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Application of Foundry Waste for Adsorption of Hexavalent Chromium

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It is well known if the amount of heavy metals in liquid waste is higher than allowed, there is a potential danger for the health of humans and other living organisms. They can also cause different troubles in technological processes. That is why monitoring and controlling the content of heavy metals in liquid waste of industrial system is very important.

Furthermore, foundries also have great difficulties with the disposal of their harmful waste material. Safe disposal of hazardous waste and substances is a task equally important as maintaining quality and profit. The aim must be to reduce the amount of waste through regeneration or some other applications.

The purpose of this paper was to examine adsorption of Cr (VI) ions from water solution on the non-toxic foundry waste material. The results showed that foundry waste material can be used for adsorption of Cr (VI) ions.

Key words:

Foundry waste, Cr (VI) ions, adsorption

Introduction

Chromium and its compounds are toxic metals introduced into natural water course from a variety of industrial wastes. They cause severe environmental and public health problems. The major sources are from leather tanning, textile dyeing, electroplating, and metal finishing industries. The hexavalent form of chromium is considered a group “A” human carcinogen because of its mutagenic and carcinogenic properties. It leads to liver damage, pulmonary congestion, edema, and causes skin irritation, resulting in ulcer formation.¹

In Croatia, the upper limit for the discharge of Cr (VI) into inland surface waters and public drainage systems is 0.1 mg L⁻¹.² A wide range of physical and chemical processes are available for the removal of Cr (VI) from wastewater, such as electro-chemical precipitation, ultra-filtration, ion exchange, electro-dialysis, reverse osmosis, chemical precipitation, and adsorption.^{3–5} The major drawbacks with these processes are high cost, toxic

sludge generation or incomplete metal removal.⁶ Comparison of all techniques reveals the economically more favorable alternative for the removal of metals from aqueous solutions. Activated carbons are widely used because of their high adsorption abilities of a large number of heavy metal ions. However, the price of activated carbon is relatively high, which limits their usage. This has led many researchers to search for low cost adsorbents such as anode dust, electric furnace slag and steel shot and biosorbents.^{7–10} In this study, waste mould sand, a byproduct of the gray iron foundry, was used as a low-cost adsorbent for treating wastewater contaminated with Cr (VI) ions. Thus, re-using foundry waste mould sand as adsorbents is attractive in terms of sustainable development, and allows the foundry industry to accrue savings through reduced disposal costs.¹¹

Experimental materials and methods

Used waste mould sand is a non-toxic waste material from the gray iron foundry. For analysis, a

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representative sample of waste mould sand was obtained by a quartering technique. It was dried at 105 °C for 4 hours. The chemical composition of the sample was determined by atomic absorption spectroscopy. A series of Erlenmeyer's flasks containing 1 g waste mould sand in 50 mL solution of Cr (VI) ions with different initial concentration (50–500 mg L⁻¹) were sealed until equilibrium was obtained. Then the adsorbent was removed by filtration. The concentration of Cr (VI) ions was determined by atomic absorption spectrometer. Temperatures of Cr (VI) solutions were 20, 30 and 40 °C.

The adsorption isotherm was tested in accordance with the following models:

Freundlich model:

$$\ln q_e = \ln K_F + 1/n \ln c_e \quad (1)$$

Langmuir model:

$$\frac{1}{q_e} = \frac{1}{K_L \cdot q_m \cdot c_e} + \frac{1}{q_m} \quad (2)$$

Eadie-Hoffstee model:

$$q_e = q_m - \frac{q_e}{K_E c_e} \quad (3)$$

Temkin model:

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln c_e \quad (4)$$

where q_e is equilibrium concentration of Cr (VI) ions on adsorbent (mg g⁻¹), c_e is the equilibrium concentration of Cr (VI) ions in solution (mg L⁻¹), q_m is the adsorption capacity (mg g⁻¹), T is temperature (K), R is universal gas constant (J mol⁻¹K⁻¹), K_F , K_L , K_E , K_T , b_T are adsorption constants. The free energy of adsorption, considering the adsorption equilibrium constant K_L is given by the following equation:

$$\Delta G^\circ = -RT \ln K_L \quad (5)$$

Other thermodynamic parameters were calculated using the following equation:

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

ΔG° is standard free energy change (J mol⁻¹), ΔH° is enthalpy change (kJ mol⁻¹), ΔS° is entropy change (J mol⁻¹K⁻¹), K_L is Langmuir constant (L mg⁻¹).

Mineralogical composition and information about the chemistry of the surface were investigated by means of X-ray diffraction analysis, XRD, and Fourier transformation infrared, FTIR, spectroscopy.

XRD analysis was performed on instrument using Cu K α radiation, operated at 40 kV and 30 mA. Diffraction measurement was conducted within the 2θ range of 5–75° with 0.04° step and in 1 s/step. The FTIR spectra were recorded on instrument equipped with an attenuated total reflection (ATR) accessory with a diamond crystal. Each spectrum from 4000 to 400 cm⁻¹ was averaged over 16 scans at 4 cm⁻¹ resolution.

Results and discussion

Table 1 presents chemical composition of examined waste mould sand. Mineralogical composition of the waste mould sand was determined using the X-ray diffraction method (XRD method). Fig. 1 shows the result of the diffraction analysis.

Table 1 – Chemical and mineralogical composition of waste mould sand

Composition	SiO ₂	Fe	Al ₂ O ₃	Ca	C	Mg	Cr	Mn
wt. %	96.1	2.57	0.85	0.31	0.12	0.03	0.009	0.008

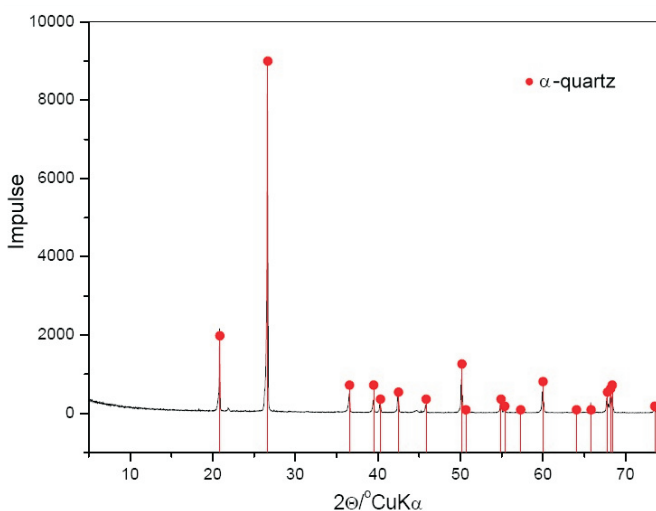


Fig. 1 – XRD analysis of waste mould sand

Used waste mould sand is a mixture of silica sand, clay binder and organic carbon source (typically coal dust) used to make moulds for gray iron casting. As a reactive medium, the coal dust provides organic carbon for adsorption, and the iron particles act as a reducing agent.

Adsorption isotherms

Fig. 2 shows experimental results of Cr (VI) ions adsorption on waste mould sand at three different temperatures, at 20, 30 and 40 °C.

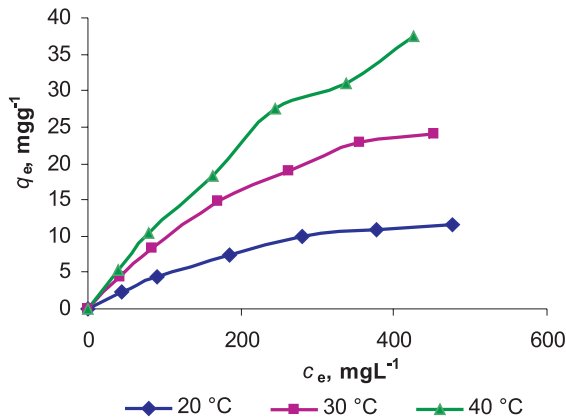


Fig. 2 – Adsorption isotherms for system Cr (VI) / waste mould sand at 20, 30 and 40 °C

It can be seen that the adsorption of Cr (VI) ions increases with temperature. The obtained adsorption capacity for Cr (VI) ions is a good indicator of waste mould sand’s potential for use in aqueous adsorption systems. This phenomenon is probably due to the increase in temperature which results in increased mobility of chromium ions in aqueous solution, and better ability to bind these ions on the surface of the waste molding sand.

Fig. 3 shows FTIR analysis of waste mould sand before and after Cr (VI) adsorption.

FTIR analysis provides information on the chemistry of the surface of the tested samples. The characteristic bands used for identification of Cr₂O₃ phase are in the 650–300 cm⁻¹.^{12,13} Fig. 3 shows visible peaks at 625 and 475 cm⁻¹ compared to the original sample, which confirmed that there was a binding of Cr (VI) ions on the waste mold sand. These data are also a good indicator of waste mould

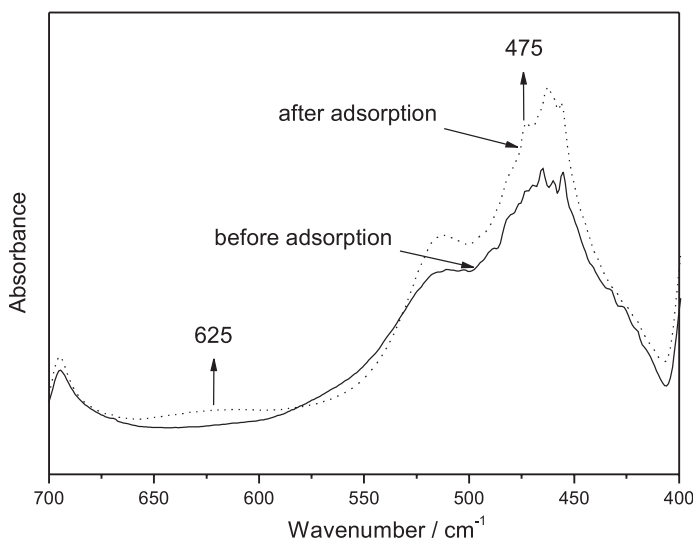


Fig. 3 – FTIR analysis of waste mould sand before and after adsorption of Cr (VI) ions

sand’s potential for use in aqueous adsorption system.

For understanding and interpreting the binding of toxic metals on the adsorbent it is necessary to carry out equilibrium analysis to determine the parameters that significantly affect the balance of individual adsorption processes. In this paper, Langmuir, Freundlich, Eadie-Hoffstee and Temkin model were used for analysis of equilibrium binding of Cr (VI) ions on waste mould sand. Figs. 4–7 show the adsorption isotherms.

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. In the Langmuir theory, the basic assumption is that adsorption takes place at specific homogeneous sites within the adsorbent. Temkin isotherm assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbens-adsorbate interactions and adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding en-

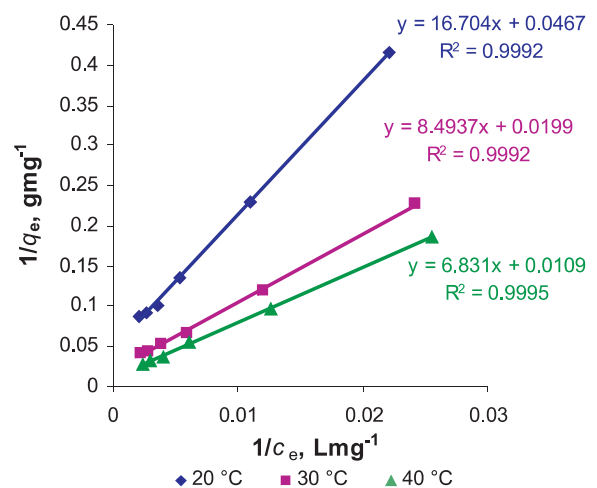


Fig. 4 – Langmuir isotherms for system Cr (VI) / waste mould sand at 20, 30 and 40 °C

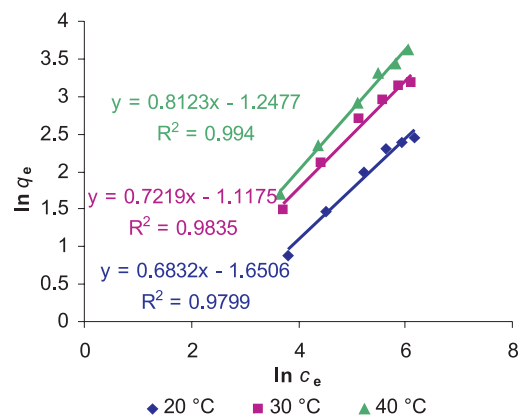


Fig. 5 – Freundlich isotherms for system Cr (VI) / waste mould sand at 20, 30 and 40 °C

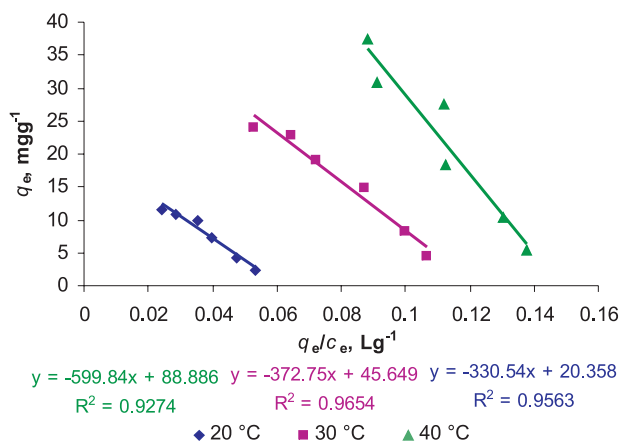


Fig. 6 – Eadie-Hofstee isotherms for system Cr (VI) / waste mould sand at 20, 30 and 40 °C

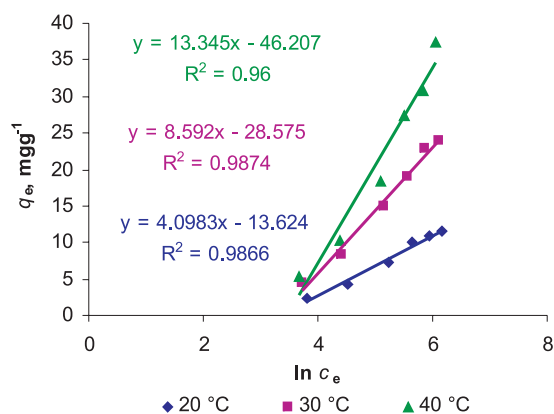


Fig. 7 – Temkin isotherms for system Cr (VI) / waste mould sand at 20, 30 and 40 °C

Table 2 – The values of parameters for isotherms

T, °C	Langmuir			Freundlich isotherm			Eadie-Hofstee isotherm			Temkin isotherm		
	K_L	q_m	r^2	K_F	$1/n$	r^2	K_E	q_m	r^2	K_T	b_T	r^2
20	0.008	21.413	0.9992	0.1919	0.683	0.9799	-0.0030	20.358	0.9563	0.127	-5.44	0.8635
30	0.0023	50.251	0.9992	0.3271	0.722	0.9835	-0.0027	45.649	0.9654	0.0004	-2.94	0.8473
40	0.0015	91.743	0.9995	0.2871	0.812	0.9940	-0.0017	88.886	0.9274	$0.205 \cdot 10^{-6}$	-2.12	0.7774

ergy.¹⁴ The Eadie-Hofstee isotherm considers the variation in affinity constants and overlying resistance of the unstirred water layer at different sites.¹⁵

The values of parameters for all isotherms are given in Table 2.

Comparison of correlation coefficients shows that the Langmuir and Freundlich isotherm fits better to the experimental data than other isotherms.

The mono-component Langmuir constant q_m , is the monolayer saturation at equilibrium. The other mono-component Langmuir constant, K_L , corresponds to the concentration and indicates the affinity for the binding of Cr (VI) ions on waste mould sand. A small K_L value indicates a low affinity. K_F and $1/n$, the mono-component Freundlich constants, are indicators of adsorption capacity and adsorption intensity, respectively. The higher value of $1/n$, the higher will be the slope expressed by $1/n$ and thus higher the affinity. As the value of $1/n$ is close to zero, the system is less heterogeneous. The data obtained in this study (Table 2) indicated that the waste mould sand represents a homogeneous surface. Temkin and Eadie-Hofstee isotherms have lower correlation coefficients and are not recommended for describing the adsorption process of Cr (VI) ions on the waste mould sand.

Thermodynamic study

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, ΔG° , is an indicator of chemical reaction spontaneity. Both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occur spontaneously at a given temperature if ΔG° has a negative value. The values of thermodynamic parameters calculated from equations 5 and 6 for adsorption of Cr (VI) ions on waste mould sand are given in Table 3.

The negative values of ΔG° (Table 3) show that the adsorption is highly favorable and spontaneous. A negative value of ΔH° implies that the adsorption

Table 3 – Thermodynamic parameters of adsorption of Cr (VI) ions on waste mould sand

T (°C)	$-\Delta G^\circ$ (J mol ⁻¹)	$-\Delta H^\circ$ (kJ mol ⁻¹)	ΔS° mol ⁻¹ K ⁻¹
20	6.82081	67.459	184.596
30	57.9403		
40	41.6365		

phenomenon is exothermic. A positive value of ΔS° reflects the affinity of the adsorbent towards the adsorbate. In addition, positive value of ΔS suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and adsorbent. The adsorbed ions, which are displaced by the adsorbate, gain more translational entropy than is lost by the adsorbate ions/molecules, thus allowing for the prevalence of thermodynamics randomness in the system.¹⁶

Conclusions

– Obtained results show that waste mould sand was an effective adsorbent for removal of Cr (VI) ions from aqueous solutions.

– The adsorption of Cr (VI) ions increased with temperature.

– The equilibrium data were analyzed using Langmuir, Freundlich, Eadie-Hoffstee and Temkin isotherms, and the Langmuire and Freundlich isotherm model showed better agreement with the equilibrium data.

– The negative values of ΔG° show that the adsorption is highly favorable and spontaneous. A negative value of ΔH° implies that the adsorption phenomenon is exothermic.

List of symbols with measurement units

- q_e – equilibrium concentration of Cr (VI) ions on adsorbent (mg g^{-1}),
 c_e – the equilibrium concentration of Cr (VI) ions in solution (mg L^{-1}),
 q_m – the adsorption capacity (mg g^{-1}),
 T – temperature (K),
 R – universal gas constant ($\text{J mol}^{-1}\text{K}^{-1}$),

- K_F, K_L, K_E, K_T, b_T – adsorption constants,
 ΔG° – standard free energy change (J mol^{-1}),
 ΔH° – enthalpy change (kJ mol^{-1}),
 ΔS° – entropy change ($\text{J mol}^{-1}\text{K}^{-1}$),

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