110                               | −13.22                             | 2  | 75   |
| Metal organic resin 2                | 3.725                      | 3.64                      | 13.56                       | /                           | /        | /                                 | /                                  | /                                  | /  | 3    |
| Polytetraallylpropane diaminium      | 5.253                      | 21.48                     | 112.8                       | 0.357                       | 20       | −7.042                            | 52.401                            | −22.395                             | 6  | 55   |
| Polyelectrolyte hydrogels            | 0.790                      | 2.132                     | 1.684                       | 0.612                       | 30       | /                                 | /                                  | /                                  | /  | 6    |
| Amine-magnetite nanoparticles        | 4.079                      | 16.33                     | 66.61                       | 0.149                       | 25       | 137.1                             | 26.91                             | −3.26                              | 3  | 2    |
| L-Cysteine magnetite                 | 0.663                      | 215.3                     | 142.7                       | 2.512                       | 45       | 73.31                             | 280                               | −14.7                              | 2  | 10   |
| Ustilago nuda                        | 2.530                      | 0.300                     | 0.759                       | 2.4 × 10\(^{-2}\)           | 0.52     | 20                                | −9745                             | −38.685                             | 2  | 27   |
| Amine silica magnetite               | 3.561                      | /                        | /                           | /                           | Room     | /                                 | /                                  | /                                  | /  | 2    |
| Nano-γ-Al\(_2\)O\(_3\)              | 0.267                      | 101.4                     | 27.07                       | 0.318                       | 25       | /                                 | /                                  | /                                  | /  | 78   |
| Pteris vivata L.                     | 3.206                      | 1.56                      | 5.001                       | 1.179                       | 30       | 21.0                              | 200                               | −26.5                              | 2  | 59   |
| Chitosan magnetite                   | 3.846                      | 1.3                       | 5.000                       | 1.743                       | 30       | 25.72                             | 182                               | −29.4                              | 3  | 7    |
| Aspergillus niger                    | 0.097                      | 1142.3                    | 110.8                       | 2.14 × 10\(^{-3}\)          | 0.666    | 28                                | /                                  | /                                  | /  | 3    |
| MgAlFe-double hydroxide              | 3.385                      | 0.9952                    | 0.322                       | 0.489                       | 25       | /                                 | /                                  | /                                  | /  | 79   |
| Alum-water treatment sludge          | 0.220                      | 1.12                      | 0.246                       | 0.011                       | 25       | /                                 | /                                  | /                                  | /  | 3    |
| Palm kernel shell                    | 0.955                      | 113.7                     | 108.6                       | 0.0958                      | Room     | /                                 | /                                  | /                                  | /  | 6    |
| Bacterial cellulose/chitosan         | 2.925 *                    | /                        | /                           | /                           | 25       | /                                 | /                                  | /                                  | /  | 6    |
| Kaolinite nanotubes                  | 4.579                      | 0.143                     | 0.655                       | 0.0536                      | 30       | /                                 | /                                  | /                                  | /  | 2    |
| Bacterial cellulose/attapulgite      | 1.750                      | 2.205                     | 3.859                       | 0.526                       | 45       | 25                                | /                                  | /                                  | /  | 6    |
| Char derived from South African coal | 0.006                      | 7.323                     | 0.044                       | 0.0096                      | 665      | /                                 | /                                  | /                                  | /  | 43   |
| Granular activated carbon            | 0.138                      | 15.334                    | 2.116                       | 0.2433                      | 0.611    | /                                 | /                                  | /                                  | 7.5| 43   |

* Experimental data.
3.3. Sorbent Affinity toward Cr(VI)

The sorbent affinity toward Cr(VI) can be evaluated from the Langmuir equilibrium constant ($K_L$): the higher $K_L$, the higher the sorbent affinity for Cr(VI). Among tested sorbents (Table 1), *Sargassum bevanom* ($K_L = 1160 \text{ L mmol}^{-1}$) [19] and *Aspergillus niger* ($K_L = 1140 \text{ L mmol}^{-1}$) [37] exhibit the highest affinity for Cr(VI), followed by L-cysteine functionalized magnetite ($K_L = 215 \text{ L mmol}^{-1}$) [10], magnetic ion exchange resin ($K_L = 181 \text{ L mmol}^{-1}$) [38] and calcinated Al/Fe oxide–oxyhydroxide composite ($K_L = 123 \text{ L mmol}^{-1}$) [67]. For practical purposes, it is also relevant to evaluate sorbent affinity at low Cr(VI) initial concentration. This parameter can be estimated from the initial slope of the Langmuir isotherm, which is the product of the maximum sorption capacity, $q_m$, and $K_L$. The highest values for Cr(VI) affinity at low Cr(VI) concentration have been reported for polypyrrole graphene oxide nanocomposite [62] and *Sargassum bevanom* [19] (see Table 1).

3.4. Sorption Thermodynamics

The change of sorption isotherms (i.e., of the equilibrium conditions) with temperature provides information on the temperature-dependence of the sorption equilibrium and related thermodynamic parameters, namely the standard change in Gibbs energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$).

The temperature-dependence of the sorption equilibrium constant ($K$) is generally derived from the Gibbs-Helmholtz equation [84]:

$$\frac{\partial}{\partial T} \left( \frac{\Delta G^\circ}{T} \right) = -\frac{\Delta H^\circ}{T^2}$$ (21)

By using the well-known thermodynamic relationships:

$$\Delta G^\circ = -RT \ln(K)$$ (22)

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$ (23)

and assuming that neither $\Delta H^\circ$ or $\Delta S^\circ$ varies appreciably with temperature, Equation (21) can be integrated to give:

$$\ln(K) = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R}$$ (24)

A plot of $\ln K$ vs. $1/T$ (van’t Hoff plot) will produce a straight line whose slope and intercept with $y$-axis permit the determination of $\Delta H^\circ$ and $\Delta S^\circ$, respectively.

The value of $K$ in Equation (24) depends on the model chosen for describing the sorption isotherm. The Langmuir equilibrium constant $K_L$ is often used for this purpose in Cr(VI) sorption studies [35,51,75]; the sorption distribution coefficient $K_D = q_e/C_e$ (determined by extrapolating to zero the plot $\ln(q_e/C_e)$ against $C_e$) is also utilized, though less frequently [32,64,70].

Applying Equation (24), Kumar et al. [58] obtained positive values of $\Delta H^\circ$, indicating that Cr(VI) sorption on zirconium oxide-immobilized alginate beads is an endothermic process. The same was reported by Dragan et al. [63] using anion exchanger microspheres embedded into chitosan/poly(vinyl amine), by Song et al. [68] using amine-functionalized magnetic corn stalk composites, and by many other authors (Table 1). Negative values of $\Delta H^\circ$ are encountered less frequently in the literature, for example Gheju et al. [24] using MnO$_2$ and Albadarin et al. [51] using dolomite.

Crucially thermodynamic analyses of Cr(VI) sorption reported in the literature is often wrong [2,7,19,20,24,26,30,35,52,53,58,62,68,73,74,77]. The value of $K$ (Equation (24)) has been erroneously determined on many occasions [2,7,20,24,30,52,53,58,62,68,73,74,77] using the following expression:

$$K = \frac{q_e}{C_e}$$ (25)

As easily inferred from any experimental isotherm curve (with the exception of linear isotherms), the $q_e/C_e$ ratio is not constant (i.e., it varies with sorbent coverage [85]), thus Equation (25) does not
represent an equilibrium constant and cannot be used in the van’t Hoff equation (Equation (24)). As already observed, a correct determination of $K$ from the $q_e/C_e$ ratio could be obtained by extrapolating its value at zero sorbent coverage [86–88].

For the same reasons, we consider incorrect the determination of $K$ as:

$$K = \frac{F_e}{1 - F_e} \tag{26}$$

where $F_e$ is the fraction of Cr(VI) sorbed at equilibrium [19,74].

Another mistake frequently observed in the literature concerns the meaning ascribed to the sign of $\Delta G^o$. Several authors [2,7,19,20,24,26,32,35,52,58,62,64,68,73] found a $\Delta G^o < 0$ and interpreted this as an indication of spontaneous Cr(VI) sorption. Others obtained a $\Delta G^o > 0$ and concluded that the instance of Cr(VI) sorption they examined was a non-spontaneous process [4,74,77]. These claims have been so long held that one tends to forget that the calculated change in Gibbs energy refers to standard conditions. A negative or positive $\Delta G^o$ only indicates the spontaneity or non-spontaneity, respectively, of a hypothetical sorption process in which the reagents (sorbent and solute) and the product (adsorbent-solute adduct) are both in standard conditions [88]. The sign of $\Delta G^o$ may even depend on the selected standard state [88,89]. It is worth remarking that the choice of the standard state not only influences the sign of $\Delta G^o$ (hence the value of $K$ [90]), but also the sign and magnitude of $\Delta S^o$ ($\Delta H^o$ is independent on the standard state because the ratio between $K$ values at two different standard states is constant (see Equation (24)). From the above considerations, it follows that, for a correct comparison of thermodynamic parameters for sorption on different sorbents, these should be relative to similar standard conditions.

4. Kinetic Modelling

The study of sorption kinetics is of practical significance because it provides information on the time required for effective removal of a solute from the aqueous phase.

Among the models proposed for describing the kinetics of Cr(VI) sorption, the most popular ones are the pseudo-first order (PFO) and the pseudo-second order (PSO) model; other frequently used models are the Weber-Morris and the Elovich model.

The PFO model [91] assumes that the observed rate of sorption ($dq/dt$) is proportional to the distance from equilibrium expressed as the difference between the amount of Cr(VI) sorbed at equilibrium ($q_e$) and at any time ($q$):

$$\frac{dq}{dt} = k_{PFO}(q_e - q) \tag{27}$$

where $k_{PFO}$ is the PFO kinetic rate constant. By integrating Equation (27) for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$, we obtain:

$$q = q_e(1 - e^{-k_{PFO}t}) \tag{28}$$

The PSO model [92] differs from the PFO model because the sorption rate is assumed to be proportional to the square of the distance from equilibrium:

$$\frac{dq}{dt} = k_{PSO}(q_e - q)^2 \tag{29}$$

Here $k_{PSO}$ is the PSO kinetic rate constant. Equation (29) can be integrated, for the same boundary conditions as for Equation (27), leading to:

$$q = \frac{q_e^2k_{PSO}t}{1 + q_ek_{PSO}t} \tag{30}$$
It is widely maintained that the application of the PSO model to Cr(VI) sorption kinetic data gives better fitting results than the PFO model. Examples include studies carried out using as sorbent bacterial cellulose/attapulgite magnetic composites [83], palm oil kernel shell [80], cross linked-chitosan-grafted-polyaniline composite [64], teff straw [70] and material derived from harmful algal bloom biomass [27]. In contrast, Dragan et al. [63] found that the PFO model was best suited to describe the kinetic data of Cr(VI) sorption onto chitosan/poly(vinyl amine cryogel. Better applicability of the PFO model appears to be associated with weak Cr(VI)-sorbent interaction (physiosorption) [63], whereas better applicability of the PSO model is indicative of strong interaction (chemisorption) [41]. Noticeably, better performance of the PSO model may also be an artifact from improper analysis of the data. In most cases this results from the application of Equation (30) in the following linearized form [17,93]:

\[
\frac{t}{q} = \frac{1}{k_{PSO}q_e^2} \frac{t}{q_e} + 1
\]

According to Equation (31), if the data obey the pseudo-second order model, a plot of \( t/q \) vs. \( t \) should produce a straight line. The main drawback of this method is that for data points at (or very close to) equilibrium, the plot of \( t/q \) vs. \( t \) becomes linear independently of sorption kinetics [93]. The goodness of the results obtained by the plot of \( t/q \) vs. \( t \) may be verified by using a linearized form of the PSO model [17]:

\[
\frac{q}{t} = k_{PSO}q_e - k_{PSO}q
\]

If the PSO model is appropriate for the data, the plot of \( q/t \) against \( q \) will be linear. As an example, the comparison between \( t/q \) vs. \( t \) and \( q/t \) vs. \( q \) for the sorption of Cr(VI) onto MnO\(_2\) [24] is reported in Figure 5. The authors claimed that the sorption kinetics was adequately described by the PSO model because the linear curve-fitting of \( t/q \) vs. \( t \) data gave excellent results (\( R^2 = 0.999 \), see Figure 5). However, as can be seen from Figure 5, this conclusion is incorrect because the same data, rearranged in the form \( q/t \) vs. \( q \), significantly deviate from linearity.

![Figure 5](image-url)  
Figure 5. Comparison between the plots of \( q \) vs. \( t \) and \( q/t \) vs. \( t \) for the sorption of Cr(VI) onto MnO\(_2\); initial Cr(VI) aqueous concentration = 0.02 mM, sorbent dosage = 2 g L\(^{-1}\). Adapted from Gheju et al. [24].
As a general rule, the non-linear curve fitting is recommended over the linear curve fitting to prevent possible misinterpretation of the data. It is also worth observing that, because Cr(VI) sorption rate varies with operative conditions such as the initial solute concentration and the sorbent dosage, it is usually not possible to compare the values of $k_{PFO}$ or $k_{PSO}$ from different reports. To partially overcome this problem, one could, for example, compare the values of initial sorption rate ($v_0$) as predicted by the PFO and the PSO model, using Equations (33) and (34), respectively:

\[
v_0(PFO) = k_{PFO}q_e \tag{33}
\]

\[
v_0(PSO) = k_{PSO}q_e^2 \tag{34}
\]

Values of $v_0(PFO)$ and $v_0(PSO)$ from recent works are reported in Table 2. With very few exceptions [32,53], most of the studies report higher values of $v_0(PSO)$ compared to $v_0(PFO)$. 
Table 2. Kinetic data for Cr(VI) sorption.

| Sorbent Type | C0 (mmol L⁻¹) | Sorbent Dosing (g L⁻¹) | qe (mmol g⁻¹) | kF (h⁻¹) | qF (mmol g⁻¹ h⁻¹) | t (h) | pH Ref. |
|--------------|---------------|------------------------|---------------|---------|-------------------|------|--------|
| Magnetic iron exchange resin | 1.00 | 1 | 0.77 | 0.81 | 7.392 | 29.4 | 25 | 4 | [38] |
| Zero-valent iron-carboxymethyl cellulose | 1.92 | 0.75 | 1.648 | 1.629 | 0.822 | 2.181 | 25 | 5.6 | [41] |
| Zinc oxide-alginate beads | 0.365 | 2.5 | 0.0409 | 0.0624 | 2.552 × 10⁻² | 0.0388 | 3.156 | 4.751 × 10⁻² | 25 | 5 | [50] |
| Mg-Al hydrotalcite | 3.85 | 2 | 1.471 | 1.468 | 9.36 | 20.17 | Room 6 | [35] |
| Anion exchanger chitosan/poly(vinyl amine) | 1.92 | 1.25 | 1.482 | 1.112 | 1.648 | 1.595 | 1.091 | 2.775 | 25 | 5.5 | [63] |
| Cross linked-chitosan-polyaniline | 7.89 | 2 | 10.44 | 12.35 | 13.8 | 30 | 4.2 | [64] |
| Mg-Zn-Al hydrotalcite derived oxides | 0.152 | 5 | 0.856 | 2.1 | 1.963 | 1.147 | 1.751 | 2.304 | 30 | 6 | [65] |
| Fe (III)-modified natural zeolite | 2.88 | 200 | / | / | 0.057 | 700 | 0.0173 | Room 5.5 | [66] |
| Anion-exchange resins | 1.92 | 1.67 | 0.0577 | 3.624 | 0.209 | / | / | / | 27 | 5 | [29] |
| MnO₂ | 0.04 | 2 | 8.07 × 10⁻³ | 3.72 | 0.008 | 8.769 × 10⁻³ | 0.0102 | 567.4 | 0.591 | 20 | 6.9 | [24] |
| Iron/carbon Fe/C composites | 1.92 | 1 | 0.628 | 0.0074 | 4.642 × 10⁻³ | 0.836 | 0.0392 | 0.0528 | Room 5 | [27] |
| Cereal by-product carbon | 2.54 | 2 | 8.358 × 10⁻³ | 0.120 | 1.00 × 10⁻³ | 0.149 | 13.55 × 10⁻³ | 30.08 × 10⁻³ | 20 | 6 | [4] |
| Amine-functionalized corn stalk | 3.85 | 1 | 214.24 | 0.462 | 0.988 | 0.368 | 134.16 | 1834.7 | 45 | 3 | [68] |
| Docolite | 0.961 | 1 | 0.194 | 0.0452 | 8.769 × 10⁻³ | 0.249 | 0.179 | 0.011 | 20 | 2 | [51] |
| Acetate/ethanol yeast VITSHKMY2 | 1.92 | 2 | 0.202 | 1.08 | 0.218 | 0.492 | 12.48 | 3.021 | 27 | 2 | [48] |
| Polypyrrole graphene oxide | 1.92 | 0.3 | 5.215 | 2.136 | 11.14 | 3.846 | 6.21 | 92.30 | 23 | 2 | [60] |
| Sargassum tannin | 1.92 | 7 | 5 | / | / | / | / | / | 20 | 3 | [19] |
| Iron oxide-activated carbon | 0.961 | 5 | 5.96 × 10⁻³ | 6.36 | 0.0380 | 6.995.2 | 14.59 | 25 | 2 | [49] |
| Chitosan-ylvan-TeO₃ | 1.92 | 2 | 1.76 | 0.593 | 0.044 | 1.273 | 0.551 | 0.893 | 45 | 7 | [32] |
| Tiff straw | 1.92 | 10 | 0.137 | 1.68 | 0.230 | 0.175 | 15.6 | 0.478 | 45 | 2 | [70] |
| Cañafate fomentarium | 10 | / | / | / | / | / | / | / | 20 | 2 | [54] |
| β-Cyclodextrin-polyurethane | 0.0192 | 0.2 | / | / | 4.688 × 10⁻³ | 884 | 0.0190 | 25 | 3 | [72] |
| Resin Tunus A-27 | 1.1 | 0.033 | / | / | / | / | / | / | 30 | 5.5 | [30] |
| Sclad broxolastic root salt | 9.61 | 6 | 0.531 | 1.02 | 0.542 | 2.404 | 4.642 | 26.83 | 30 | 2 | [73] |
| Pedicularis longipes | 7.69 | 4 | 0.329 | 2.73 | 0.896 | 0.581 | 7.488 | 252.8 | 25 | 2 | [28] |
| Trexus madiflora | 2.15 | 0.75 | 0.433 | 1.66 | 0.722 | 2.709 | 13.01 | 95.48 | 30 | 2 | [77] |
| Alum-water treatment sludge | 0.001 | 10 | 0.027 | 0.564 | 0.0152 | 0.079 | 58.02 | 0.362 | 25 | 3 | [19] |
| Polyethylene-aldehyde diaminium | 1.92 | 0.7 | 2.612 | 18.80 | 40.10 | 0.0521 | 16.55 | 0.0449 | 20 | 6 | [53] |
| Amine-magnetite nanoparticles | 0.096 | 0.1 | 0.123 | 3.6 | 0.443 | 0.543 | 6.24 | 1.840 | 25 | 3 | [2] |
| Litchi myallii | 0.48 | 10 | / | / | / | 0.0375 | 42.74 | 0.0601 | 20 | 5.5 | [77] |
| Amine silica magnetite | 2.88 | 1.07 | 0.631 | 19.92 | 32.57 | 2.497 | 203.3 | 1280 | Room 2 | [97] |
| Nano-γ-Fe₂O₃ | 0.38 | 3 | 0.011 | 1.2 | 0.0132 | 0.156 | 93.6 | 2.278 | 25 | 3 | [70] |
| Poria jissum L. | 1.92 | 1 | / | / | / | 1.479 | 3.12 | 6.825 | 30 | 2 | [59] |
| Aquiprilia niger | 0.96 | 10 | 8.52 × 10⁻³ | 0.014 | 4.495 × 10⁻³ | 8.30 × 10⁻³ | 17.238 | 1.187 | 28 | 2.5 | [37] |
| Palm kernel shell | 0.096 | 20 | / | / | 1.2 × 10⁻² | / | Room 6 | [80] |
| Bacterial cellulose/soybean | / | / | / | / | / | / | / | / | 25 | 6 | [61] |
| Kaolinite nanotubes | 1.92 | 0.333 | / | / | 1.074 | 4.802 | 5.334 | 30 | 2 | [92] |
| Bacterial cellulose/attapulgite | 0.96 | 0.2 | 1.473 | 56.7 | 43.52 | 1.635 | 3.25 × 10⁶ | 8.688 × 10⁸ | 25 | 6 | [83] |
The Weber-Morris equation \[94\] is a semi-empirical model often used in Cr(VI) sorption studies for evaluating whether the rate of the process is affected by solute diffusion within sorbent pores (intra-particle diffusion):

\[
q = k_D \sqrt{t} + \kappa \tag{35}
\]

Here \(k_D\) is a kinetic diffusion parameter and \(\kappa\) is a constant proportional to the thickness of the diffusion boundary layer. A linear correlation between \(q\) and the root square of time suggests that the rate of Cr(VI) sorption is controlled by diffusion \[19,32,73\]. Some authors argued that the presence of multiple linear portions in the \(q\ vs. \sqrt{t}\) plot indicates that the sorption process proceeds through two or more consecutive diffusive steps \[75\].

Another model used for modelling the sorption kinetic data is the Elovich equation \[95\], which envisages an exponential decrease of the sorption rate with an increase of bound sorbate \(q\), without reaching equilibrium (for \(t \to \infty, q \to \infty\)):

\[
\frac{dq}{dt} = \alpha e^{-\beta q} \tag{36}
\]

where \(\alpha\) is the initial \((t = 0)\) sorption rate and \(\beta\) indicates the extent to which the rate varies with \(q\). It is agreed that the applicability of the Elovich model to experimental data provides evidence of heterogeneity of sorption sites \[75\]. Equation (36) can be integrated for the boundary conditions \(t = 0\) to \(t = t\) and \(q = 0\) to \(q = q\), yielding:

\[
q = \frac{1}{\beta} \ln(1 + \alpha \beta t) \tag{37}
\]

Owing to historical difficulties (lack of computational power) associated with the application of non-linear curve fitting \[96\], an approximated-linearized form of Equation (37) was introduced by Chien and Clayton \[97\] for testing the applicability of the Elovich model. The approximated form of the integrated Elovich equation was derived on the assumption that for sufficiently high values of \(t\), the term \(\alpha \beta t\) becomes much greater than 1 so that Equation (37) reduces to:

\[
q = \frac{1}{\beta} \ln \alpha \beta + \ln t \tag{38}
\]

Thus, the validity of Equation (38) is verified by the linear plot of \(q\ vs. \ln t\). Although non-linear curve fitting is now easy to perform, linearization is still the first-choice procedure for testing the Elovich model, which may lead to incorrect interpretation of data. As a matter of fact, several recent studies of Cr(VI) sorption reported that the linearized Elovich equation (Equation (38)) gave less satisfactory fitting results than the PSO model \[4,19,75,82\]. However, as stated above, the exact integrated form for the Elovich equation (Equation (37)) ought to be employed for a rigorous comparison with the PSO model.

5. Conclusions

The primary mechanism of chromium sorption involves electrostatic interactions between the sorbate and the sorbent surface. The pH strongly affects chromium sorption behavior. The most frequently used models to describe the equilibrium of Cr(VI) sorption are the Langmuir model and the Freundlich model, the former usually providing better fitting results. The Pseudo First-Order and the Pseudo Second-Order model are the models of choice for the kinetics of Cr(VI) sorption. The Pseudo Second-Order model generally fits the data much better than the Pseudo First-Order model.

A critical survey shows that thermodynamic and kinetic analyses of Cr(VI) sorption reported in the recent literature are often incorrect. Common mistakes include miscalculation of the sorption equilibrium constant, erroneous extrapolation of data to standard conditions, and the application of regression models in linearized form.
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