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Removal of Cadmium Ions from Aqueous Solutions Using Burnt Rock

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Abstract

Adsorption treatment of industrial wastewater and reservoir water from toxic metals can reduce the anthropogenic load on water bodies. The efficiency of using an adsorbent obtained on the basis of local mineral raw material, namely burnt rock from the Erunakovskoe coal deposit in the Kemerovo Region, to remove heavy metal ions from aqueous solutions is shown. The kinetics of cadmium ion extraction from aqueous solutions, the adsorption models of Freundlich, Langmuir and Dubinin-Radushkevich, and their significance for the description of heavy metal ion recovery from aqueous solutions using burnt rock were studied. The dependence of adsorption on the acidity (pH) of the medium has been established. A maximum adsorption capacity of 30 to 40 mg/g was achieved at pH 12.0. Chemical modification with alkali (NaOH) at pH 12 leads to an increase in the degree of cadmium ions extraction. Within the studied concentration range, the Freundlich and Langmuir isotherms are more consistent with the experimental data on the equilibrium adsorption of metal ions on burnt rock, compared to the Dubinin-Radushkevich model.

Keywords: adsorption, heavy metals, adsorption models, burnt rock, water treatment

INTRODUCTION

The presence of non-biodegradable and carcinogenic heavy metals in the ecosystem is still a substantial danger for human health [1]. The major sources of water pollution with heavy metals are industry (mining, galvanic, metallurgical, textile), as well as agricultural facilities.

Many methods and technologies have been developed for the purification of industrial waste waters and reservoir waters to decrease anthropogenic load on water objects. As a rule, the final stage in the implementation of these technologies is post-treatment of waste waters with the help of sorption materials.

Comprehensive studies have been carried out in the area of pollutant adsorption by various adsorbents. In comparison with other methods to remove pollutants, adsorption as a technological process is easier to implement, results in the formation of smaller amounts of precipitates, and is considered to be ecologically friendly process with low investment expenses [2].

However, relatively cheap sorbents capable of efficient water purification from heavy metal compounds and other pollutants are used in the Russian Federation not to a full extent. There are many natural sorbents that remain insufficiently studied yet and therefore have not won broad industrial application, but clearly pronounced adsorption properties and broad occurrence in nature define the reasonability of their use. For instance, quartz sand, burnt and clayey rocks, zeolites are rather well known in our country. The advantages of these substances include high selectivity and stability against heating, ionizing radiation, and organic solvents [3].

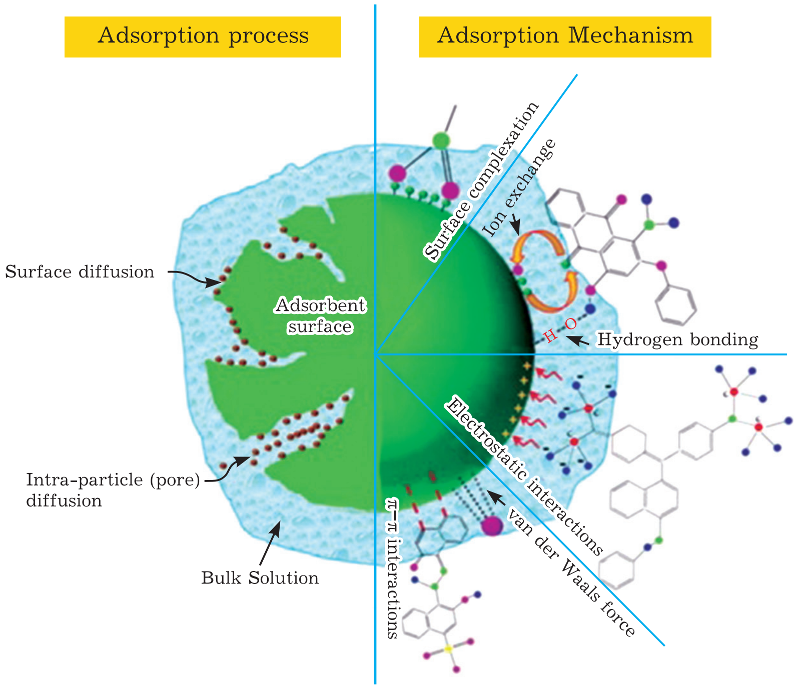

Fig. 1. Adsorption mechanisms. Reproduced from [11] with permission from the Royal Chemical Society.

Numerous studies report on alternative adsorbing materials obtained from the wastes and by-products from natural sources, and used to purify waste waters from pollutants [4]. These natural and modified materials demonstrate rather good efficiency in removing pollutants.

Carbon-containing materials are preferable adsorbents to remove chemical pollutants because of the high porosity, great diversity of functional groups, adjustable surface functionality through modification, and high adsorption capacity.

Carbon adsorbents, such as grapheme and its derivatives, carbon nanotubes, activated coal and biochar, zeolites, chitosans, are often used to remove heavy metals from aqueous solutions [2, 5].

In addition, carbon materials are cheap, readily available and chemically stable. The prevailing adsorption mechanism that works during the removal of chemical substances with the help of coal is electrostatic interaction, less significant are physical sorption, chemisorption, π-electron dispersion interactions [6–11] (Fig. 1).

The results on the purification of natural water bodies from radionuclides, in particular sorption-based strontium radionuclide concentrating from aqueous solutions under static and dynamic conditions using natural aluminosilicate, are presented in [12]. Natural aluminosilicates are available and environmentally safe, which is their most substantial advantage. This allows efficient application of the adsorbents obtained on the basis of local mineral raw materials to purify natural and waste waters for various regions of the country.

Some minerals and inorganic materials, such as clay, zeolites, magnesium oxide nanoparticles, aluminium oxide, silicon dioxide or ion exchange resins, also can to remove pollutants from water. Ion exchange resins are used to remove heavy metals and other toxic ions, and to soften water. In addition, many synthetic resins possessing high adsorption capacity and improved mechanical properties have been developed [13, 14].

Clayey minerals are also used as adsorbents of heavy metals and organic pollutants. Clay is characterised by high porosity, and large specific surface area. Natural and modified clays are efficiently used as adsorbents for waste waters, dumps, oil spillages, etc. The best studied kinds of clay are montmorillonite, illite, saponite, bentonite, kaolinite, and vermiculite [15, 16].

Mineral raw material extracted in open pit mines at coal deposits were used in [3]. The authors explained the choice of adsorbing system by the ability of heavy metal cations to form low-soluble compounds through ion exchange with sorbents. Natural materials were activated with the solution of hydrochloric acid to enhance sorption activity. Experimental data were described involving the classical Langmuir, Temkin, Freundlich and Dubinin-Radushkevich theories.

Various methods of chemical modification are applied to introduce heteroatoms, first of all oxygen, nitrogen, and sulphur, onto carbon surfaces to improve the surface functional possibilities and sorption properties with respect to heavy metals in aqueous solutions [5].

For instance, the authors of [17] achieved higher degree of metal ion binding by introducing the functional groups on adsorbent surface by treating the solid material with the solutions of alkali, sodium hypochlorite, hydrogen peroxide or nitric acid after carbonisation.

The goal of the work was to study the adsorption capacity of burnt rock from the Erunakovskoe coal deposit (the Kemerovo Region) with respect to cadmium ions. The objectives that have been put forward in the study include:

– investigation of the kinetic parameters of the extraction of heavy metal cations from aqueous solutions by adsorption using the burnt rock;

– an increase in adsorption capacity by the modification of materials;

– investigation of adsorption models and their relevance to describe the recovery of heavy metal ions from aqueous solutions.

EXPERIMENTAL

Materials and methods of investigation

The model aqueous solutions of cadmium nitrate (chemically pure reagent grade) were used to simulate polluted waters. The concentration of Cd(2+) ions was varied within the range of 0.0001–0.1 mol/L. Changes in the concentration of polluting ions were determined by titration with the solution of disodium salt of ethylenediamine tetraacetic acid (EDTA-Na_2, Trilon B) before purification process and after purification by adsorption. Constant acidity (pH 8) during titration was maintained with the help of a buffer ammonia system. The equivalence point was detected from the change of eriochrome black T colour from violet to light-blue.

Decarbonisation of initial raw material was performed at a temperature of 600–800 °C for 3 h to achieve more complete burning of coal residue. To modify the adsorbents, the solutions of sodium hydroxide [18] with different acidity values – pH 8, 10, 12 and 14 were prepared. The treatment was performed for 30 min at 20 °C. The modified adsorbent was washed with distilled water to achieve the neutral pH.

Kinetic studies and adsorption models

The kinetic studies were carried out under isothermal conditions with contact time up to 180 min.

The analytical description of adsorption isotherms and calculation of the adsorption equilibrium parameters were made using Langmuir (1), Freundlich (2) and Dubinin-Radushkevich equations (3) [19–21]:

$$a = a_{max}KC_{eq}/(1 + KC_{eq}) \qquad (1)$$

$$a = \beta C_{eq}^{1/n} \qquad (2)$$

$$\lg a = \lg a_{max} - [2.303R^2T^2 \cdot \lg (C_s/C_{eq})]/E^2 \qquad (3)$$

where a is adsorption amount; a_{max} is the limiting adsorption amount; K is the adsorption equilibrium constant; C_{eq} is the equilibrium ion concentration; β is the constant in the Freundlich equation; n is a dimensionless coefficient in the Freundlich equation; 2.303 is recalculation coefficient; R is the universal gas constant; T is absolute temperature; C_s is salt solubility; E is the free energy of adsorption.

RESULTS AND DISCUSSION

Preliminary investigation of the kinetics of cadmium ion recovery from the model aqueous solutions with the help of burnt rock show that the processes are rather rapid, and the concentration of cadmium ions decreases to 40–30% during the contact within the first 20–30 min. Then adsorption rate is observed to decrease and approach the equilibrium state, which is achieved after 45–60 min.

Adsorption isotherms were plotted, relying on the experimental data on the studies of metal ion adsorption from aqueous solutions by the natural and modified forms of adsorbents (Fig. 2). Adsorption process depends on the pH of the medium. The maximal adsorption capacity (30 to 40 mg/g) was achieved at pH 12.0. Therefore, the best results were obtained for modification with NaOH at pH 12.0: for cadmium ions the degree of aqueous solution purification after 30 min was more than 60%.

Rather high selectivity of sorbents treated with a NaOH solution at pH 12.0 is explained by the fact that tightly held metal hydroxide layers are formed on adsorbent surface. This ensures additional chemical interaction between the introduced functional groups and metal ions. So, the surface of the modified material exhibited a higher affinity to cadmium ions.

The reduction of the Freundlich empirical equation to the linear form gives us the possi-

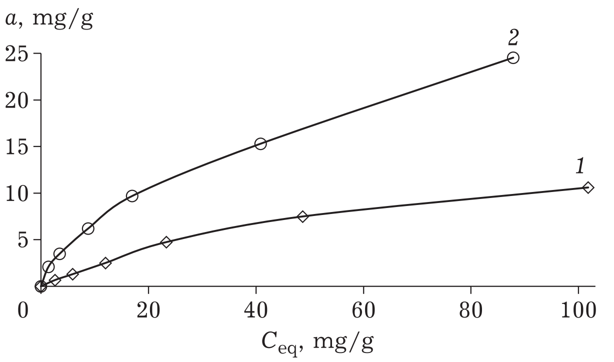

Fig. 2. Isotherms of cadmium ion adsorption: *1* – non-modified adsorbent; *2* – adsorbent after modification with NaOH. Here and in Fig. 3–5: C_{eq} – the equilibrium concentration of cadmium ions; a – amount of adsorption.

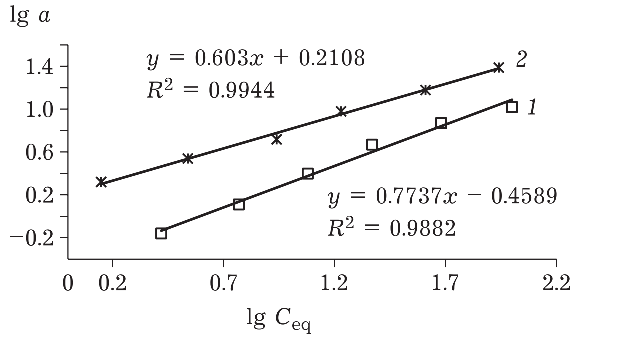

Fig. 3. Adsorption isotherms for cadmium ions in the coordinates of Freundlich equation: *1* – adsorbent without modification; *2* – adsorbent after modification with. For designations, see Fig. 2.

bility to determine the constant β and the parameter $1/n$ (Fig. 3). Langmuir model in the linear coordinates allowed us to calculate the limiting adsorption amount a_{max} and the constant of adsorption equilibrium K for adsorbent samples under investigation. Deviation factor (R^2) for Langmuir isotherm model points to the homogeneity of active centres with monolayer coverage of the adsorbent surface by the adsorbate (Fig. 4). By applying the Dubinin-Radushkevich model (Fig. 5), from the linear form of equation we calculated the characteristic adsorption energy E and determined the volume of pores (W) occupied by the adsorbed substance. The calculated parameters of adsorption are listed in Table 1.

To determine the limiting stage of diffusion, we studied the dependence of the degree to which adsorption equilibrium was achieved (γ) and the dimensionless kinetic parameter (T) on the duration of solution mixing (t) [18]. The mass transfer coefficient (β_m) was calculated as parameter characterising the rate of absorption of the substance to be removed by the unit volume of the adsorbent:

$$\beta_m = \frac{dC}{dt(C_t - C_{eq})} \tag{4}$$

The value of T, proportional to the time of process course, was determined according to equation:

$$T = A\beta_m t \tag{5}$$

where A is the proportionality coefficient.

The adsorption of ions, according to the linear dependence $T = f(t)$, is limited by the external mass exchange for 5–10 min. Ten minutes later, the deviation from the curve is observed, which points to the processes of internal diffusion of the

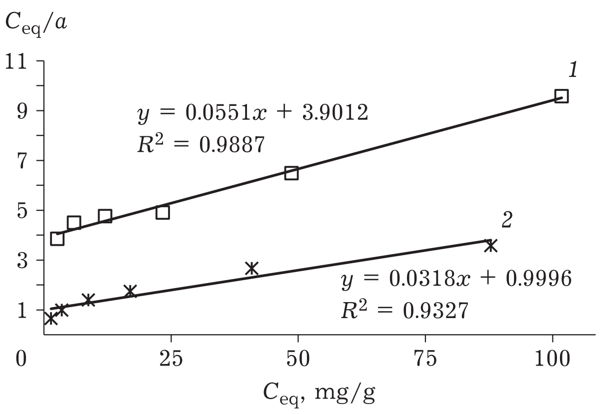

Fig. 4. Adsorption isotherms for cadmium ions in the coordinates of Langmuir equation: *1* – non-modified adsorbent; *2* – adsorbed modified with NaOH. For designations, see Fig. 2.

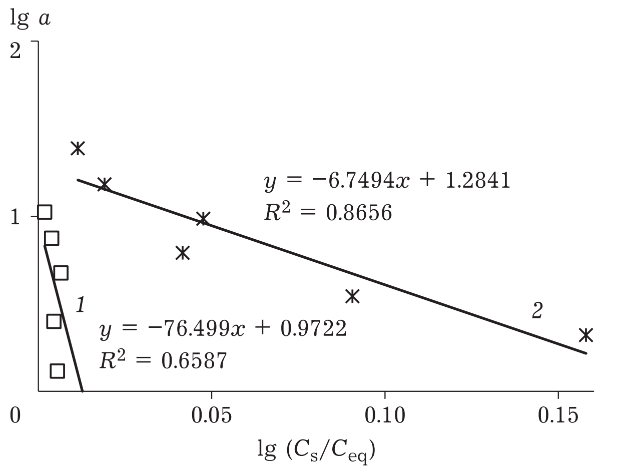

Fig. 5. Adsorption isotherms for cadmium ions in the coordinates of Dubinin-Radushkevich equation: *1* – non-modified adsorbent; *2* – adsorbent modified with NaOH. For designations, see Fig. 2. C_s – the solubility of salt.

TABLE 1

The parameters of heavy metal adsorption (recovery of Cd(2+) ions) from aqueous solutions on burnt rock

System under study	Purification degree, %	Langmuir equation		Dubinin-Radushkevich equation		
		a_{max}, mg/g	K	a_{max}, mg/g	E, kJ/mol	W, cm^3/g
Non-modified burnt rock	40.2	22.15	0.018	22.68	0.38	0.019
Modified burnt rock	76.3	31.05	0.027	35.13	1.38	0.022

adsorbate. The determined coefficient of external-diffusion mass transfer for non-modified burnt rock was 0.0039–0.0079 min^{-1}, for the modified burnt rock – 0.0091–0.033 min^{-1}.

CONCLUSION

The obtained results show that burnt rock may be considered as adsorption material to recover cadmium ions from aqueous solutions. The maximal adsorption capacity (from 30 to 40 mg Cd/g) is achieved by chemical modification with alkali (NaOH) at pH 12.0.

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