



Use of steel converter slag as nickel adsorber to wastewater treatment

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Abstract

Magnetite, the main component of converter slag in the steel industry, can be used for the adsorption of Ni(II) from aqueous solutions, over a range of conditions: initial metal concentration ($10\text{--}100\text{ mg l}^{-1}$), stirring times (2–240 min), adsorbent dosage (1 g for 0.5 l of metal solution) and temperatures (20, 30 and 38°C). The adsorption rate increased with initial concentration but decreased with increase in temperature, due to competition of the dissolution process. The adsorption process obeyed the Freundlich isotherm model. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Increase in the use of heavy metals over the past few decades has inevitably resulted in an increase in the amount of these substances in the aquatic environment. Drain outs from mines, industrial and municipal effluents, agricultural run-off, acid rain, etc. have all contributed to various extents towards increased metal contents in water bodies. Metals are of special concern as they are non-degradable and therefore continue to exist in these water bodies [1].

The heavy metals are extremely toxic and have a tendency to bio-accumulate in the food chain. Strict environmental regulations related to heavy metal discharge has made it necessary to develop measures for their removal from wastewater. Conventional methods such as chemical precipitation, cementation, ion exchange, electrodeposition, use of membrane systems and activated carbon are not cost effective [2]. Hence, low cost, long-lasting, non-conventional materials are being considered to remove heavy metals. Industrial wastes such as fly ash, charred wastes of oxalic acid plants, bottom ash and granulated slag of steel plants as well as agricultural

wastes such as rice husk, tree bark and enriched iron clays have been studied as economical and convenient adsorbents for the treatment of heavy metal containing wastewaters [2].

The main objective of this investigation was to evaluate steel industry converter slag as an adsorbent material and to examine the effects of initial metal concentration and temperature on adsorption. The converter slag was obtained as small particles from air filters of the Bessemer Converter [3]. This slag is inexpensive and abundant, and is therefore ideal for low-cost wastewater treatment. It is a solid waste and can be used as an adsorbent, prior to eventual discharge of effluents with heavy metal content under permissible limits and thereby adhering to environmental regulations.

2. Materials and methods

2.1. Converter slag

Steel plants produce large quantities of solid wastes, many of which are non-toxic and some, even present desirable properties that render them suitable for other purposes. The steel converter slag is one such waste. A set of air filters are used for removing suspended particles from the Bessemer converter environment. The collected particles present in those air filters were washed and the

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Table 1
Some properties of converter slag

Measurements	Properties
X-ray diffraction (RINT-2000 RIGAKU)	The sample is mainly composed of crystallized iron compound — magnetite with some measured contamination — quartz
X-ray fluorescence (RIX-3000 RIGAKU)	All granulometric fractions over 0.04 mm (ASTM No. 325) have more than 88% of Fe ₂ O ₃ followed by CaO and MgO (5%) and others — a total of less than 2%
Particle size analysis (standard sieves method)	30% of total mass of sample — composed of particles under 0.037 mm (ASTM No. 400) followed by 12% of granulometric fraction under 0.300 and over 0.210 mm (ASTM Nos. 65 and No. 48)
Surface area (multi point BET adsorption — Quantachrome NOVA 2200)	55.01 m ² g ⁻¹

produced heavy slurry was filtrated. The slag was produced as filter press cake during the slurry filtration. A portion of the samples was dried at 60°C for 8 h, and then characterized [4].

Table 1 shows the characteristics of a converter slag. It is suitable for use as a metal adsorber in industrial wastewater treatment [5,6]. The slag is mainly composed of iron oxide (Fe₃O₄ — magnetite), and has also, low particle size and high surface area [7,8].

2.2. Adsorption process

Batch adsorption studies were conducted using 1 g of humid converter slag (as collected) and 500 ml of nickel solutions at desired initial pH values and temperature. The process lasted at least 4 h and six different solution samples were collected at different time intervals using a calibrated chronometer (Table 2). The first sample was collected at the end of 1 min of stirring the slag-solution mixture and the last (sixth) sample after 4 h of continuous stirring. All the samples were centrifuged and 20 ml of the supernatant solution were collected, and this was divided into two samples (as duplicates) for chemical analysis.

2.3. Metal measurements

The adsorption process was studied using nickel as the metal and this was chosen mainly due to its chemical

Table 2
Experimental data obtained after different time intervals for adsorption process with initial Ni concentration of 10 mg l⁻¹

Time (min)	UV absorbance	Nickel concentration (mg l ⁻¹)	Removal (%)
1	0.550±0.002	10.31±0.04	0
2	0.422±0.005	7.90±0.01	23
10	0.123±0.007	2.33±0.02	77
60	0.112±0.001	2.13±0.02	79
120	0.021±0.003	0.41±0.06	96
240	0.027±0.002	0.52±0.04	95

properties, which are common to metals of group VIII. This element is used in silver refineries, the electroplating industry, zinc base casting and storage battery industries. The permissible Brazilian limit for Ni (II) in wastewater discharge is 2.0 mg. l⁻¹ [9,10].

The measurements of nickel concentration were performed using a spectrophotometer (Varian-Cary 1E UV-visible). The collected nickel samples were treated to prepare the colored nickel dimethylglyoxim complex. This treatment consisted of adding 0.05 ml of 28% NH₄OH, 0.1 ml of 10% citric acid solution, 0.25 ml of dimethylglyoxim, and 1% ethanol. After agitation, chloroform was added to obtain a total volume of 25 ml. The addition of citric acid was to reduce the influence of dissolved iron, on nickel concentration results. The absorbance of all duplicate samples was measured at 360 nm.

The adsorbance values were converted to nickel concentration using a standard curve. This curve was obtained using data from nickel analysis of four standard solutions. Table 2 shows a summary of the experimental data. The concentration of the prepared Ni and dissolved iron samples were analyzed using a UV-Visible spectrophotometer and by atomic absorption spectroscopy. Finally, the values obtained were analyzed using an outliers criteria for rejection of 2% (level of significance).

3. Results and discussion

3.1. Adsorption process

Fig. 1 shows the curves of adsorbed nickel after different intervals of stirring. Different initial nickel concentrations were used and the resultant mean and standard deviations of all the observations carried out with different starting nickel concentrations are also shown.

The plotted results indicate that a system based on adsorption can be used to remove at least 78% of Ni ions from solutions of varying nickel concentration. The tested systems were found to be more efficient for

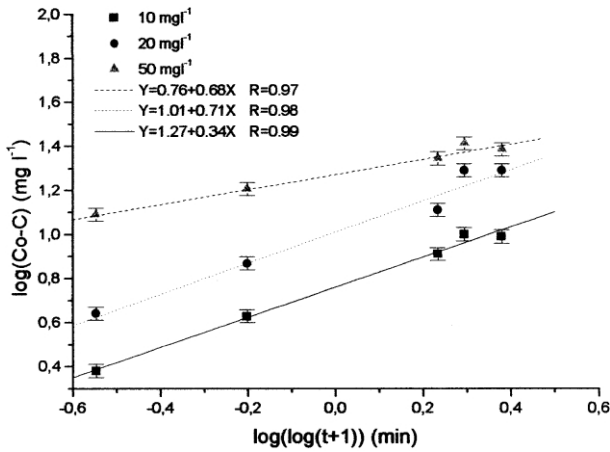


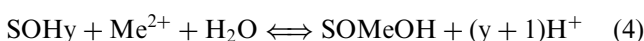
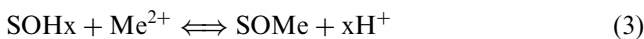
Fig. 1. Logarithmic lines corresponding to nickel removed using converter slag as adsorber from solutions with different initial concentrations.

removing Ni ions from dilute solutions than from concentrated solutions and the equilibrium time observed was 2 h. No increase in Ni ion adsorption rate was observed even after continuous stirring.

3.2. pH Studies

The metal adsorption depends directly on the surface charge of the oxide, and the charge is determined by the amount of H⁺/OH⁻ present in solution. The solid surface can exhibit zero point charge (ZPC), and under these conditions, only a slight increase in adsorption is expected. In adsorption systems with pH above ZPC, metal cations are adsorbed to counterbalance the net negative surface charge at the oxide/H₂O interface. The ZPC for magnetite is 6.5±0.2 [11,12].

The adsorption process in which converter slag was used, started in the acid range and was followed by an increase in pH. The increase of pH was considered to be due to the slag dissolution, when some of the slag compound as iron, hydroxide and oxidehydroxide will be released to solution. The effect of adsorption can be noticed when the pH decreases in the agitation time interval of 30–40 min of adsorption, when the adsorption mechanism, consisting of Eqs. (1)–(4) showing the H⁺ release. When the converter slag was used as adsorber, in strong acid range, the adsorber dissolution increased with the adsorbed metal releasing [13,14]. It was observed that adsorber dissolution rate increased accordingly, with aggressive adsorption conditions such as low pH or high system temperature.



where

SOH, SOH_x and SOH_y are the corresponding surface charges of the solid adsorber surface; Me²⁺ is the Ni ions in solution; S₂O₂Me, SOMeOH, SOMe and SOMeOH are adsorbed metals on the solid surface.

Some exploratory pH studies were carried out to try and prevent the converter slag from behaving as adsorbed material in wastewater treatment. This was done using the adsorption process at three different pH values: 6, 4 and 2. The dissolution process was followed by iron measurements at different time intervals. The data obtained for pH 6 indicated that the dissolution process occurred on a small scale, with mean concentration of Fe < 0.1 mg l⁻¹. The pH 4 adsorption system exhibited 0.5 mg l⁻¹, mean iron concentration, and finally, for adsorption system at pH 2, mean iron concentration of 10 mg l⁻¹ was measured. The adsorption process measurements were carried out at pH 5.5–6.0, above ZPC and with a low dissolution rate.

3.3. Kinetic model

Fig. 2 shows the effect of temperature increase on the adsorption process of a slag adsorber. Using log (Ce–C) as a dependent variable and time as an independent variable, it is possible to find a line equation.

The kinetics of converter slag as adsorber can be studied as a first order adsorption process with the expression [1]:

$$\log(C_e - C) = \log C_e - (K_{ab}/2.303)t$$

$$y = B + Cx \quad (5)$$

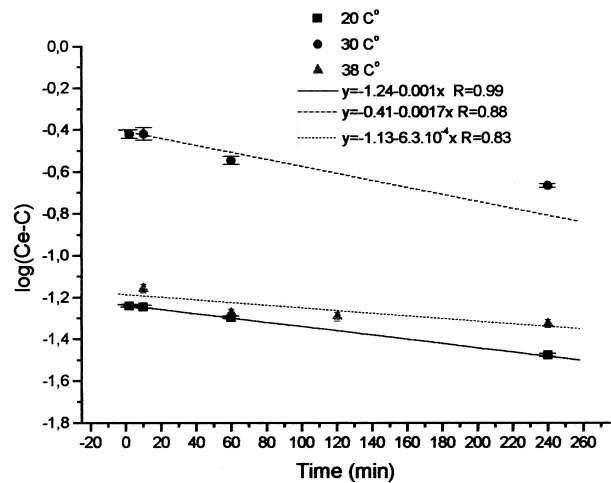


Fig. 2. Line equation for metal concentration at different adsorption temperatures.

where

- K_{ab} = constant rate of adsorption ($\text{mg g}^{-1} \text{min}^{-1}$)
- C = the adsorbed Ni at t (mg g^{-1})
- C_e = the adsorbed Ni at equilibrium time (mg g^{-1})
- t = time (min)

The K_{ab} factor is an empirical value used to describe the best temperature to remove Ni from solution, Table 3 [1]. The K_{ab} obtained shows 30°C as the optimum temperature for the adsorption process. At temperatures lower than 30°C, the adsorption system entropy is not favorable, and over 30°C, the dissolution process increases and the resultant K_{ab} factor shows a reduction in Ni adsorption rate [13].

3.4. Ni adsorption empirical model

The adsorption data have been analyzed using a mathematical empirical model [1]. The removal rate of Ni from the solution using a converter slag as adsorber at three different initial concentrations: 10 mg l^{-1} ; 20 mg l^{-1} and 50 mg l^{-1} follows an empirical relationship. Table 4 and Fig. 1.

$$\log(t + 1) = K''(C_0 - C)^A \tag{6}$$

where

- C_0 = initial concentration of Ni (mg l^{-1})
- C = Ni concentration of t (mg l^{-1})
- K'' and A are empirical constants that depend on the density and particle size of the adsorbent
- t = time (min)

$$\log[\log(t + 1)] = \log K'' + A \log(C_0 - C) \tag{7}$$

$$a \log(C_0 - C) = -1/A \log K'' + 1/A \log[\log(t + 1)]$$

$$y = B + Cx \quad C = 1/A$$

$$B = -(\log K''/A)$$

Table 3

Line parameters and calculated empirical value of K_{ab}

Temperature (°C)	Equation	K_{ab} ($\text{mg g}^{-1} \text{min}^{-1}$)
20	$y = -1.24 - 1 \times 10^{-3}x$	2.3×10^{-3}
30	$y = -0.41 - 1.7 \times 10^{-4}x$	3.9×10^{-3}
38	$y = -1.13 - 6.3 \times 10^{-4}x$	1.5×10^{-3}

Table 4

Line parameters and calculated empirical value of A and K''

C_0 (mg l^{-1})	Line equation	A	K''	Concentration equation	C (mg l^{-1})
10	$y = 0.79 + 0.67x$	1.27	0.099	$\log(t + 1) = 0.099 (C_0 - C)^{1.27}$	0.23
20	$y = 1.01 + 0.71x$	0.99	0.100	$\log(t + 1) = 0.100 (C_0 - C)^{0.99}$	1.57
50	$y = 1.27 + 0.34x$	0.79	0.099	$\log(t + 1) = 0.099 (C_0 - C)^{0.79}$	10.67

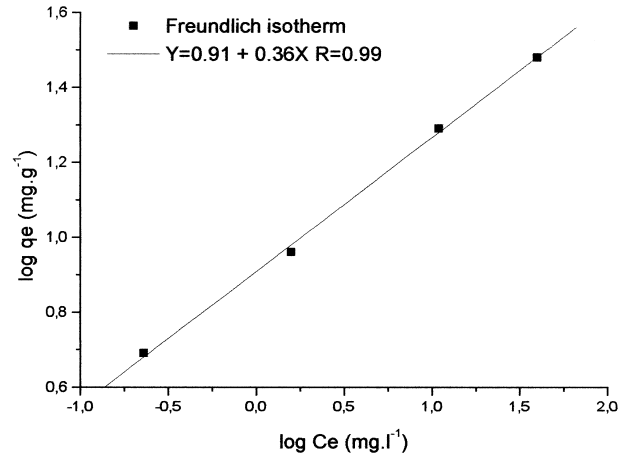


Fig. 3. Plots for $\log q_e$ vs $\log C_e$ for nickel adsorption.

The results obtained can be analyzed and the concentration equations permit the Ni concentration to be calculated, after the different time intervals. For example, with initial concentration of 50 mg l^{-1} , after $t = 3600$ s (1 h), the Ni concentration will be 10.97 mg l^{-1} . Similarly, when the initial Ni concentrations were 20 and 10 mg l^{-1} , after equilibrium time, the Ni concentrations will be 1.57 and 0.83 mg l^{-1} , respectively. In spite of the low adsorption rate, after the adsorption process, the remaining Ni concentration could be below the environmental regulation limits.

3.5. Isotherm study

The Freundlich isotherm model and equation were applied to the adsorption equilibrium [1].

$$\log q_e = \log K + (1/n) \log C_e \tag{8}$$

where

- C_e = equilibrium concentration (mg l^{-1})
- q_e = the amount adsorbed at equilibrium (mg g^{-1})
- K and n are Freundlich constants related to adsorption capacity and energy of adsorption.

Fig. 3 shows the plots of $\log q_e$ vs $\log C_e$ and the resultant line which followed a Freundlich model. For the obtained line equation, the related constants were $K = 8.1$ and $n = 2.8$. The expected n value should be between 2 and 10 to achieve complete adsorption [13].

The dissolution process was observed only when the conditions were aggressive, at low pH values and high temperatures. In most cases, the dissolution rate was low compared to the adsorption rate. In some cases the dissolution rate could be ignored, but in others, mainly in aggressive conditions, it needs to be controlled.

4. Conclusions

Converter slag can be used like an adsorber material for wastewater treatment. As a steel plant residue, it is abundant and can be obtained at low cost. The adsorption systems studied, show the efficiency of Ni adsorption from solutions with different initial concentrations. The low pH adsorption system and increase in temperature revealed reduced efficiency in adsorption of heavy metals from solutions. This effect is due to adsorber dissolution and will have to be controlled in industrial applications. In spite of some difficulties, 1 g of the converter slag used as adsorber material reduced the Ni concentration from 20 to 1.57 mg l⁻¹. The Ni concentration in the treated solution reduced to levels permissible in industrial discharges.

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