Comparison of acetic acid adsorption kinetics on different waste materials

Štrkalj, Anita; Glavaš, Zoran

JST&M 1(2021), 13 - 19
DOI: 10.57131/jstm.2021.1.2

Original scientific paper

COMPARISON OF ACETIC ACID ADSORPTION KINETICS ON DIFFERENT WASTE MATERIALS

Anita Štrkalj[1], Zoran Glavaš[1]

[1]The University of Zagreb Faculty of Metallurgy, Aleja narodnih heroja 3, Sisak, Croatia

ABSTRACT

In this paper, the adsorption properties of two metallurgical wastes (slag and anode dust) and two municipal wastes (eggshells and coffee grounds) were described. Acetic acid was used as the adsorbate Adsorption kinetic was monitored during the adsorption process. The obtained results showed that all tested waste materials can be used as potential cheap adsorbents. Adsorption took place relatively quickly. Equilibrium was reached in 15 minutes, and the adsorption kinetics followed the pseudo-first-order reactions, i.e., can be described by the Lagergren model. All q_e values calculated using Ho's model have a negative sign. That indicates that the Ho model is not suitable for describing the kinetics of the tested adsorption systems

Keywords: adsorption; metallurgical waste; municipal waste; kinetics

Corresponding Author:
Anita Štrkalj,
University of Zagreb Faculty of Metallurgy
Aleja narodnih heroja 3, 44 000 Sisak, Croatia
E-mail address: strkalj@simet.unizg.hr

1. INTRODUCTION

Waste materials are substances that generate in industry, households, agriculture, etc. Often, the waste cannot be used for further use and must be further processed or/and disposed of. As human activities become more intense, the amount of waste increases [1]. Landfilling is the least acceptable form of waste management from an economic, especially from an environmental point of view. Proper waste disposal requires adequate preparation of the disposal area, large areas, drainage of gas and water, etc., which is a significant financial expense. Often the waste is disposed of on unprepared surfaces or in nature, which is a direct danger to the environment. However, studies have shown that it is not always necessary to dispose of non-hazardous waste, i.e., that could be used for other purposes. That is especially true for industrial and municipal waste.

Industrial waste generates in production processes. Some industries produce large amounts of waste materials [2]. That is especially true of the metallurgical industry. In the metallurgical industry, in addition to a large amount of waste material, there are different types of waste. It occurs in almost every segment of production, such as iron production (blast furnace sludge, blast furnace slag, dust, etc.), steel production (electric arc furnace slag, electric arc furnace dust, and refractory material), production of castings (waste molding mixture, waste after castings cleaning), etc. Part of this waste returns to the production process, but the rest still requires adequate disposal.

Municipal waste is generated primarily in households, but this group includes all other waste materials similar in composition and properties to municipal waste. Its quantities are also significant and require proper management. Despite the opinion that about 80% of the content from household waste can be further processed, the rest still requires disposal [3].

The total waste generated in the EU in 2018 by all economic activities and households amounted to 2337 million tons. Of that, 38.5 % of waste materials were disposed of, and 37.9 % were recycled [4].

The other major environmental problem is the increasing amount of wastewater loaded with both organic and inorganic pollutants. Both types of pollution are dangerous for human health, but also flora and fauna. The most common inorganic contaminants are heavy metals such as chromium, nickel, lead, cadmium, etc. Most heavy metals are not dangerous in small amounts and are necessary for the normal functioning of organisms. However, in increased concentrations, they have a detrimental effect on the human body, causing various diseases and even death.

Organic pollutants in wastewater are usually phenols, pharmaceuticals, food acids such as acetic, citric, ascorbic, formic, and others. Acetic acid (HAc) is a colorless organic liquid compound with a distinctive sour taste and pungent smell. Acetic acid is used primarily for the production of polyvinyl acetate, cellulose acetate, synthetic fibers, and in the food industry. A lot of industrial wastewater containing acetic acid is discharged directly from chemical industries without treatment. Consequently, it can cause environmental pollution, such as water pollution, soil pollution, and air pollution. Prolonged exposure to 10 ppm of acetic acid vapor can lead to eyes, nose, and throat irritation. If the concentration is as high as 1000 ppm, it can seriously damage the eyes, nose, and respiratory tract [5].

Because of the above-mentioned, the common denominator of similar research is finding new methods for the utilization of waste for wastewater treatment. The adsorption properties of individual wastes are of high interest, which would enable its application in wastewater treatment processes. Adsorption has proven to be a simple and effective method for removing organic and inorganic contaminants from wastewater. The disadvantage of this method is the cost of the adsorbent. Using waste as an adsorbent would decrease the treatment cost, and reduce the amount of waste material for disposal [6-8].

In this article, the possibility of removing acetic acid from wastewater was presented. Adsorption was used as a method for removal. Industrial and municipal wastes were used as adsorbents in the research. Industrial waste is waste from the metallurgical industry (slag and anode dust), while municipal waste is common household waste (eggshells and coffee grounds). In the experiments, the adsorption kinetics was monitored using two kinetic models: the Lagergren model and the Ho model.

2. MATERIALS AND METHODS

In this paper, the adsorption kinetics of four adsorption systems were studied, as follows: slag/acetic acid, anode dust/acetic acid, eggshells/acetic acid, coffee grounds/acetic acid.

Slag is a waste generated in the metallurgical industry during steel production. It acts as a refining agent, collecting unwanted components from steel. Anode dust is a waste generated during the anode production (firing and transport) used for the electrolysis of alumina during the production of aluminium.

Eggshells and coffee grounds are wastes generated in the household during the preparation and consumption of food and appropriate beverages. The chemical composition of the waste materials was determined by inductively coupled plasma spectrometry ((ICP-OES) Optima 2100-Perkin Elmer).

All four waste materials were shredded, homogenized, and dried at 105 °C to constant weight. In this form, they were used as adsorbents.

Acetic acid as the adsorbate was used. It was prepared as an aqueous solution with a concentration of 0.5 mol/L using ultra-pure water.

The adsorption experiment was performed by a static (batch) method (without mixing), using 0.5 g of adsorbent in contact with 50 mL of the adsorbate. Adsorption temperature was 25 °C for a time of 60 min. After 5, 10, 15, 30, and 60 min, the solutions were filtered through a blue ribbon filter paper. In the filtrates, the concentration of acetic acid after adsorption is measured by the volumetric method. The obtained data were mathematically processed as follows:

- determination of adsorption capacity

$$q_e = \frac{(c_0 - c_e)}{m} \cdot V \tag{1}$$

where is:
c_0 - initial concentration of acetic acid, mg/L,
c_e - equilibrium concentration of acetic acid, mg/L,
m – the mass of adsorbent, g,
V – the volume of acetic acid, L.

- determination of adsorption kinetics:

Lagergren model:

$$\ln(q_e - q_t) = ln q_e - k_1 t \tag{2}$$

Ho model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where is:
q_t- adsorption capacity in time t, mg/g,
q_e - equilibrium adsorption capacity, mg/g,
t - contact time, min,
k_1 – first-order reaction rate constant, min,
k_2 – second-order reaction rate constant, g/mg·min

3. RESULTS AND DISCUSSION

Tables 1 and 2 show the chemical composition of the slag and the anode dust.

Table 1. Chemical composition of the slag

Element	Si	Ca	Mn	Mg	Al	Fe	Cr	Na	K	Ba	other elements
wt. %	47.0	23.80	14.30	5.33	4.18	1.33	0.13	0.07	0.06	0.01	3.79

Table 2. Chemical composition of the anode dust

Element	C	Al	Si	Ca	Fe	Na	Mg	Ni	other elements
wt. %	96.8	1.27	1.27	0.22	0.19	0.13	0.07	0.02	0.03

The chemical composition of eggshells showed that the major component is calcium (calcium oxide 96 %). The chemical composition of coffee grounds showed that the main component was carbon (98 %).
Figure 1 shows the adsorption capacity of acetic acid on slag, anode dust, eggshells, and coffee grounds depending on time. Figure 1 shows that all tested adsorbents show some adsorption properties. In all adsorption, a system at the time of contact (in the first five min.), very fast adsorption of acetic acid on the surface of the adsorbent occurs, followed by slightly slower adsorption. In all tested systems, dynamic equilibrium is achieved relatively quickly, in just 15 min.

At the moment of equilibrium, the best adsorption capacity had coffee grounds (1.95 mg/g), followed by anode dust (0.95 mg/g), slag (0.95 mg/g), and eggshells (0.69 mg/g). That was the result of the chemical composition. Namely, anode dust and coffee grounds are carbon materials that belong in the group of potential carbon-based adsorbents. Some other studies recorded that carbon materials had the best adsorption properties, whose leader is activated carbon - the best known and the most effective commercial adsorbent [9-11].
Slag, as well as eggshells, belongs to the group of potential adsorbents based on metal oxides. Slag showed slightly better adsorption properties because it consists of

several different oxides. The main component in slag is SiO_2 which is also a potential adsorbent. Zengin and Erkan [12] monitored the adsorption of acids and bases on SiO_2. The obtained results indicate good adsorption capacity. Eggshells show adsorption potential but with a slightly lower adsorption capacity. The reason is only one oxide (CaO) in the chemical composition of eggshells, which has a bit lower adsorption potential compared to other oxides and carbon.

To better understand the adsorption kinetics, the obtained results by kinetic models were processed (Figures 2 and 3).

Table 3 shows the kinetic parameters for the adsorption systems of slag/acetic acid, anode dust/acetic acid, eggshells/acetic acid, and coffee grounds/acetic acid.

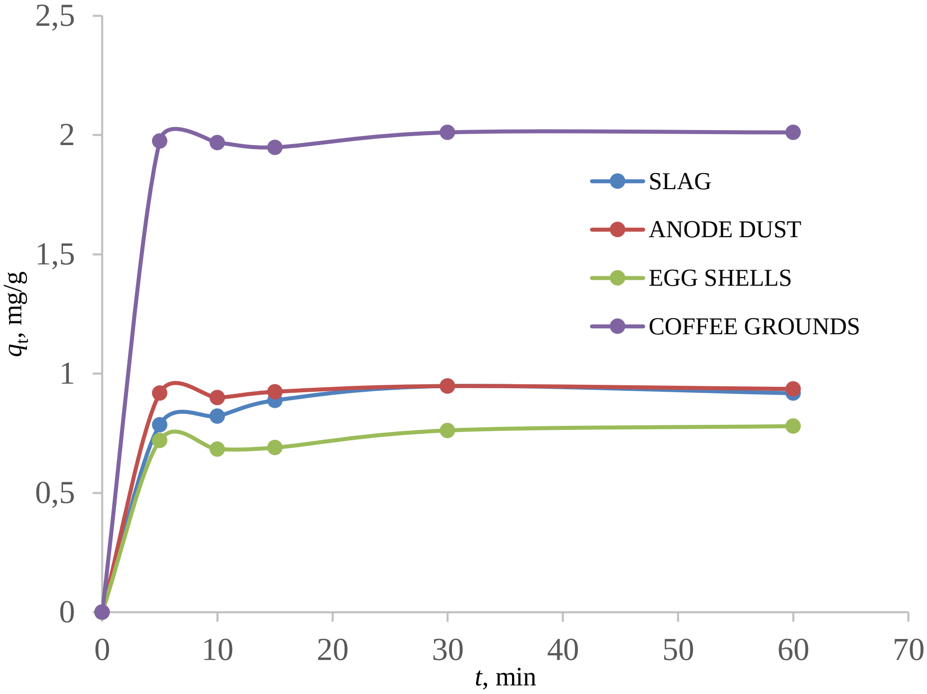

Figure 1. The adsorption capacity of acetic acid on the tested adsorbents depends on time.

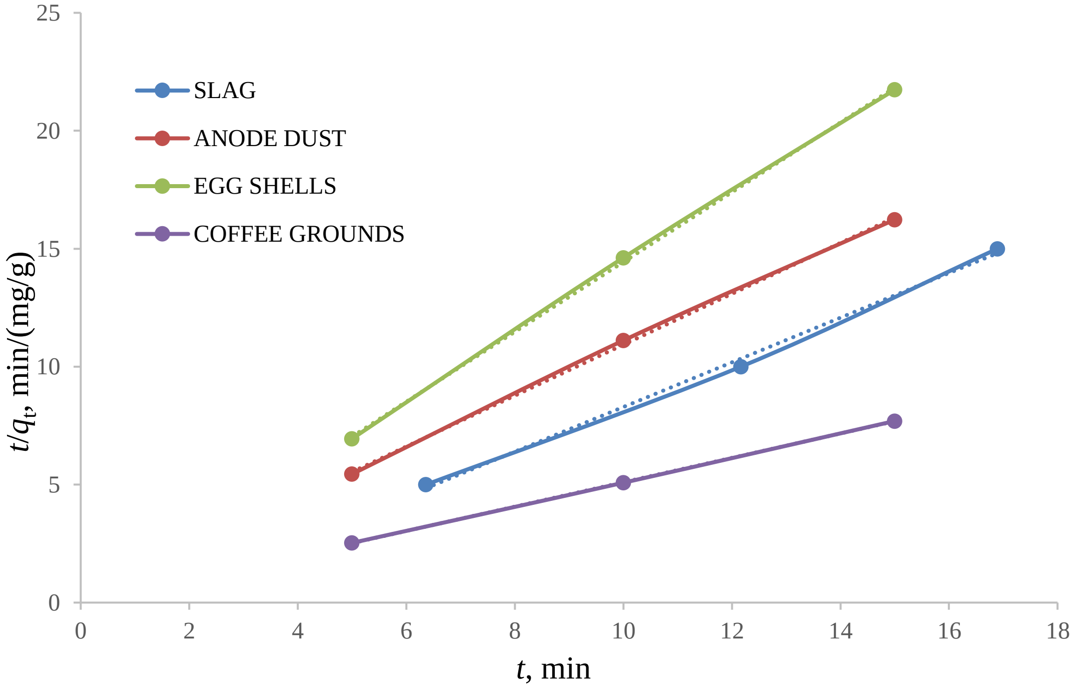

Figure 2. The Lagergren kinetic model for the tested systems

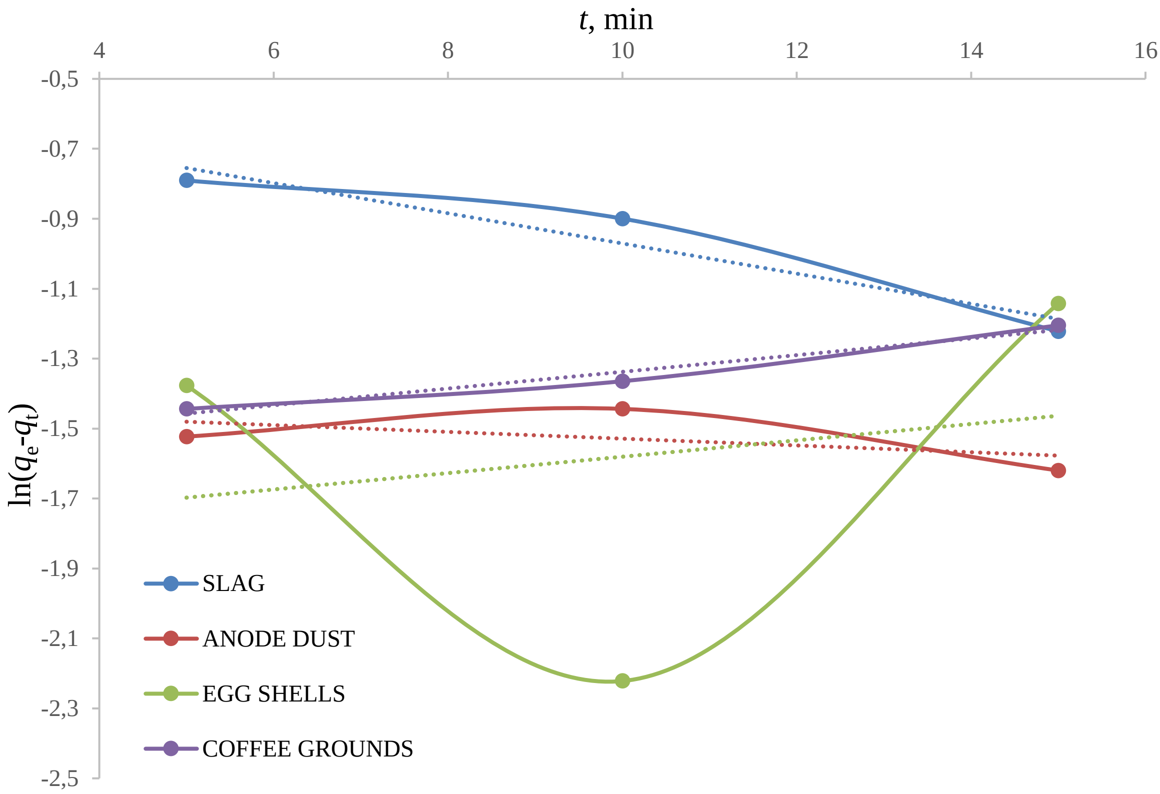

Figure 3. The Ho kinetic model for the tested systems

Table 3. Kinetic parameters for the adsorption systems of slag/acetic acid, anode dust/acetic acid, eggshells/acetic acid, and coffee grounds/acetic acid

	KINETIC MODEL			
	The Lagergren model		The Ho model	
slag/acetic acid	q_e, mg/g	0.310	q_e, mg/g	-23.202
	k_1, min	0.9463	k_2, g/mg·min	-8.991
	R^2	0.9965	R^2	0.9248
anode dust/acetic acid	q_e, mg/g	1.154	q_e, mg/g	-103.093
	k_1, min	1.0787	k_2, g/mg·min	-6.571
	R^2	0.9992	R^2	0.3019
eggshells/acetic acid	q_e, mg/g	0.696	q_e, mg/g	42.735
	k_1, min	1.4795	k_2, g/mg·min	-3.018
	R^2	0.9995	R^2	0.0425
coffee grounds/acetic acid	q_e, mg/g	0.940	q_e, mg/g	41.841
	k_1, min	0.5166	k_2, g/mg·min	-3.623
	R^2	0.999	R^2	0,9635

It is visible from Table 3 that the coefficients of determination (R^2) are higher for the Lagergren model, meaning that the adsorption in the examined systems follows the adsorption kinetics of the pseudo-first-order, taking place according to the Lagergren model.

The values of q_e obtained experimentally and q_e calculated by kinetic models were compared. The results for the q_e values obtained by the Lagergren model better correspond to the q_e values obtained experimentally, which also confirms the better description of the adsorption by the pseudo-first-order. In addition, all q_e values calculated using the Ho model have a negative sign, indicating that the Ho model is not suitable for describing the kinetics of the tested adsorption systems. Although most adsorption processes take place according to the kinetics of pseudo-second-order reactions (the Ho model), there are also a small number of adsorption systems whose kinetics follow pseudo-first-order reactions (the Lagergren model) [13]. Following the theoretical principles of the pseudo-first-order model, at low concentrations of adsorbate, the adsorption kinetics is affected only by a large number of free sites on the adsorbent surface [14, 15]. In this investigation, the acid of very low concentration (0.5 mol/L) was used. That probably was the reason why adsorption takes place according to the Lagergren model.

4. CONCLUSIONS

All tested adsorbents, slag, anode dust, eggshells, and coffee grounds showed appropriate adsorption properties under the tested conditions, meaning that they could play a role as potential adsorbents. Using that type of material would reduce the amount of waste material for disposal, and would help the removal of acetic acid from wastewater. The obtained results showed that the adsorption of acetic acid on the tested adsorbents is relatively fast. Equilibrium was reached in 15 minutes. Adsorption takes place in two steps. The first step is fast in general, and the second is somewhat slower. According to the obtained results, it was visible that the adsorption of acetic acid on slag, anode dust, eggshells, and coffee grounds follows the kinetics of pseudo-first-order reactions, taking place according to the Lagergren model.

Conflicts of Interest

The authors declare no conflict of interest.

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