Review

Adsorption of rare earth metals: A review of recent literature

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A B S T R A C T

Rare earth elements (REEs) have gained considerable attention due to their unique properties and their use in huge range of industrial applications. They are widely used in different sectors such as, nuclear energy, metallurgy, medicine, chemical engineering, electronics, and computer manufacturing. As a result, the recovery of REEs is a significant issue that needs appropriate attention. There are many methods to recover REEs such as precipitation, filtration, solvent extraction etc. but these methods are not economically attractive. Among the available methods, adsorption has gained wider attention because of its simplicity, high efficiency and low cost. This review article presents the recently published literature (after 2013) regarding the removal of rare earth metals from aqueous solution by different low cost adsorbents. For this purpose, best applying model (isotherm, kinetic), thermodynamic studies and other factors which influence the adsorption process (such as the effect of solution pH, contact time, temperature and adsorbent's dose) are also discussed.

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1. Introduction

Rare earth (RE) group consists of seventeen elements and is divided into two categories namely the light rare earths (LRE) and the heavy rare earths (HRE). The former include cerium (Ce), lanthanum (La),

neodymium (Nd), praseodymium (Pr), samarium (Sm), and the latter include gadolinium (Gd), europium (Eu), terbium (Tb), dysprosium (Dy), thulium (Tm), ytterbium (Yb), lutetium (Lu), yttrium (Y), holmium (Ho) and erbium (Er) [1]. RE group belongs to a multi applicable group which contributes to important sectors such as the mundane (lighter flints, fluorescent lamps), the high-tech (batteries, lasers, super-magnets), and the futuristic (high-temperature superconductivity, information storage, conservation and transport of energy) fields,

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due to their diverse chemical, electrical, metallurgical, magnetic, optical, and catalytic properties [2]. China, United States of America (USA) and Australia are the leading producers of rare earth elements (REEs), with China holding 90% of the global production [3].

Moreover, aquatic nuclear industry radioactive waste consists of various toxic pollutants, including long-lived radiotoxic trivalent actinides [4]. Consequently, the treatment of the aforementioned waste is of great importance for environmental and safety reasons. Trivalent actinides have high radiotoxicity and as a result they are not easy to be used in a lab setting. For this purpose, in recovery of trivalent actinides from radioactive waste, REEs, such as europium and neodymium, are used as homologues for trivalent actinides due to their similar physicochemical properties [5].

In recent years, with ever-increasing demand for high-purity REEs (rare earth elements) and their compounds, purification of individual REEs have gained considerable attention [6,7]. There are many methods which are applied in order to separate, purify and preconcentrate the REEs, such as adsorption, liquid — liquid extraction, chemical precipitation and ion exchange [8]. Among them, adsorption has been recognized as one of the most promising methods due to its simplicity, high efficiency, and wide-range availability [2,9–25].

There are various adsorbent materials (raw and modified) used for the removal of REEs from aqueous solutions such as, granular hybrid [26], carbonized polydopamine nano carbon shells [27], modified red clays [12], cysteine-functionalized chitosan magnetic nano-based particles [11], silica gel particles modified with diglycol amic acid groups [9], marine sediments [28] and biopolymer microcapsules containing $D_2EHPA/TOPO$ extract [29]. But after a detailed screening of the literature, there is only an old review article published in 2013, summarizing the published literature (1995–2011) on the use of biosorbents for REEs adsorption [30]. However, to the best of authors' knowledge, no other review is yet available discussing the progress on the removal of REEs from aqueous solution by different adsorbents.

The main goal of this review is to provide the recent progress regarding the REEs adsorption by various adsorbents. For this purpose, only recent studies (after 2013) were extensively discussed in terms of adsorption capacity, fitted isotherm, kinetic models and thermodynamic aspects.

2. Equilibrium modeling.

In order to organize, establish and understand an adequate design model for the removal of rare earth metals from aqueous media, isotherm, kinetics, desorption and thermodynamic studies are essential basic prerequisites (Table 1).

Adsorption isotherms models are extensively used to provide information about the amount of adsorbed ion by a certain adsorbent and about the interaction between the adsorbents and adsorbate [36]. In a recent review, Rangabhashiyam et al. [37] studied the use of two, three, four and five parameters isotherms models and concluded that in case of two parameters isotherm model, Langmuir and Freundlich models have the best fit. Langmuir isotherm assumes that all binding sites have equal affinity for the adsorbate, resulting to the formation of monolayer of adsorbed molecules (saturation of the adsorbent). Freundlich isotherm describes adsorption onto heterogeneous surfaces that provide adsorption sites of varying affinities and also by using this isotherm model, the adsorbent will not be saturated.

Kinetics studies are useful tool to find the optimum conditions for full-scale adsorption process [38]. Kinetic modeling reveals the mechanism of adsorption and potential rate-controlling steps such as mass transport or chemical reaction processes [38,39]. The most common are the pseudo-first and pseudo-second order kinetic equations. It is

Table 1
Isotherms, kinetics and thermodynamic equations.

Expression	Equation form	Plot	Parameters
Non linear Langmuir [31]	$q_e = q_m \frac{b_L C_e}{1 + b_L C_e}$	–	q_m (mg/g): saturated monolayer adsorption capacity b_L (L/mg): constant related to the energy of sorption and equilibrium constant
Linear Langmuir-1	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{b_L q_m}$	$\frac{C_e}{q_e}$ vs. C_e	
Linear Langmuir-2	$\frac{1}{q_e} = \left(\frac{1}{b_L q_m}\right)\frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$	
Linear Langmuir-3	$q_e = q_m - \left(\frac{1}{b_L}\right)\frac{q_e}{C_e}$	q_e vs. $\frac{q_e}{C_e}$	
Linear Langmuir-4	$\frac{q_e}{C_e} = b_L q_m - b_L q_e$	$\frac{q_e}{C_e}$ vs. q_e	
Non linear Freundlich [32]	$q_e = K_F C_e^{1/n}$	–	K_F: constant related to adsorption capacity or sorption equilibrium n: constant related to the adsorption intensity or degree of favorability of adsorption
Linear Freundlich	$\ln q_e = , \ln K_F + \frac{1}{n}, \ln C_e$	$\ln q_e$ vs. $\ln C_e$	
Non Linear pseudo-first-order kinetic	$q_t = q_e(1 - \exp^{-k_1 t})$	–	q_t (mg/g): is the amount adsorbed at time t (min) k_1 (min^{-1}): is pseudo-first-order rate constant
Linear pseudo-first-order kinetic [33]	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$\ln (q_e - q_t)$ vs. t	
Non linear pseudo-second-order kinetic [34]	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	–	q_t (mg/g): is the amount adsorbed at time t (min) k_2 (g/mg min): is pseudo-second-order rate constant
Linear pseudo-second-order kinetic [35]	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	t/q_t vs. t	
Gibbs	$\Delta G^0 = -RT \ln b_L$ [a] or $\Delta G^0 = -RT, \ln\left(\frac{q_e}{C_e}\right)$ [b] $\Delta G^0 = -RT \ln K$ [c] $\Delta G^0 = -RT \ln K_0$ [d]	–	Free energy change
Van't Hoff	$\ln(b_L) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$ or $\ln\left(\frac{q_e}{C_e}\right) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$ $\ln(K) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$ $\ln(K_0) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$	$\ln (b_L)$ vs $\frac{1}{T}$ or $\ln\left(\frac{q_e}{C_e}\right)$ vs $\frac{1}{T}$ or $\ln (K)$ vs $\frac{1}{T}$ $\ln (K_0)$ vs $\frac{1}{T}$	Enthalpy change Entropy change
Clausius Clapeyron	$\Delta H^0 = \frac{RT_1 T_2}{T_2 - T_1}\left(, \frac{\ln C_{e1}}{\ln C_{e2}}\right)$	–	Enthalpy change

For isotherms and kinetics studies: C_e (mg/L) and q_e (mg/g) are the equilibrium liquid phase concentrations and amount of solute adsorbed at equilibrium, respectively. R is the gas constant (8.314 J/mol K) and T is the absolute temperature (K).

[a] b_L in (L/mol) from Langmuir model.

[b] $\frac{q_e}{C_e}$ is the ratio where q_e is adsorbed rare earth metal at concentration (mg/L) and C_e is the residual rare earth metal concentration in the solution (mg/L).

[c] $K = q_m X b_L$ calculated from Langmuir constants (q_m) is the maximum adsorption capacity in mg/g and b_L units in L/mg.

[d] K_0 can be evaluated by plotting $\ln(q_e/C_e)$ versus q_e by extrapolating to $q_e = 0$.