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WASTE METALLURGICAL MATERIALS - POTENTIAL ADSORBENTS FOR REMOVAL Cr^{6+}

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ABSTRACT: Chromium is a common pollutant introduced into natural waters due to the discharge of a variety of industrial wastewaters. On the other hand, chromium based catalysts are also usually employed in various chemical processes, including selective oxidation of hydrocarbons. This paper describes the use of three metallurgical waste materials (electric arc furnace slag, waste mould sand and waste steel shot after cleaning of castings) as adsorbents for removal of Cr^{6+} from aqueous solutions. All mention waste materials were potential low-cost effective materials for Cr^{6+} removal. The removal of Cr^{6+} was studied by batch tests. The obtained results show that the analyzed metallurgical waste materials are effective adsorbents for the removal of Cr^{6+} from aqueous solutions within the range of working concentrations. The rate of Cr^{6+} adsorption increased rapidly during the initial 60 minute. Comparing the all isotherms, electric arc furnace slag was shown higher adsorption of Cr^{6+} than other used waste metallurgical materials.
KEYWORDS: waste metallurgical materials, adsorption, efficiency

INTRODUCTION

Chromium is a toxic metal and widely used in the industry (electroplating, leather tanning, metal finishing and chromate preparation, etc.). Of its two oxidation states, Cr^{3+} and Cr^{6+}, the hexavalent form is considered to be a group "A" human carcinogen because of its mutagenic and carcinogenic properties [1, 2].

Chromium is a common pollutant introduced into natural waters due to the discharge of a variety of industrial wastewaters. On the other hand, chromium based catalysts are also usually employed in various chemical processes, including selective oxidation of hydrocarbons. According to the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for total chromium is 0.05 mg/l. Hence, it becomes imperative to remove Cr^{6+} from wastewaters before discharging them into aquatic systems or onto land [3].

Adsorption is a well-established technique for heavy metal removal. Activated carbon is a widely used adsorbent material. In fact use of activated carbon can be expensive due to the regeneration required and loses in the application processes. A variety of natural, synthetic materials and industrial waste materials has been used as Cr^{6+} inexpensive adsorbents [4].

This paper presents the use of three metallurgical waste materials (electric arc furnace slag, waste mould sand and waste steel shot after cleaning of castings) as adsorbents for removal of Cr^{6+} from aqueous solutions. All mention waste materials were potential low-cost effective materials for Cr^{6+} removal.

MATERIALS AND METHODS

Electric arc furnace slag, steel shot and waste mould sand, as non-toxic waste materials, was used as adsorbents. The electric arc furnace slag is a waste material generated from the steel making process. The steel shot is waste material from castings cleaning process. The waste mould sand is residue from gray iron foundry.

The chemical composition of adsorbents was determined with classical chemistry analysis, according to Standard Methods [5] (Table 1-3).

Table 1. Chemical composition of electric arc furnace slag

Components	CaO	FeO	MnO
wt, %	36.1	27.2	18.0
Components	SiO_2	Al_2O_3	MgO
wt, %	17.0	1.4	0.3

Table 2. Chemical composition of steel shot

Components	Fe	C	Mn
wt, %	98.05	0.85	0.60
Components	Si	S	P
wt, %	0.40	0.05	0.05

Table 3. Chemical composition of waste mould sand

Components	SiO_2	Al_2O_3	Fe	Ca	Mg
wt, %	90.0	1.6	6.8	0.55	0.08
Components	Mn	Ni	Cr	C	
wt, %	0.04	0.004	0.01	0.916	

The removal of Cr^{6+} was studied by batch tests. The mixtures of 1 g samples (adsorbents) and 50 ml of prepared chromium solutions of differential initial concentrations (100, 200, 300 mg/l) were shaken at 60 rpm during 180 min at a temperature of 20°C in the closed vessels. Chromium ion solutions with different initial concentrations of chromium were prepared by diluting chromium standard solution. After filtration of the suspensions, the concentrations of chromium ions in the filtrate were determined by atomic adsorption spectrometer (ZEEnit 650, Analytic Jena).

Adsorption capacity of metallurgical waste materials was compared with adsorption capacity of commercial activated carbon (Merck, Deutschland), which was tested in identical adsorption condition as waste metallurgical materials.

RESULTS AND DISCUSSION

Figure 1 shows adsorption isotherms of Cr^{6+} ions on electric arc furnace slag, waste steel shot, waste mould sand and commercial activated carbon.

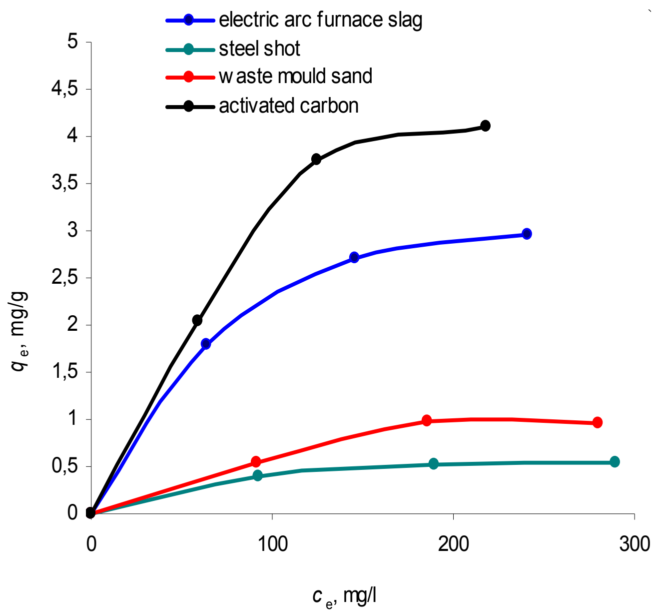

Figure 1. Adsorption isotherms of Cr^{6+} on electric furnace arc slag, waste steel shot, waste mould sand and commercial activated carbon

Figure 1 shows that the adsorption capacity increased with an increase in the initial Cr^{+6} concentrations for all using adsorbents. This is because an opportunity existed for increased reaction between the adsorbent and the adsorbate [6].

Comparing the all isotherms, Cr^{6+} adsorption of electric arc furnace slag was higher than adsorption capacity of other waste materials used as adsorbents. For electric arc furnace slag, equilibrium adsorption of Cr^{6+} was 2.95 mg/g when initial concentration of Cr^{6+} was 300 mg/l. The uptake of Cr^{6+} on waste steel shot and waste mould sand was much lower (adsorption capacity was 0.53 and 0.99 mg/g, respectively), for the same initial Cr^{6+} concentrations.

Figure 2 shows the amount of Cr^{6+} adsorbed on used adsorbents versus time.

It can be observed from Figure 2 that the rate of Cr^{6+} adsorption increased rapidly during the initial 60 minutes. After that, the removal of Cr^{6+} ions was decreased.

During the initial stage of adsorption, a large number of vacant surface sites were available for adsorption. After a lapse of some time, the remaining vacant surface sites were more difficult to occupy due to repulsive forces between the adsorbed molecules on the solid surface and in the bulk phase or desorption [7 - 9].

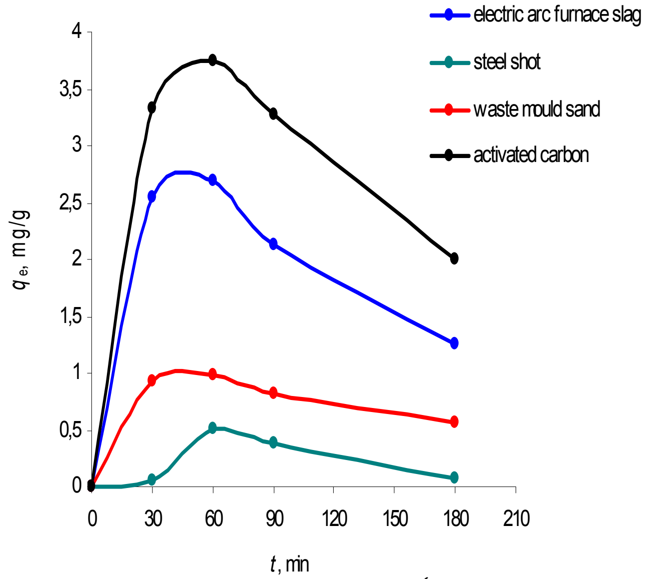

Figure 2. The amount of Cr^{6+} adsorbed on used adsorbents versus time (initial concentration is 300 mg/l)

Figure 3 shows the removal efficiency of Cr^{6+} as a function of initial adsorbents concentration (100, 200 and 300 mg/l).

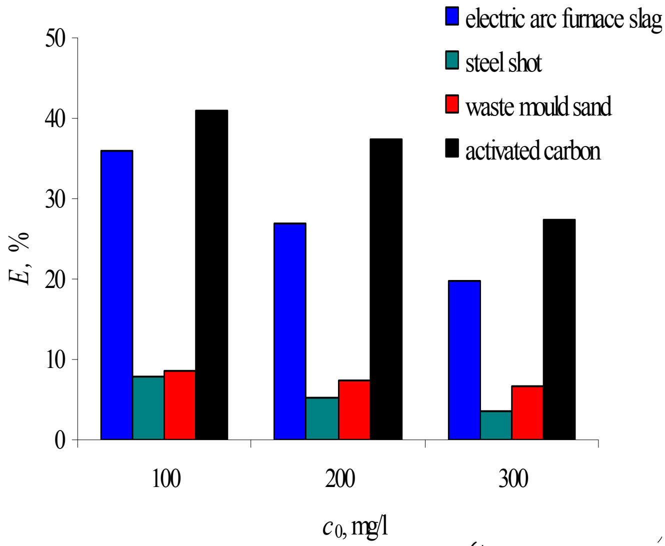

Figure 3. The removal efficiency of Cr^{6+} as a function of initial adsorbents concentration

It can be observed from Figure 3 that the removal efficiency of Cr^{6+} decreases with the increase of concentration of Cr^{6+} in solution. The cause may be the aggregation/agglomeration of adsorbent particles at higher concentrations, which would lead to a decrease in the surface area and an increase in the diffusion path length [10].

All results indicate that the electric arc furnace slag was the best low-cost adsorbent for removal of Cr^{6+}.

This research also proves that the removal efficiency depends on chemical composition of adsorbents [11].
Electric arc furnace slag composed of different oxides, mostly iron oxide (Table 1). Waste mould sand (Table 2) is mixture of silica sand, clay binder and organic carbon source (typically coal dust) [12, 13]. Adsorption medium was probably the iron particles and the coal dust [14].
Examination of different adsorbents shows the connection between their composition and adsorption capacity [15 - 18]. Carbon, metal oxides and SiO_2 in metallurgical wastes contribute to their adsorption ability (Tables 1-3).
Activated carbon adsorption seems to be an attractive choice for chromium removal, both for its exceptionally high surface areas, well-developed internal micro porosity structure, as well as the presence of a wide spectrum of surface functional groups like carboxylic group. For these reasons, activated carbon adsorption has been widely used for the treatment of chromium containing wastewaters [19].
Recently the market price of activated carbon for industrial grade is considered to be very expensive, depending on the quality of activated carbon itself [4]. Although a significant number of low-cost adsorbents from various materials have been found, commercial activated carbon has still been used intensively today.
Comparison of used waste metallurgical materials with commercial activated carbon shows that are good adsorbents for adsorption Cr^{6+}, especially electric arc furnace slag.

CONCLUSIONS

- *The metallurgical waste materials (electric arc furnace slag, waste steel shot and waste mould sand) were effective low-cost adsorbents for removal Cr^{6+} from aqueous solutions in concentration range from 100 to 300 mg/l at a temperature 20 °C.*
- *The rate of Cr^{6+} adsorption increased rapidly during the initial 60 minutes.*
- *The electric arc furnace slag was much better adsorbents for removal of Cr^{6+} than then waste mould sand and waste steel shot.*
- *Commercial activated carbon was the best adsorbents for removal Cr^{6+} from aqueous solution.*

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