ADSORPTION OF Cu(II) IONS BY MEANS OF FOUNDRY WASTE

Anita Štrkalj, Zoran Glavaš
University of Zagreb, Faculty of Metallurgy
Sisak, Croatia

Keywords: adsorption, Cu(II) ions, waste after shot blasting of castings

ABSTRACT
This article deals with the analysis of the adsorptive properties of the waste produced during the shot blasting of castings in foundries. During this process, particles of moulding mixture and scale that remained on the surface of the casting after removal from the mould are removed. Since this waste contains particles of moulding mixture (SiO_2, carbon, ...) and scale (i.e. iron oxides), which as individual components are known as satisfactory adsorbents, its adsorption properties towards Cu(II) ions in aqueous solution were investigated. The obtained results show that the investigated waste has a significant adsorption capacity for binding Cu(II) ions.

1. INTRODUCTION

Casting is one of the oldest processes that man uses to shape metal. With this process, metal objects, i.e. castings of different shapes, dimensions and mass, chemical composition and mechanical properties are obtained relatively quickly according to customer requirements. Precisely because of these possibilities, the production of castings in the world is growing. In 2020, 105.5 million tons of castings were produced in the world [1]. However, the production of castings is not a completely ecological way of production. Due to the large number of materials used during production (sand, binder, etc.) and partial processing of castings (cleaning (shot blasting), grinding), as well as due to mass production, considerable amounts of various hazardous and non-hazardous waste are generated. Part of the non-hazardous waste is returned to production, while the rest cannot be reused and is disposed of in landfills. In order to reduce disposal, today non-hazardous waste from foundries is being researched a lot in terms of its further use. Very often, waste moulding mixture and slag are used in construction, but also in road construction [2,3]. In addition, tests of the adsorption properties of waste foundry materials are very widespread [4-7]. This type of research and the possibility of using it for the purpose of adsorption is certainly very significant since this type of waste usually consists of metal oxides, such as SiO_2, Al_2O_3, MgO, CaO, FeO, Fe_2O_3 (sand, slag, scale, waste after shot blasting), clay (binders) and carbon-based materials (various additives to improve the properties of the moulding mixture) which are known as good adsorbents.
In this article, using equilibrium adsorption models, waste after shot blasting was investigated as a potential adsorbent for the removal of Cu(II) ions from aqueous solutions.

2. MATERIALS AND METHODS

The waste produced during the shot blasting of castings was used as an adsorbent in this article. The shot blasting process consists of hitting shot pellets of appropriate dimensions on the surface of the casting, during which the scale, i.e. metal oxides and particles of the moulding mixture that remain on the casting after removing the casting from the sand mould, are removed. Since the steel pellets hit the surface of the casting at high speed, some of them are damaged and due to the inappropriate granulometric composition, they can no longer be used for shot blasting. Damaged shot pellets, scale and sand that have fallen off the surface of the casting constitute waste. This type of waste and Cu(II) ions from the aqueous solution were used to form an adsorption system for the batch adsorption process.

For the experiment, 1 g of waste after shot blasting was used, which was placed in contact with 50 ml of a solution of Cu(II) ions of different concentrations (10, 30, 50, 70 and 100 mg/l). The research was carried out at a temperature of 22 °C and a pH of 5.69. After dynamic equilibrium was established (20 minutes), filtration was performed, and the concentration of Cu(II) ions in the obtained filtrates was determined by atomic absorption spectrometry.

From the data for the initial concentration of Cu(II) ions, the concentration of Cu(II) ions after adsorption (in the filtrate), the mass of the adsorbent and the volume of the adsorbate, the adsorption capacity q_e was determined according to the following equation [8]:

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

where is:

c_0 - initial mass concentration of Cu(II) ions in the solution, mg/l,

c_e - equilibrium mass concentration of Cu(II) ions in the solution, mg/l,

m - the mass of waste after the shot blasting, g,

V – a volume of the solution of Cu(II) ions, l.

Several adsorption isotherms models were used for the equilibrium study, and their mathematical models are presented in Table 1.

Table 1. Mathematical representation of the isotherms used to describe the equilibrium data of the adsorption system waste after shot blasting/Cu(II) ions [9]

Isotherm model	Mathematical representation
Langmuir	$q_e = \frac{q_m K_L c_e}{1 + K_L c_e}$
Freundlich	$q_e = K_F c_e^{1/n}$
Dubin-Radushevich	$q_e = q_m \exp^{(-k \cdot \varepsilon^2)}$
Eadie-Hoffstee	$q_e = q_m - \frac{q_e}{K_c c_e}$
Temkin	$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln c_e$

3. RESULTS AND DISCUSSION

The study of adsorbent-adsorbate interactions is very important for the potential application of the investigated adsorbent. Most often, this interaction is studied through the adsorption capacity, and the experimental data are processed with different adsorption models, whereby a more detailed insight into the adsorption process is obtained.

Figure 1 shows the equilibrium state of the adsorption system waste after shot blasting/Cu(II) ions via the dependence q_e= f(c_e).

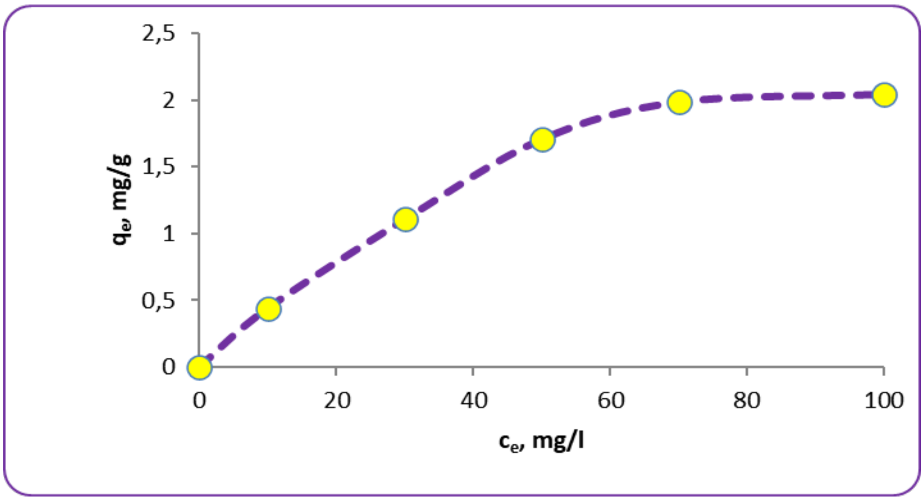

Figure 1. The equilibrium state of adsorption system waste after shot blasting/Cu(II) ions

It can be seen from Figure 1 that the waste after shot blasting shows the appropriate adsorption affinity towards Cu(II) ions. By increasing the concentration of ions in the solution, the adsorption capacity increases and at a concentration of 100 mg/l it reaches slightly more than 2 mg/g. An increase in the concentration of Cu(II) ions favours adsorption since more Cu(II) ions are available in the solution and, at the same time there are a lot of free places on the surface of the adsorbent, which is also an important factor in adsorption. This adsorbent-adsorbate behaviour is expected and is consistent with the behaviour of other waste materials that are being investigated as potential adsorbents [10 - 12].
However, from these data it is not possible to conclude about the type and method of adsorption (chemical or physical). For this reason, the equilibrium experimental data were processed using five isotherms models: Langmuir, Freundlich, Dubin-Radushevich, Eadie-Hoffsteev and Temkin according to the equations shown in Table 1.
Figures 2 - 6 graphically show the used adsorption isotherms models.

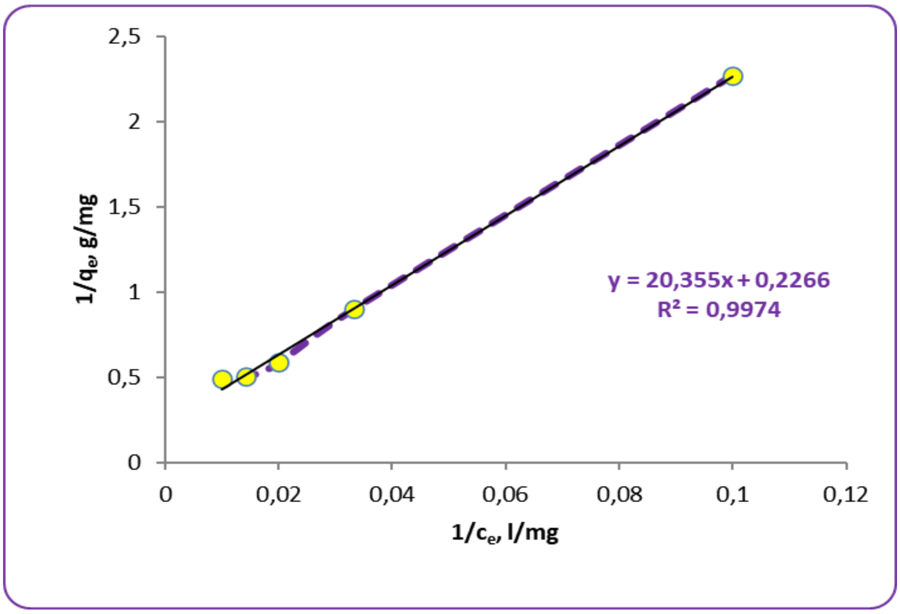

Figure 2. Langmuir adsorption isotherm model for the system waste after shot blasting/Cu(II) ions

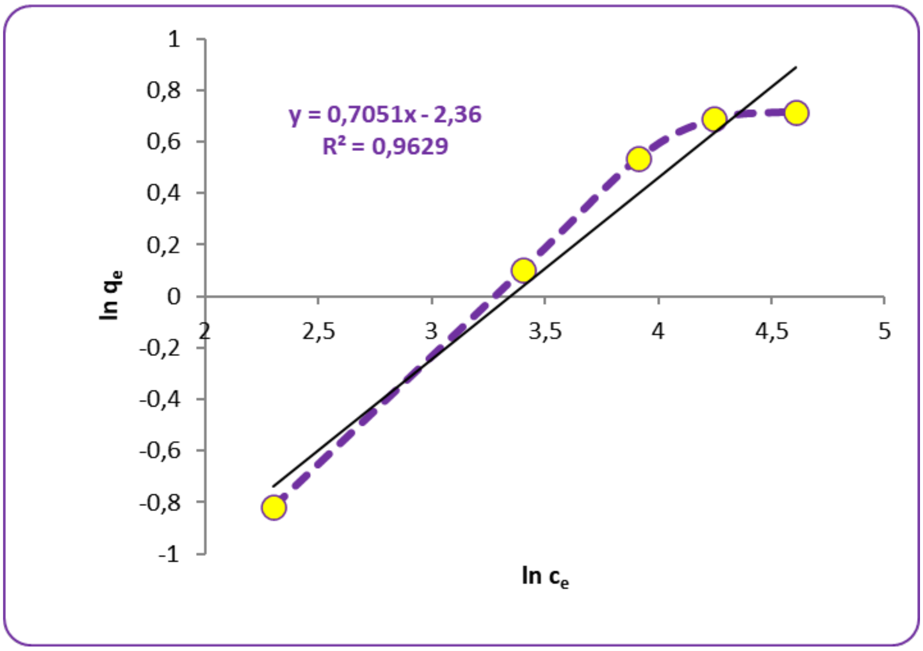

Figure 3. Freundlich adsorption isotherm model for the system waste after shot blasting/Cu(II) ions

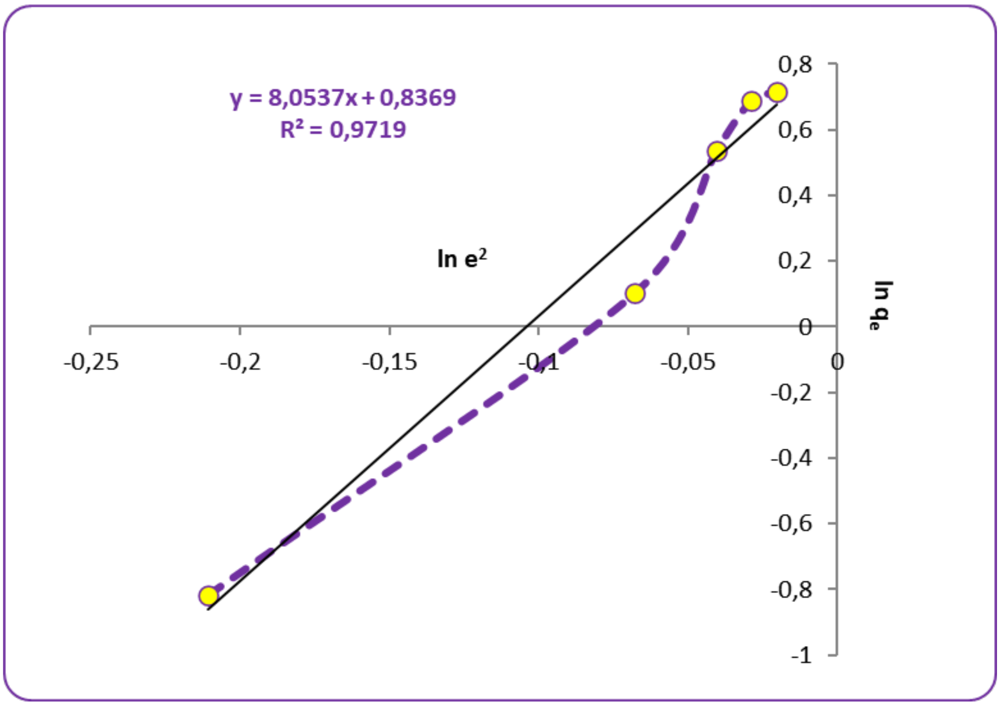

Figure 4. Dubin-Radushevich adsorption isotherm model for the system waste after shot blasting/Cu(II) ions

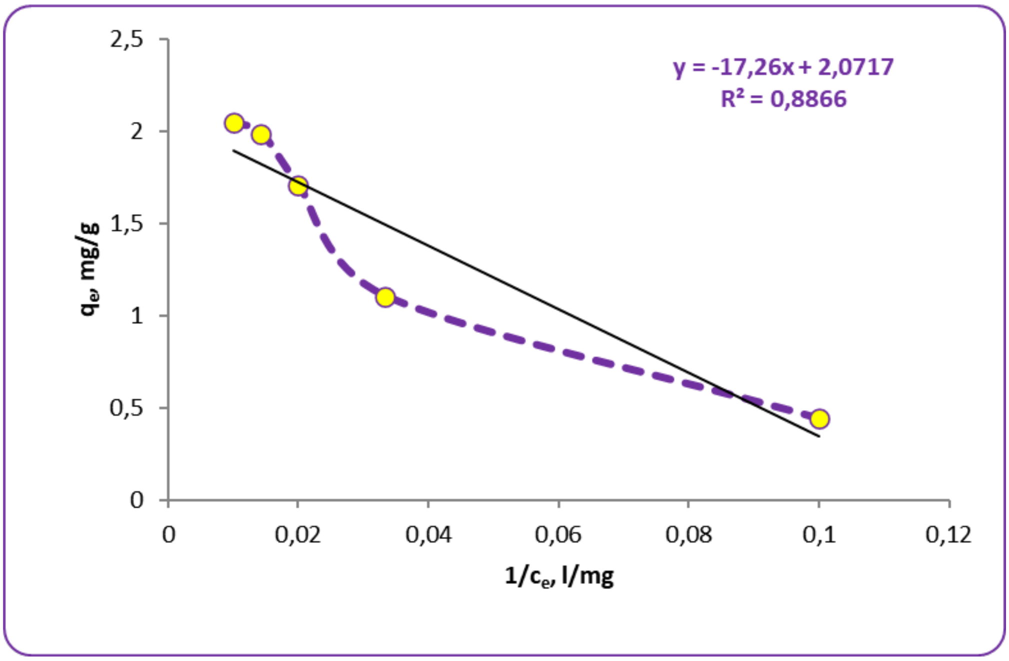

Figure 5. Eadie-Hoffstee adsorption isotherm model for the system waste after shot blasting/Cu(II) ions

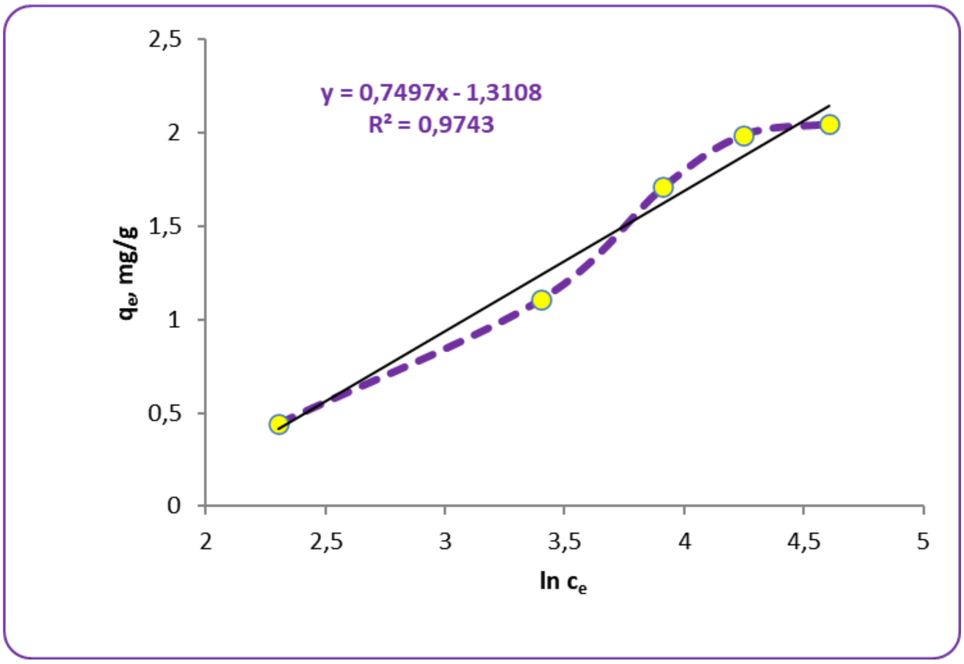

Figure 6. Temkin adsorption isotherm model for the system waste after shot blasting/Cu(II) ions

In order to choose the isotherm model that best describes the investigated system, the so-called fitting is usually used. There are numerous parameters that are used to assess the quality of fitted experimental data: coefficient of determination (R^2), mean absolute relative error (MARE), root mean squared relative error (RMRSE), Marquardt's per cent standard deviation (MPSD), hybrid fractional error function (HYBRID), average relative error (ARE), average relative standard error (ARS), sum squares errors (ERRSQ/SSE), the standard deviation of relative errors (SRE), Spearman's correlation coefficient (r_s), nonlinear chi-square test (χ^2).

In this article, the coefficient of determination was used to assess the quality of the fitted experimental data. Table 2 shows the coefficients of determination for all used isotherms models.

Table 2. Coefficients of determination for all used isotherms models (system waste after shot blasting /Cu(II) ions)

Isotherm model	Coefficients of determination, R^2
Langmuir	0,997
Freundlich	0,962
Dubin- Radushevich	0,971
Eadie-Hoffstee	0,886
Temkin	0,974

A comparison of the coefficients of determination (Table 2) shows that all coefficients are > 0.64, which means that all isotherms models can be used to describe the adsorption of the system waste after shot blasting/Cu(II) ions [13]. This conclusion coincides with literature definitions of certain isotherms, according to which the Langmuir adsorption isotherm indicates that adsorption is limited to the formation of only one adsorbate layer. It is also based on the assumption that all active sites have the same affinity for adsorbate molecules. In addition, if the Langmuir isotherm describes the investigated system well, it is assumed that adsorption takes place as chemisorption. Temkin model also indicates that adsorption is the result of the chemical bonding of adsorbate. According to the Freundlich and Dubin-Radushevich isotherms, adsorption takes place on a heterogeneous surface [9]. The data obtained in this research are in accordance with the literature claims mentioned above. Namely, the waste after shot blasting is very heterogeneous due to its composition, so the description of adsorption by the Freundlich and Dubin-Radushevich models is appropriate. It can be seen from Figure 1 that the adsorption capacity is constantly increasing, which indicates that desorption does not occur. Adsorption in which desorption does not occur is the result of chemical binding in one layer of adsorbent and adsorbate, which is in accordance with Langmuir and Temkin theory.

4. CONCLUSION

Based on the conducted research, the following can be concluded:

- adsorption of Cu(II) ions on the waste after shot blasting is possible under the tested conditions,
- as the concentration of Cu(II) ions increases, the adsorption capacity increases, since more Cu(II) ions are available in the solution, but there are also a lot of free places on the surface of the adsorbent,
- all investigated isotherms models (Langmuir, Freundlich, Dubin-Radushevich, Eadie-Hoffstee and Temkin) can be used to describe the adsorption system waste after shot blasting/Cu(II) ions. However, the Langmuir model best describes the examined system,
- since the Langmuir model best describes the examined system, it can be concluded that adsorption takes place as chemisorption, in one layer on a heterogeneous surface.

5. REFERENCES

[1] …, Census of World Casting Production, Modern Casting 111(2021) 12, 26-28.

[2] D. S. Leidel, M. Novakowski, D. Pohlman, Z. D. MacRunnels, M. H. MacKay, External Beneficial Reuse of Spent Foundry Sand, AFS Transactions 102(1994), 235-243.

[3] D. Križaić, V. Pavlic, Mogućnosti primjene korištenog ljevačkog pijeska kao industrijski proizvedenog agregata u građevinarstvu, Znanstveno-stručni ljevački skup: nove tehnologije i materijali u ljevaonicama, Sisak, 2011.
[4] A. Štrkalj, Z. Glavaš, Lj. Slokar, Microstructural and equilibrium adsorption study of the system of waste foundry molding sand/Cu(II) ions, Archives of metallurgy and materials 61(2016) 4, 1805-1812.
[5] A. Štrkalj, Z. Glavaš, I. Brnardić, Application of Foundry Waste for Adsorption of Hexavalent Chromium, Chemical and Biochemical Engineering Quarterly 27(2013) 1, 15-19.
[6] Z. Glavaš, A. Štrkalj, Kinetika adsorpcijskog procesa za sustav otpadna kalupna mješavina /Cu(II) ioni, Hrvatske vode 93(2015) 23, 185-190.
[7] S. Bello, I. A. Belloand, K. A. Adegoke, Adsorption of Dyes Using Different Types of Sand: A Review, South African Journal of Chemistry 66(2013), 117–129.
[8] B. Gezer, Adsorption capacity for the removal of organic dye pollutants from wastewater using carob powder, International Journal of Agriculture, Forestry and Life Science 2(2018), 1-14.
[9] K. Y. Foo, B. H. Hameed, In sights into the modeling of adsorption isotherm systems, Chemical Engineering Journal 156(2010) 1, 2-10.
[10] W. M. Ibrahim, A. F. Hassan, Y. A. Azab, Biosorption of toxic heavy metals from aqueous solution by *Ulvalactuca* activated carbon, Egyptian Journal of Basic and Applied Sciences 3(2016) 3, 241-249.
[11] M. Švábová, Z. Weishauptová, O. Pribyl, The effect of moisture on the sorption process of CO_2 on coal, Fuel 92(2012) 1, 187-196.
[12] J. B. Fernandes, S. G. Tilve, Adsorption behavior of methylene blue on glycerol based carbon materials, Journal of Environmental Chemical Engineering 6(2018) 2, 1714-1725.
[13] I. Šošić, V. Serdar, Uvod u statistiku, Školska knjiga, Zagreb, 2002.