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Sorption Cleaning of Galvanic Wastewater from Fe Ions (II), (III) and Reuse of Sorbent Ipi-T

Elena G. Filatova*,
Olga I. Pomazkina and Vladimir I. Dudarev
National Research Irkutsk State Technical University
83 Lermontova, Irkutsk, 664074 Russia

The sorption method of wastewater cleaning from ions of Fe (II) and (III) using carbon sorbent IPI-T synthesized in the Irkutsk State Technical University. Particular attention is paid to the regeneration of the carbon sorbent saturated with ions of Fe (II) and (III),by the chemical treatment method. Was studied the reuse of the sorbent for the purification of galvanic wastewater.

Keywords: water treatment, galvanic wastewater, adsorption, carbon sorbents, Fe ions (II) and (III).

1. Introduction

One of the most pressing environmental problems of engineering companies, having in its production cycle electroplating processes, the problem is a deep cleaning of waste water from heavy metal ions. Water treatment of Fe ions (II) and (III), is traditionally carried out by transferring them into water-insoluble compounds, which are then removed by sedimentation, flotation, filtration and other methods of separation of solid and liquid phases. Translated into the solid phase is mainly carried out by introducing alkali with the formation of hydroxides, hydroxo-carbonates, carbonates. However, the use of reagents for the withdrawal of metal ions from the liquid phase leads to an increase saline in a purified water and makes it difficult to use in circulating water systems businesses. The priority method of neutralization of waste water from heavy metal ions are the physico-chemical, which include electrochemical and sorption methods of wastewater treatment. Sorption methods are one of the most effective methods of disposal of waste water from heavy metal ions.

Objective: To study the main regularities of the sorption process of cleaning galvanic wastewater from Fe ions (II) and (III) by using carbon sorbents IPI-T, synthesized in the Irkutsk State Technical University [1].

2. Experimental procedure

Carbon adsorbents IPI-T is a black granules of irregular shape with an average particle size of from 2 to 5 mm, with a specific surface area 480 m^2/g, total pore volume is 0,65 cm^3/g, micropore volume – 0,28 cm^3/g.

*   Corresponding author E-mail address: efila@list.ru

As objects of investigation used a waste water containing from 1 to 34 mg/l of Fe ions (II) and from 1 to 36,5 mg/l of Fe ions (III). It is known that the ions of Fe (II) are stable in water with low oxygen content. In the contaminated waste water of dissolved oxygen, or does not exist at all, or its concentration does not exceed 0,5-1 mg/l. The concentration of Fe (II) was controlled by a standard permanganat-metric quantitative analysis [2], the relative measurement error did not exceed ±0,1%. The concentration of Fe (III) was controlled the spectrophotometric method of analysis using the sulfosalicylic acid [3].

The study of the adsorption capacity of the sorbent with respect to the ions of Fe (II) and (III) in static conditions was performed using isotherms and kinetic curves of adsorption. We used the method of variable portions (2 g, 1 g, 0,75 g, 0,5 g, 0,25 g) and constant concentration. Kinetic experiments in static conditions determined the time to establish equilibrium in the system carbon adsorbent – solution of metal salt. The magnitude of adsorption in static conditions (A, mmol/kg) was calculated by the formula

$$A = \frac{c_u - c_k}{m} \cdot V,$$

where c_u and c_k – initial and final metal concentration in solution, mmol/l; V – volume of solution, l; m – portion of adsorbent, kg.

Dynamic activity of the sorbent was characterized by the time from the beginning of the adsorptive transmission to the «breakthrough», ie till appearance him after sorbent layer. The process of sorption under dynamic conditions was carried out in a column with an inner diameter of 16 mm. The column was filled with the sorbent in an amount of 10 g (layer height – 12 cm). The optimum flow rate of the adsorbate through the sorbent layer was 5-7,5 ml/ min, which corresponds to a linear velocity in the industrial conditions of 1,5-2,0 m/h.

The degree of desorption of metals was calculated by the formula

$$\varepsilon_{\text{Д}} = \frac{c_\partial \cdot V_\partial}{m \cdot A} \cdot 100\%$$

where c_∂ – the concentration of metal in the passed volume, mg/l, V_∂ – the passed volume, l; m – portion of adsorbent, g; A – the capacity of the adsorbent, mg/g.

3. Results and discussion

We found that the maximum adsorption of ions of Fe (II) by carbon sorbents IPI-T happened in a weakly acidic medium at pH = 3.9 [6]. The maximum value of the adsorption of Fe (III) from wastewater is achieved at pH = 1.79 [7]. Further study of the sorption in the dynamic and static conditions was carried out at the optimum pH.

In Fig.1. shows the adsorption isotherm of Fe (II), constructed from experimental data obtained under static conditions at a temperature of 293K.

As can be seen from Fig. 1., the shape of the curve corresponds to the adsorption of a multilayer or poly-molecular, adsorption. In Fig. 2. shows the adsorption isotherm of Fe (III) at a temperature of 293K.

From Fig. 2. shows that the shape of the adsorption of ions of Fe (III) is similar to the form of isotherms for Fe ions (II). For multilayer adsorption isotherms can be applied the BET theory. The isotherm equation of BET adsorption:
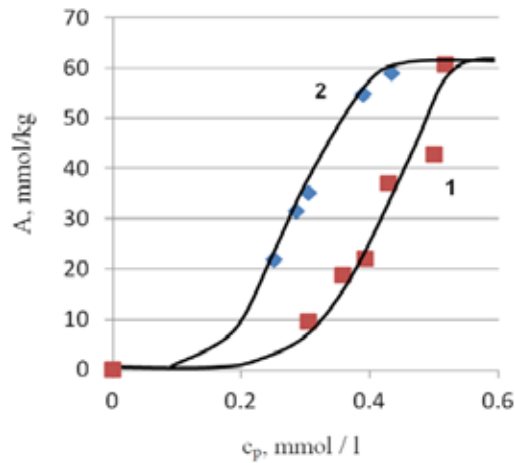
Fig. 1. Adsorption isotherm of Fe (II): 1 – the curve of adsorption; 2 – desorption curve
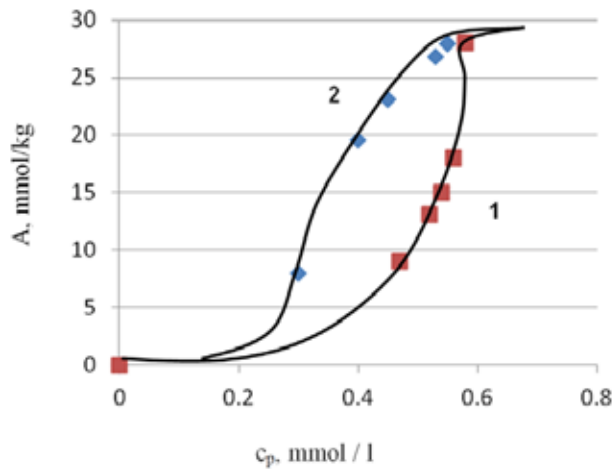

Fig. 2. Adsorption isotherm of Fe (III): 1 – the curve of adsorption 2 – desorption curve

$$A = \frac{A_\infty \cdot C \cdot (c/c_0)}{(1 - c/c_0) \cdot [1 + (C-1)(c/c_0)]},$$

where A – the value of adsorption, mmol/kg; A_∞ – ultimate adsorption capacity of the monolayer, mmol/kg; C – constant for a given adsorption system, directly related to the heat and entropy of adsorption; c, c_0 – the equilibrium and initial concentration of Fe (II) and (III), mmol/l.

The equation of BET adsorption in linear form:

$$\frac{c/c_0}{A(1 - c/c_0)} = \frac{1}{A_\infty \cdot C} + \frac{C-1}{A_\infty \cdot C} \cdot c/c_0.$$

The adsorption isotherms of Fe (II) and (III) were constructed for the study of IPI-T sorbent (Fig. 3.) using the equation of the BET adsorption in the linear form.
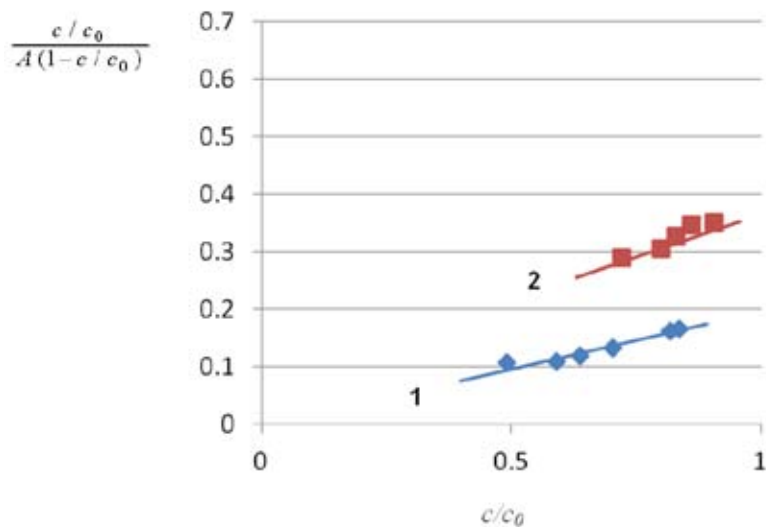
$$\frac{c/c_0}{A(1-c/c_0)}$$

Fig. 3. Sorption isotherms of the linear form of BET equation 1 – for the ions of Fe (II); 2 – ions to Fe (III)

Table 1. BET equation constants for the study of IPI-T sorbent

Ions	The equation $\dfrac{c/c_0}{A(1-c/c_0)} = f(c/c_0)$	Max. sorption capacity of the monolayer A_∞, mol/kg	Constant $C \cdot 10^{-3}$	Coefficient of corellation
Fe (II)	$\dfrac{c/c_0}{A(1-c/c_0)} = 0{,}186\ (c/c_0) + 0{,}006$	0,052	32,0	0,980
Fe (III)	$\dfrac{c/c_0}{A(1-c/c_0)} = 0{,}036\ (c/c_0) + 0{,}012$	0,021	4,0	0,933

From the linear dependence shown in Fig. 3., using the tangent of slope of the straight lines and the value of segments crossed with the straight axis, was measured maximum sorption capacity of the monolayer A_∞ and a constant C (Table 1).

In connection with the fact that the constant C in equation BET is the ratio of two equilibrium constants $C=k_1/k_2$, it can also be regarded as the equilibrium constant, ie to calculate the standard Gibbs energy can be used equation

$$\Delta G^0{}_C = -\,R \cdot T \cdot ln\ C = -\,R \cdot T \cdot ln\ k_1/k_2.$$

Thus, for ions of Fe (II) $\Delta G^0{}_C = -\,25{,}7$ kJ/ mol, and for the ions of Fe (III) $\Delta G^0{}_C = -\,20{,}5$ kJ/ mol, $\Delta G^0{}_C$ reflects the standard Gibbs energy of pure adsorption as a result of interaction between the adsorbate and the surface of the adsorbent.

In the course of the work performed studied the effect of temperature on the sorption of ions of Fe (II) and (III) IPI-T sorbent, the results presented in Fig. 4. and 5.
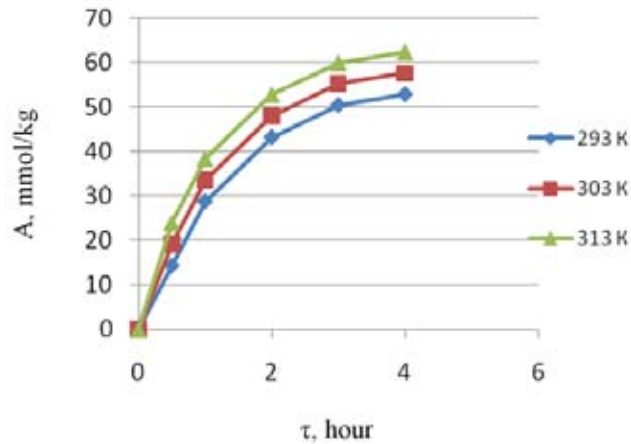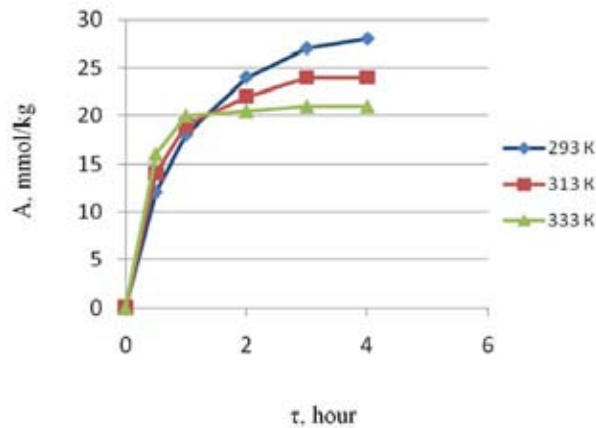
Fig. 4. Kinetic curves of sorption of Fe (II)

Fig. 5. Kinetic curves of sorption of Fe (III)

From Fig. 4. shows that with increasing temperature is increased the adsorption of Fe (II). However, physical adsorption is exothermic and reversible, and the increase in temperature should lead to a decrease in speed, however, the experimental data indicate that the temperature increases the rate of process. Consequently, the adsorption of ions of Fe (II) takes place activated adsorption. We found that the maximum adsorption occurs at 343 K, a further increase in temperature leads to a decrease in the adsorption of ions of Fe (II) sorbent of IPI-T.

From Fig. 5. shows that with increasing temperature at first is an increase in the adsorption of Fe (III), as the heat always helps to speed up the establishment of equilibrium in the system. Further, when the temperature increase adsorption, corresponding to the equilibrium state decreases. Thus, the kinetic curves of adsorption of ions of Fe (III) at different temperatures cross each other, as shown in Fig. 5.

The obtained temperature dependence of the adsorption of ions of Fe (II) and (III), confirms the fact that the Fe hydroxide (II) is a strong base, so the ions of Fe (II) is characteristic of activated

adsorption. Hydroxide, Fe (III), is a weak base, it is reflected in the fact that the salts of Fe (III) is strongly hydrolyzed and Fe ions (III) is characterized by physical adsorption.

In this paper we studied the adsorption of Fe (II) and (III) in dynamic conditions. Established that the protective effect of IPI-T sorbent for sorption of Fe (II) is two hours, then within an hour the concentration of ions of Fe (II) of the adsorbent layer remains within the MPC. The time of the protective action of IPI-T sorbent for sorption of Fe (III) was slightly less than two hours. The time, during which the concentration of the substance in the filtrate changes from the adsorbate concentration at an acceptable breakthrough, corresponding to the concentration of Fe (II) and (III) within the MPC to the initial concentration was about 6 hours.

4. Desorption and reuse of sorbents

Sorption method for the extraction of metals economically rational only if used the repeated use of sorbents. Therefore, the regeneration of carbon sorbents is one of the main issues arising from the sorption method of extraction of metals from waste water. The purpose of regeneration is, on the one hand, the desorption of adsorbed ions, or the destructive removal and, on the other hand, the recovery of the adsorption capacity of the sorbent.

In this paper we studied the regeneration of the carbon sorbent IPI-T, saturated with Fe ions (II) and (III), by the method of chemical treatment. Capacity of the saturated sorbent IPI-T for Fe (II) was 3,41 mg/g, and the Fe (III) – 1,16 mg/g . The process of desorption of the saturated sorbent IPI-T ions of Fe (II) and (III) (mass portions – 0,5 g) was carried out with solutions of hydrochloric acid (acid volume – 40 ml) of various concentrations under static conditions, regeneration time was 120 minutes, the results in Tables 2.

The data in Table. 2 that the maximum desorption of ions of Fe (II) occurs when using 0,56 M hydrochloric acid solution, and the maximum desorption of ions of Fe (III) – by using 0,74 M solution. Since the desorption process is endothermic, then it should be lead at an elevated temperature. An increase in temperature is an effective means of increasing the depth of the desorption of carbon

Table 2. Results of regeneration IPI-sorbent with hydrochloric acid at T 298 K

| Dilution HCl	Concentration HCl,		Ions of Fe (II)		Ions of Fe (III)	
	%	mol/l	Concentration in eluate, mg/l	Degree of desorption, %	Concentration in eluate, mg/l	Degree of desorption, %
1:2	12,0	3,2	18,3	21,3	3,4	31,6
1:4	7,2	1,9	19,4	21,1	6,1	56,3
1:6	5,1	1,4	20,0	21,8	6,4	59,2
1:8	4,0	1,1	18,8	20,6	7,5	69,5
1:10	3,3	0,87	21,1	23,1	7,6	70,5
1:12	2,8	0,74	21,7	23,7	9,2	85,6
1:14	2,4	0,64	24,0	26,2	7,7	71,5
1:16	2,1	0,56	24,3	26,5	7,3	68,0
1:18	1,9	0,51	22,9	25,0	6,2	57,7
1:20	1,7	0,46	22,3	24,3	4,1	37,7
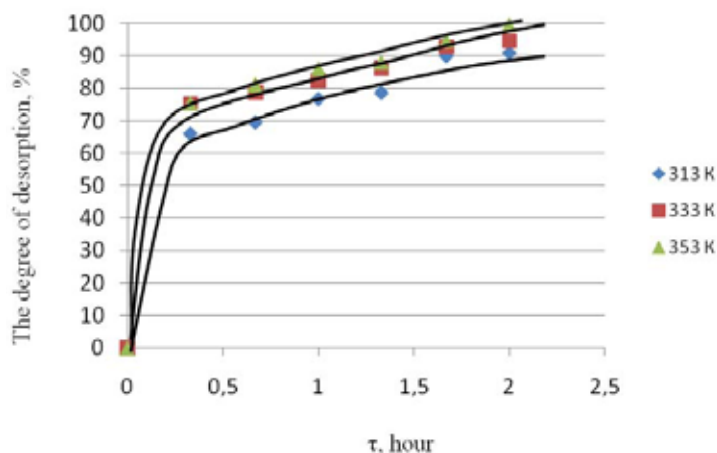
Fig. 6. The curves of desorption of ions of Fe (III) by carbon sorbent IPI-T

sorbents. The process of desorption of the carbon sorbent IPI-T was performed in the temperature range 303-353 K using a 0,74 M solution of Fe (III), the results are shown in Figure 6.

From Fig. 6. it follows that the degree of desorption of ions Fe (III) at 353K up to 99,6%. Carrying four cycles «sorption-desorption» showed a reduction of sorption activity of the carbon sorbent IPI-T for about 4%.

5. Conclusions

1. Was established the possibility of galvanic treatment of Fe (II) and (III) using the carbon sorbent IPI-T synthesized in the Irkutsk State Technical University.

2. In the study of adsorption in static conditions, was defined the limited adsorption capacity of monolayer of carbon sorbent IPI-T by the sorption isotherms of the linear form of BET equation: for the ions of Fe (II) $A_\infty = 0,052$ mmol/kg; for ions of Fe (III) $A_\infty = 0,021$ mmol/kg.

3. In the study of adsorption under dynamic conditions, it was found the protective effect of IPI-T sorbent for the sorption of ions of Fe (II), is two hours, then within an hour the concentration of ions of Fe (II) of the adsorbent layer remains within the MPC. The time of the protective action of IPI-T sorbent for sorption of Fe (III) was slightly less than two hours.

4. The optimum concentration of acid to regenerate the carbon adsorbent IPI-T: for the extraction of Fe ions (II) is better to use 0,56 M solution of hydrochloric acid for the extraction of Fe (III) – 0,74 M solution.

5. Desorption, using the optimum concentration of hydrochloric acid, saturated with carbon sorbent IPI-T ions of Fe (III) at 353 K is 99,6%. Carrying four cycles «sorption-desorption» showed a reduction of sorption activity of the carbon sorbent IPI-T for about 4%.

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Сорбционная очистка гальваностоков
от железа (II), (III)
и повторное использование сорбента ИПИ-Т

Е.Г. Филатова,
О.И. Помазкина, В.И. Дударев
Национальный исследовательский
Иркутский государственный технический университет,
Россия 664074, Иркутск, Лермонтова, 83

Изучен сорбционный способ очистки гальваностоков от ионов железа (II) и (III) углеродным сорбентом ИПИ-Т, синтезированным в ИрГТУ. Особое внимание уделено регенерации углеродного сорбента, насыщенного ионами железа (II) и (III) методом химической обработки. Изучено повторное использование сорбента для очистки гальваностоков.

Ключевые слова: очистка воды, водоподготовка, гальваностоки, адсорбция, углеродные сорбенты, ионы железа (II) и (III).