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Thermodynamic parameters for adsorption equilibrium of heavy metals and dyes from wastewaters

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HIGHLIGHTS

- We reviewed adsorption works with thermodynamic parameters evaluations.
- Adsorption mechanisms reported for copper ions and methylene blue were listed.
- Adsorption works with low-cost adsorbents are nearly equilibrium.
- The standard enthalpy and entropy changes values reported are highly contestable.
- Suggestions were made on the works needed for adsorption thermodynamics.

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ABSTRACT

This meta-analysis evaluates adsorption studies that report thermodynamic parameters for heavy metals and dyes from wastewaters. The adsorbents were derived from agricultural waste, industrial wastes, inorganic particulates, or some natural products. The adsorption mechanisms, derivation of thermodynamic relationships, and possible flaws made in such evaluation are discussed. This analysis shows that conclusions from the examined standard enthalpy and entropy changes are highly contestable. The reason for this flaw may be the poor physical structure of adsorbents tested, such that pore transport controlled the solute flux, leaving a surface reaction process near equilibrium.

1. Introduction

Heavy metals and dyes are pollutants found in various industrial wastewaters. Methods for removing metals or dyes from a water stream include adsorption, a highly effective and economical process when the appropriate adsorbents are applied. The search for low-cost adsorbents, preferably derived from locally available waste materials, has become a primary research focus (Annadurai et al., 2002; Volesky and Holan, 1995; Gadd, 1993; Ho, 2006; Sheng et al., 2004; Vijayaraghavan and Yun, 2008; Wang and Chen, 2009; Guibal et al., 1998; Chang et al., 1997; Aksu, 2005; Chojnacka, 2010; Hossain et al., 2012). To date, thousands of studies have used countless adsorbents to remove heavy metals or dyes (Saini and Melo, 2013; Park et al., 2012; Fernandez et al., 2012; Bulgariu and Bulgariu, 2012; Flores-Garmica et al., 2013; Ye et al., 2013; Lou et al., 2013; Wang et al., 2013a,b; Yu et al., 2013). The effectiveness of biosorption processes to remove pollutants from wastewaters has recently been investigated (Mishra and Malik, 2013; Promies et al., 2013; Patel, 2012; Vithanage et al., 2012; Asgher, 2012; Mudhoo et al., 2012; Kikuchi and Tanaka, 2012; Hubbe et al., 2012; Julinova and Slavik, 2012; Das, 2012; Kanmani et al., 2012). A biomass typically exists with excess extracellular polymeric substances (EPS) that have a strong affinity for heavy metals (Zhang et al., 2012, 2013; Lin et al., 2013).

Adsorption quantities and adsorption rates are two most important performance indices of any adsorption system. In a well-mixed reactor, the external mass transfer resistance of a solute to the surface of an adsorbent is low. The interaction between a solute and adsorbent surface “sites” is controlled by the quantity and rate of uptake of the solute. Interaction between a solute and surface site is a complicated function of all process parameters (Volesky, 2007). Thermodynamic parameters are the focus of engineering evaluations that assess the uptake of adsorbents, hopefully providing insight into adsorption mechanisms for further use to modify and optimize processes. Most studies estimated changes in free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) under standard states based on a set of temperature-dependent equilibrium

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adsorption quantities. However, Ramesh et al. (2005) identified the probable flaws in many adsorption studies when they assessed their thermodynamic parameters. This review surveyed current literature and confirmed the findings by Ramesh et al. (2005). The use of single set of equilibrium constants *versus* testing temperature data to evaluate thermodynamic parameters is questioned.

2. Adsorption tests

Each year numerous studies are published on all aspects of biosorption. In 2012, 916 papers were published on the Web of Science (WoS) database on subject of “biosorption”, compared with only 20 in 1990. The total number of citations for biosorption papers exceeded 130,000 hits, with more than 21,000 citations in 2012 alone. India and China account for about 33% of all biosorption papers. Table S1 lists the biosorption studies that reported their thermodynamic parameters. Although this list is not exhaustive, a discussion should be sufficient in identifying trends in biosorption equilibrium studies.

In these studies, numerous metal ions were tested as the adsorbate (Cd^{2+}, Cr^{6+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Cr^{3+}, Sb^{3+}, Sb^{5+}, Hg^{+} Al^{3+}, Se^{4+}, Sb^{3+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Sr^{2+}, Fe^{3+}, Cs^{+}, Au^{3+}, As^{5+}), with adsorption of Cu^{2+}, Cr^{6+}, Pb^{2+}, and Cd^{2+} studies most likely attributable to environmental concerns of these heavy metals in industrial effluents. In dye adsorption studies, many dyes have been tested (methylene blue (MB), reactive dye yellow 42, red 45, blue 19, blue 49, malachite green, methyl orange, eriochrome black T, direct red-31, direct orange-26, rhodamine B, basic green 4, reactive black 5, basic red 46, basic yellow 28), with MB as the most widely studied. A WoS search identified over 450 studies published in the last decade. Most adsorbents tested were from “wastes,” and agricultural or natural products (coir pith carbon, pine tree bark, meranti wood, *Moringa oleifera* bark, *M. oleifera* leaves powder, *Candida albicans* biomass, tea factory waste, dehydrated wheat bran carbon, dehydrated peanut hull, modified oak sawdust, *Agave lechuguilla* biomass, chitin, *Aspergillus niger*, wheat shells, kaolinite clay, diatomite, moss (*Drepanocladus revolvens*) biomass, brown algae (*Padina pavonica*) biomass, green algae (*Cladophora hutchinsiae*) biomass, lichen *(Physcia tribacia*) biomass, *Penicillium simplicissimum*, vermiculite, dolomite, *Citrus sinensis*, olive tree pruning waste, magnetic chitosan resin, *Tamarindus indica* seed powder, mushroom biomass (*Agaricus bisporus*), seed husk of *Calophyllum inophyllum*, chestnut shell, mycelial biomass (*Streptomyces rimosus*), rice husk, *Cinnamomum camphora* leaf powder, *Acidithiobacillus ferrooxidans* BY-3, coffee grounds, inactivated sewage sludge, Mansonia wood sawdust, anaerobic sludge, *Ananas comosus* (pineapple) leaf powder, walnut hull, macrofungus (*Lactarius scrobiculatus*) biomass, pine bark, *Acacia leucocephal* bark, olive oil industry waste, coconut copra meal, *Corynebacterium glutamicum* waste biomass, lichen (*Cladonia furcata*) biomass, chaff, phoenix tree leaves, neem oil cake (NOC), guava (*Psidium guajava*) leaf powder, and Ficus religiosa leaves. These studies emphasized the recycling process from waste to resource to fit the green targets of sustainable development.

The number of adsorbate–adsorbent pairs for study is infinite. Understanding the adsorption mechanism provides basic information on how a system responds to changes in process parameters and clues on how the efficiency of an existing system can be further improved.

3. Adsorption mechanisms

Affinity, which induces adsorption of a solute on an adsorbent surface, is a key focus in adsorption studies. Heavy metals ions are hydrophilic, charged solutes, while dyes are organic compounds with light-emitting groups with very different levels of acidity in water and molecular weight. The proposed adsorption mechanisms were ion exchange, surface adsorption, chemisorption, complexation and adsorption + complexation.

3.1. Adsorption of copper ions

This discussion takes adsorption systems adsorbing Cu^{2+} as an example. Argun et al. (2007) used oak sawdust to adsorb Cu^{2+} and noted that Cu^{2+} ions were bound to that active surface on the sawdust by O^{2-} ions and this action released H^{+} into the solution. Dursun (2006), who used *A. niger* to adsorb Cu^{2+}, noted that under highly acidic pH, the overall surface charge on cells was positive and metal cations and protons compete for binding sites on cell walls, resulting in low metal uptake. At low pH values, cell wall ligands are closely associated with H_3O^{+}, restricting access to ligands. Bhattacharyya and Gupta (2011) applied mineral powders to adsorb Cu^{2+}. At $pH < 6$, competition between protons and Cu^{2+} reduces the adsorption efficiency of Cu^{2+}. At $pH > 6.0$, the Cu(II) hydroxide precipitates. Chowdhury and Saha (2011), who applied *T. indica* seed to adsorb Cu^{2+}, noted that by Fourier transform infrared spectroscopy (FTIR) spectral analysis various functional groups, such as NH_2, OH, and CO are involved in Cu^{2+} biosorption. Ertugay and Bayhan (2010) applied a mushroom biomass to adsorb $Cu^{2+;}$ at pH values of 2, 4, 5 and 6, the zeta potentials of *A. bisporus* were −5.18, −5.2, −12.2 and −8.12 mV, respectively, such that copper ions were attracted to the surface of {what?} by electrostatic forces. Yao (2010) used chestnut shell to adsorb Cu^{2+}, noting that C=O, —COO^{-} and C—O bonds on the shell surface participated in copper binding. At $pH > pH_{ZPC}$ (4.9 for the chestnut shell), adsorption of Cu^{2+} was nearly complete due to the ion exchange reaction with dissociated —COOH groups ($pKa = 3.8 - 5.0$) on the shell surface. Chen et al. (2010) asserted that ion-exchange and surface complexation were responsible to the accounted for adsorption of Cu^{2+} ions by *C. camphora* leaves. Ofomaja et al. (2010), who used Mansonia wood sawdust to adsorb Cu^{2+}, demonstrated that copper uptake was low at low pH, and as pH increased the amount of copper ions adsorbed increased. In using *M. oleifera* leaves to adsorb Cu^{2+}, Reddy et al. (2012) determined that Cu(II) was adsorbed mainly by active groups such as hydroxyl groups (OH) and carboxylic groups (COO^{-}). At $pH < 3$, the non-ionic form of the carboxyl group, COOH, was present, and metal adsorption was low because electrostatic interaction was absent. At $pH > 3$, the carboxyl group became COO^{-}, and metal adsorption increased and peaked at around pH 4.0–6.0.

For heavy metal ions other than copper ions, mean biosorption energy calculated using Dubinin–Radushkevich isotherm models suggested that biosorption of Se^{4+} and Sb^{3+} onto a biomass was determined by an ion exchange mechanism (Tuzen and Sari, 2010; Uluozlu et al., 2010). Similar modeling methods indicated that the binding of chromium species to the *A. lechuguilla* biomass was caused by interactions between metal ions and functional groups, such as carboxyl groups, on the surface of the bioadsorbent (Romero-Gonzalez et al., 2005, 2006). The carboxyl, amine, and hydroxyl groups on the biomass surface were involved in adsorption of Pb^{2+} ions (Lawal et al., 2010; Yan et al., 2010). Ion exchange between lignin, tannins, cellulosic compounds, and heavy metals, according to Ho (2006), dominated in the use of agricultural waste as an adsorbent. Ion exchange during adsorption of Hg^{2+} onto a flax shive and then the chemical reduction of adsorbed Hg^{2+} to Hg^{0} by lignin and humic compounds occurred (Shukla et al., 2002). Ion exchange and hydrogen bonding induced adsorption of heavy metal ions by sawdust (Gupta et al., 2003).

3.2. Adsorption of methylene blue

Methylene blue, a cationic dye, is a typical adsorbate. Han et al. (2006), who used wheat chaff to adsorb MB, determined that the