Journal of Molecular Liquids xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Review

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Nanoadsorbents for pollutant's removal: A review

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ARTICLE INFO

Article history:
Received 17 December 2014
Received in revised form 1 January 2015
Accepted 3 January 2015
Available online xxxx

Keywords:
Nanoadsorbents
Heavy metals
Dyes
Modeling
Isotherms
Kinetics
Thermodynamics

ABSTRACT

The potential of nanomaterials as nanoadsorbents and their many advances are discussed in details in this review article. Adsorption is one of the most promising techniques applied for the decontamination of wastewaters from dyes and heavy metals. Nanomaterials possess a series of unique physical and chemical properties. A very important one is that most of the atoms that have high chemical activity and adsorption capacity are on the surface of the nanomaterials. Various nanoadsorbents were elsewhere overviewed in treating contaminated water; their advantages and drawbacks in such applications were evaluated. The implications of nanoadsorbents to public health and their way forward for facilitating environmental sustainability were also discussed.

Contents

1. Introduction

"Nano" is derived from the Greek word for dwarf. A nanometer is one billionth of a meter (10^{-9}) and might be represented by the length of ten hydrogen atoms lined up in a row. In nature, nanotechnology first emerged billions of years ago at the point where molecules began to arrange in complex forms and structures that launched life on earth. In the early 20th century, the first observations and size measurements of nanoparticles using an ultramicroscope were made possible in a study of gold sols and other nanomaterials with sizes down to 10 nm and less [1]. Zsigmondy was the first to characterize particle sizes using the term nanometer and he developed the first system of classification based on particle size in the nanometer range [1]. In 1980s, nanotechnology and nanoscience got a boost with two major developments: the birth of cluster science and the invention of the scanning tunneling microscope (STM). Major current tools for nanotechnology measuring

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http://dx.doi.org/10.1016/j.molliq.2015.01.004
0167-7322/© 2014 Published by Elsevier B.V.

Please cite this article as: G.Z. Kyzas, K.A. Matis, J. Mol. Liq. (2014), http://dx.doi.org/10.1016/j.molliq.2015.01.004

include many devices such as STM, scanning probe microscopes (SPMs), atomic force microscopy (AFM) and molecular beam epitaxy (MBE). Diagnosis of particles at the nanoscale level contributed extensively to the production, modification and shaping of structures that were used in different industrial, health and environmental applications.

At the nanoscale level, materials are characterized by different physical, chemical and biological properties than their normal size equivalents. For instance, materials as metals, metal oxides, polymers and ceramics, and carbon derivatives (carbon nanotubes and fullerenes) have a higher ratio of surface area to particle size at the nanoscale level. In other words, the surface area of particles increases with decreasing particle size and as such, nanoscale particles exhibit different optical, electrical, and magnetic properties from the properties exhibited by macroscopic particles [2]. These remarkable characteristics of particles at the nanoscale level possibly originated from the increase in the number of surface atoms with the decreasing of particle size.

Nanotechnology can easily merge with other technologies and modify, endorse or clarify any existing scientific concept, which is why it is so called a "platform" technology. The use of nanotechnology in the future is expected to expand into numerous industrial applications and help decrease production costs by reducing energy consumption, attenuate environmental pollution and increase the production efficiencies in developed countries. Moreover, nanotechnology may be a useful tool to address different social problems of developing countries' such as the need for clean water and the treatment of epidemic diseases [3]. Nanoscience and nanotechnology may not provide all the solutions for the ever increasing problems of this planet but could help the sustainable development of many social communities.

Many potential benefits of nanotechnology have already been identified by many researchers in the environmental and water sector, medicine, and in several industry applications but the future nanotechnology might bring innovations that can answer many existing scientific questions [3]. Hence, nanotechnology is going to play an important role in addressing fundamental issues such as health, energy and water. Major potential environmental benefits of nanotechnology were reported in the draft nanomaterial research strategy by Savage et al. [4], including: (i) early environmental treatment and remediation; (ii) stronger and lighter nanomaterials; and (iii) smaller, more accurate and more sensitive sensing and monitoring devices.

The potential of nanomaterials as nanoadsorbents and their many advances afforded in the separation and pre-concentration of a variety of analytes have been also outlined [5]. It is fact that numerous works have been recently published with a primary goal of investigating the removal of different pollutants (either in gas or liquid medium) using adsorbent materials [6–22]. But nanoadsorbents (nanomaterials) possess a series of unique physical and chemical properties. A very important one is that most of the atoms that have high chemical activity and adsorption capacity are on the surface of the nanomaterials. Various nanoadsorbents were elsewhere overviewed in treating contaminated water; their advantages and drawbacks in such applications were evaluated [23]. The implications of nanoadsorbents to public health and their way forward for facilitating environmental sustainability were also discussed.

2. Isotherm and kinetic equations

In this study, the examples taken from literature regarding the use of nanoadsorbents were explained and analyzed based on some theoretical equations (models). According to those, some crucial adsorption parameters such as the adsorption capacity and kinetic rate were evaluated.

2.1. Isotherm models

It is necessary to form the most appropriate adsorption equilibrium correlation in the attempt to discover innovative adsorbents to gain access to an ideal adsorption system [24] which is vital for consistent prediction of adsorption parameters and quantitative comparison of adsorbent behavior for various adsorbent systems (or for varied experimental conditions) [25,26]. Adsorption isotherms, which are a common name of equilibrium relationships, are essential for optimization of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents, and productive design of the adsorption systems since they explain how pollutants interrelate with the adsorbent materials [27,28] (Table 1).

Explaining the phenomenon through which the preservation (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a persistent temperature and pH takes places, in broad-spectrum, an adsorption isotherm is an invaluable curve [29,30]. The mathematical association which establishes a significant role towards the modeling analysis, operational design and applicable practice of the adsorption systems is normally represented by plotting a graph between solid-phase and its residual concentration [31].

When the concentration of the solute remains unchanged as a result of zero net transfer of solute adsorbed and desorbed from sorbent surface, a condition of equilibrium is achieved. These associations between the equilibrium concentration of the adsorbate in the solid and liquid phase at a persistent temperature are defined by the equilibrium sorption isotherms. Linear, favorable, strongly favorable, irreversible and unfavorable are some of the isotherm shapes that may form.

Understanding of the mechanism of adsorption, surface properties, along with the extent of affinity of the adsorbents is delivered by the physicochemical parameters accompanied by the fundamental thermodynamic suppositions [32].

In terms of three basic approaches, an extensive diversity of equilibrium isotherm models (Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm) has been framed in the past [33]. The first approach to be mentioned is kinetic consideration, while thermodynamics being the second one. A state of dynamic equilibrium with both adsorption and desorption rates in balance is an adsorption equilibrium and a framework of

Table 1
Lists of adsorption isotherms (non-linear forms).

Isotherm	Non-linear form	References
Langmuir	$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$	[38]
Freundlich	$Q_e = K_F (C_e)^{1/n}$	[39]
Dubinin–Radushkevich	$Q_e = (Q_s) e^{-k_{DR} \varepsilon^2}$	[40]
Tempkin	$Q_e = \left(\frac{RT}{b_T}\right) \ln(A_T C_e)$	[41]
Flory–Huggins	$\frac{\theta}{C_0} = K_{FH} (1-\theta)^{n_{FH}}$	[42]
Hill	$Q_e = \frac{Q_{S_H} C_e^{n_H}}{K_D + C_e^{n_H}}$	[43]
Redlich–Peterson	$Q_e = \frac{K_R C_e}{1 + a_R C_e^g}$	[44]
Sips	$Q_e = \frac{K_S C_e^{\beta_S}}{1 + a_S C_e^{\beta_S}}$	[45]
Toth	$Q_e = \frac{K_T C_e}{(a_T + C_e)^{1/t}}$	[46]
Koble–Corrigan	$Q_e = \frac{A C_e^n}{1 + B C_e^n}$	[47]
Khan	$Q_e = \frac{Q_s b_K C_e}{(1 + b_K C_e)^{a_K}}$	[48]
Radke–Prausnitz	$Q_e = \frac{a_{RP} r_R C_e^{\beta_R}}{a_{RP} + r_R C_e^{\beta_R - 1}}$	[49]
BET	$Q_e = \frac{Q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)(C_e/C_s)]}$	[50]
FHH	$\ln\left(\frac{C_e}{C_s}\right) = -\frac{\alpha}{RT}\left(\frac{Q_s}{Q_e d}\right)^r$	[51]
MET	$Q_e = Q_s \left(\frac{k C_e}{\ln(C_s - C_e)}\right)^{1/3}$	[52]

Please cite this article as: G.Z. Kyzas, K.A. Matis, J. Mol. Liq. (2014), http://dx.doi.org/10.1016/j.molliq.2015.01.004