Annals of Agrarian Science

Journal homepage: http://journals.org.ge/index.php

Use of plant raw materials for purification of industrial waste waters from copper and iron ions

N.G. Kalabegashvili*, G.I. Balarjishvili, L.O. Samkharadze, D.K. Ioseliani, I.I. Mikadze

Ivane Javakhishvili Tbilisi State University, Petre Melikishvili Institute of Physical and Organic Chemistry, 31, Politkovskaia Str., Tbilisi, 0186, Georgia

Received: 23 March 2019; accepted: 19 May 2019

A B S T R A C T

The purification of quarry waters of the mining enterprise "RMG Copper" (Bolnisi district, Georgia) and Kazretula River from copper and iron ions through the adsorption method is investigated. Plant raw materials (agricultural waste), such as oak bark, corn cobs, grape stalks and damp pine cones etc., have been used as adsorbents. Dependence between the plant raw material adsorption degree and contact time, environment PH of a tested solution, preliminary treatment of the adsorbent is studied. In case of quarry water the best results were shown by the following adsorbents: oak bark, pine cones, corn cobs, the adsorption degree of which comprised: for copper 54,5; 43,0; 38,9%, respectively, while for iron the mentioned figures are as follows: corn cobs – 70%; pine cones – 56,6%; Plane tree leaves – 62,9, and oak bark – 60%. The similar tests have been conducted during Kazretula River purifying. The oak bark, corn cobs, damp pine cones turned out to be the relatively best adsorbents in the mentioned tests: a purification degree from copper was 60; 56; 48%, while from iron – 73,2; 59,8; 64%, respectively. We suppose that the abovementioned agricultural waste can be recommended as adsorbents in geochemical (sorption) barriers approved in the world practice, which represent the complex of protective measures and constructions creating obstacles on the way of heavy metal ions migration.

Keywords: Adsorption, Volume capacity, Quarry water, Plant raw materials, Waste water. Cooper

*Corresponding author: Neli Kalabegashvili; E-mail address: neli_kalabegashvili@yahoo.com

Introduction

The technologies of extraction and processing existing today in mining, chemical and metallurgical industries are the powerful sources of negative, anthropological influence on the environment. This influence is manifested in the form of pollution of atmospheric air, surface and underground waters, soils and food products.

Mining industry is one of the branches, which has serious impact on environmental pollution by heavy metal ions (HMI) having high toxicity.

It was established through scientific investigations that systematic penetration of heavy metals into human body is especially hazardous for health, since they are characterized by biological peculiarities, such as: accumulation ability in the organism, mutagenic, carcinogenic, embryotoxic properties. Heavy metals' toxic effect is of a special nature in case of children and pregnant women.

The copper accumulation in large quantities in human body causes the Wilson's disease that implies excessive copper accumulation in the brain tissues, skin, liver, pancreatic gland, eyes, and kidneys. It damages the liver and nervous system and frequently becomes the reason of a lethal outcome [1].

The excessive iron content also has the negative impact on human body, it sometimes causes coma and even the death.

According to foregoing, the study and elaboration of simple processing methods of purification of waste (quarry) waters of industrial enterprises from HMI is of undoubted interest.

Local enterprise "RMG Copper" (copper-processing combine) of Bolnisi District (Georgia) faces this problem, too.

Kazretula River flows under the quarry tailing dumps and is rich in ore elements (Cu, Zn, Fe, Cd etc.). The total content of heavy metals in Kazretula River considerably exceeds the allowable concentrations for surface waters. It should be noted that water of the mentioned river is used for irrigation of agricultural lands in Bolnisi district and creates a threat of agriculture production pollution with heavy metals and causes various severe illnesses.

There are known many traditional, up-to-date and non-traditional methods of waste waters (mine, quarry and underspoil waters) treatment, for instance: chemical, membranous, ion exchange, galvanogenic, electrochemical, sorption, extraction methods and so on. However, most of these methods have number of lacks, such as origination of the secondary pollution, necessity of the special complex devices and structures that makes the production nonprofitable [2, 3].

Taking into account the generalization of literature data, carried out explorary researches and RMG Copper's technological scheme we suppose that the role of geochemical barrier technologies, i.e. complex of protective measures and structures installed on the migration way of different toxicants, including HMI, increasingly grows in the solution of mentioned problem. A geochemical barrier is the area, on which in a short time a sharp fall of migration and concentration of chemical elements takes place. The essence of this method lies in the transition of polluting components into a less moving form. Geochemical barriers play "filtering function" kind of role. Significant part in these technologies is assigned to sorption barriers made of different sorbents [4, 5].

There are developed and investigated the sorbents on the basis of a wide variety of mineral and organo-mineral raw materials, synthesized polymers, industrial and agricultural waste.

In recent years in order to remove the heavy metal ions dissolved in the water the successful use of the sorption materials on the basis of vegetable waste has been started, namely: coconut and cedar nut shells, rice husk, buckwheat, wood chips, straw and many other wastes [6-11]. The vegetable waste, such as sunflower, oat, buckwheat, rice husks contains cellulose (up to 30%) and lignin (up to 25%) in their chemical composition, i.e. substances, which are able to carry out the processes of physical sorption and chemosorption [12].

Sunflower husk is the easily-accessible large-tonnage waste at the relatively small price, that's why it is considered as a prospective raw material for production of sorption materials [13-15].

The different groups of chemical substances: lignin, polysaccharides, alkanes and long chain of alcohols have been detected in the grape stalks and pine bark [16-20].

It is also known that the oak bark is rich in tanning substances: catechin, gallotanin, quercetin, free gallic acid that are able to form insoluble complex compounds with heavy metal ions [21-23].

The use of these materials can reduce the expenses for waste water purification several times. The important economic factor is that the vegetable waste of agricultural enterprises serves as a raw material used for such prospective adsorbents. At the same time, it gives us an opportunity to relate the problem of their disposal with the improvement of ecological state of water resources.

In the previous works related to the process of quarry waters purification from heavy metal ions we have studied natural, local alumosilicates, both clays (gumbrin, Askangel) and zeolites (clinoptilolite, mordenite) and also mineral brucite. There was shown that the above mentioned alumosilicates have sorption activity towards HMI [24, 25].

Materials and methods

In the given work there is studied purification of industrial waste quarry waters and Kazretula river waters from copper Cu^{2+} and iron Fe^{+2} ions by adsorption method [26].Vegetable raw materials were used as adsorbents: oak bark, grape stalks, sunflower pellets, corn cob, spruce sawdust, walnut partition, plane tree leaus and pine cones.

Experimental part

Study of sorption properties of mentioned sorbents was conducted under optimum conditions.

The water samples of the river Kazretula were taken at a 2000 meters away from the quarry, and quarry water samples from the water reservoir, from which the quarry waters go for processing. Samples were taken in accordance with technical regalement of "sanitary rules of taking water samples" of Ministry of Infernally Displaced Persons from the Occupied Territories, Labour, Health and Social Affairs of Georgia N15/N (Law article 15 and 23)[27].Samples were several times washed by distilled water for removal of dust and other admixtures and afterwards were dried at room temperature and grinded. 5 g weights of abovementioned sorption materials were placed into test flask with a capacity of 250 cm^3, then 50 cm^3 of surveyed solution were added and a mixture stirred during an hour in the magnetic stirrer CSM305 at the 800 rpm rate, afterwards the adsorbent was removed via filtration, and copper and iron ions concentrations have been determined in the filtrate.

Analyses have been conducted by atomic-adsorption (AAC), Perkin-Elmer (Analyst-200), photometric (KFK-2) and chemical methods. Each trial of we proceed 3-times, we take the average and the results are given in table and drawings.Metal ions quantity absorbed per 1 g of sorbent (volume capacity) – A (mg/g) and adsorption (purification) degree of solution R% were calculated by formulas

$$A = \frac{C_o - C}{m} V \quad \text{mg/g}$$

$$R = \frac{C_o - C}{C_o} \cdot 100\%,$$

where C_o – initial concentration, mg/dm^3;
C – concentration after test;
m – sorbent mass, g;
V – volume of purified solution, dm^3.**[26].**

Results and discussion

Regularities of quarry and river (Kazretula) waters purification from copper and iron ions by adsorption methods are researched [26]. The studied quarry water belongs to waters of average mineralization, composition of which is changed depending on seasons. Copper and iron concentration in quarry water studied by us was varied within ranges of 201,6-560,1 mg/l and 462-560 mg/l,, while in Kazretula River 2,5 mg/l and 11,2 mg/l, respectively.

The impact of plant raw materials adsorption degree on contact time, environment pH, preliminary processing of adsorbent in relation to heavy metals sorption is studied.

The dependence of adsorption degree and volume capacity from the species of plant raw materials (adsorbents) is shown in Tables 1 and 2.

Table 1. *Dependence of copper and iron ions adsorption on the adsorbent (Quarry water ,pH = 3, τ = 1 h)*

№	Adsorbent	R, %		A, mg/g	
		$Cu(2+)$	Fe_{total}	$Cu(2+)$	Fe_{total}
1	Oak bark	54,5	60,0	3,05	2,77
2	Grape stalks battered	12,5	34,5	0,70	1,58
3	Grape stalks unbattered	30,4	40,9	1,70	1,84
4	Sunflower pellets	12,6	59,0	0,70	2,65
5	Corn cobs	38,9	70,0	2,20	3,15
6	Spruce sawdust	2,2	53,5	0,12	2,47
7	Walnut partitions	14,0	16,0	0,78	0,74
8	Plane tree leaves	8,23	62,9	0,05	2,89
9	Damp pine cones	43,0	56,6	2,41	2,55
10	Damp pine cones treated with 1N NaOH	51,0	68,0	2,85	3,06

Research results of dependence of adsorption degree on contact time for sawdust, oak bark and damp pine cones in relation to copper and iron are shown in Fig. 1.

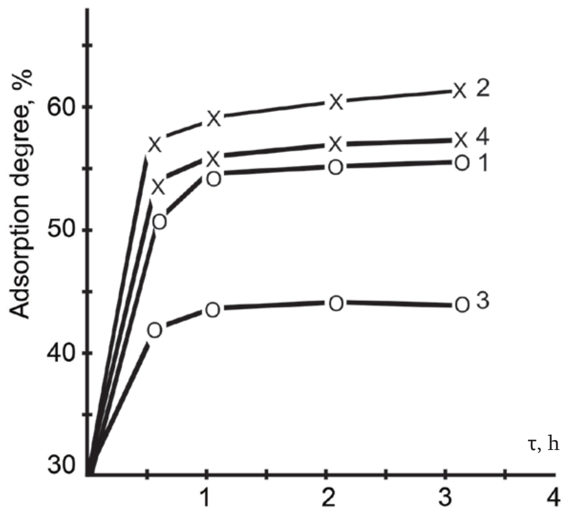

Fig. 1. *Contact time influence on adsorption degree for Cu2+ and Fe2+(pH = 3,0, ratio of adsorbent : solution volume – 1:10); 1, 2 – oak bark, 3, 4 – pine cones. o - Cu2+ x – Fe2+*

As is seen from diagrams, quarry water purification runs effectively after 30 minute contact and the maximum value of adsorption degree is reached within an hour, and afterwards isotherms negligibly go up and weak dependence between them is observed.

The maximum value of Cu^{2+} and Fe^{2+} ions adsorption degree is reached in case of oak bark and is 55 and 60%, respectively, in comparison with damp pine cones, for which it equals to 43 and 57%, respectively, when pH = 3.

According to some authors, the bark of some southern species of wood contains moderate quantity of tannins. It is shown that when purifying model solutions with the use of oak bark the metal ions enter into reaction with tannin-containing substances and form insoluble complex compounds with them [23]. It is probably one of the reasons of relatively high values of purification degree by oak bark compared with other adsorbents (see Table 1).

It is known that adsorption degree of sorbent is substantially depended on environment (solution) pH [18, 28], and due to this reason there was studied an impact of environment acidity on adsorption of sorbing materials – oak bark and damp pine cones. Adsorption isotherms in relation to Cu^{2+} and Fe^{2+} on mentioned sorbents are given in Fig. 2.

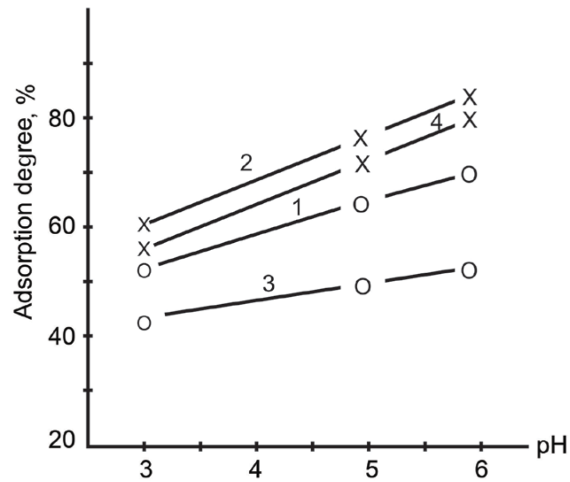

Fig. 2. *Impact of environment pH on adsorption degree of Cu2+ and Fe2+(τ = 1 hour, ratio of adsorbent : solution volume – 1:10); 1, 2 – oak bark, 3, 4 – pine cones. o - Cu2+ x – Fe2+*

As is seen from the diagrams, adsorption isotherms for copper and iron on both sorbents are almost of the same nature; they gradually go up. It is shown that maximum adsorption degree in relation to Cu^{2+} and Fe^{2+} ions in neutral environment (pH = 6) is observed in case of oak bark and is equal to 70 and 85%, while in case of pine cones it equals to 53 and 80%, respectively. Sorption degree on both sorbents in neutral environment is slightly higher than in acid medium, regarding both copper and iron.

It is established that this nature of sorption degree dependence on environment pH is related with change in state of active centers of sorbents. In case of low values of pH hydrogen ions totally dominate, and takes place promotion of sorbent surface that assists electrostatic repulsion of metal ions and reduction of their adsorption. At higher values of pH active centers of tannin-containing compounds (oak bark, grape stalks, pine cones) undergo dissociation and form corresponding phenolate anions, which are able to bind with metals ions and form chelate complexes [29].

In order to compare the effect of preliminary alkali treatment on adsorption degree, the adsorbent (pine cones) was preliminary treated with 1N NaOH solution. It was shown that after alkali treatment adsorption degree in relation to Cu^{2+} and Fe^{2+} increases by 8 and 12%, respectively.

Experimental data show that adsorption degree for all enumerated adsorbents regarding iron is higher than in relation to copper. Probably this is because of radius size of adsorbed cations, which plays important role. According to authors data copper cation radius is bigger than of iron cation and they equal to 73 r/P_m and 70 r/P_m, respectively [30].

Similar works have been carried out for the water of Kazretula River. Test results showed us that the oak barks (Cu – 60%, Fe – 73%), damp pine cones (Cu –48% and Fe – 64%) and corn cobs (Cu –56%, Fe – 60%) have purified the Kazretula water from heavy metals relatively well (Table 2).

Table 2. *Dependence of copper and iron adsorption on adsorbents (Riv.Kazretula,PH=5, τ = 1 h)*

Adsorbent	R, %		A, mg/g	
	Cu(2+)	Fe(2+)	Cu(2+)	Fe(2+)
Oak bark	60	73,2	0,015	0,082
Grape stalks battered	40	55,3	0,010	0,062
Corn cobs	56	59,8	0,056	0,067
Pine cones	48	64,0	0,012	0,072

It is known that the efficiency of adsorption processes depends not only on sorbent properties and quantity, but also on chemical nature and concentration of adsorbed substance. The more is the substance concentration in polluted water, the more quantity is adsorbed per each gram of the sorbent (A, mg/g). This fact is clearly seen from Tables 1 and 2, in case of reduction of heavy metal ions quantity in sorbent phase in Kazretula River and quarry waters.

Conclusion

On the basis of foregoing materials, one can recommend the use of geochemical sorption barriers as of obstacles on the way of migration of different heavy metal ions, where the cheap natural raw materials, such as oak bark, grape stalks, pine cones, corn cobs, and sunflower husk can be used as adsorbents. When using the mentioned raw materials as adsorbents the copper adsorption degree in case of quarry water comprised 54,5% for oak bark, 30,4% for grape stalks, 43% for damp pine cones, and 38,9% for corn cobs; while the iron adsorption degree was 60,0; 40,9; 56,6 and 70%, respectively.

In case of Kazretula River purification with the same quantity of adsorbents, the copper adsorption degree was 60; 40;48; 56; while the iron adsorption degree was 73,2; 55,3; 64% and 59,8; respectively.

References

[1] Environmental chemistry. Translation from English under the editorship of J. O.M. Bokris. Khimia, M., 1982.

[2] Kim TY, Park SK, Cho SY, Kim HB., Sorption of heavy metals by brewery biomass. Korean J. Chem. Eng., 22 (2005) 91-98.

[3] Ahuwalia SS, Coyal D., Removal of heavy metals by waste tea leaves from aqueous solution. Eng. Lige Sci, 5 (2005) 158-162.

[4] Perelman A.I., Vorobiev A.E., Landscape and geochemical conditions of location of enterprises of mining industry. Bulletin of RAS, geographic series, 2 (1994) 50-61 (in Russian).

[5] Izotov A.A., Koverdyaev O.N., Vershinina O.O., Methods for reduction of drainage waters impact on the environment in mining regions. Mining journal, 10, (2006) 103-106 (in Russian).

[6] Sciban S., Klasnja M., Skrbic B., Adsorption of copper ions from water by modified agricultural by-products. Desalination, vol. 229, iss. 1-3 (2008) 170-140.

[7] Ong S., Seng C., and Lim P., Kinetics of adsorption of Cu (II) and Cd (II) from aqueous solution on rice husk and modified rice husk. Electronic J. Environmental Agric. Food. chem., 5, (2007) 1764-1774

[8] Escuderon G., Gabaldon C., Marzal P. and Vill I., Effect of Edta on divalent metal adsorption onto grape stalk and exhausted coffee wastes. J. Hazard. Mater., 152 (2008) 476-485.

[9] Fiol N., Villaes I. and Poch I., Removal of lead(II) and cadmium(II) from aqueous solution using grape stalk waste, J. of Hazard. Materials B 133 (2006) 203-211.

[10] Valld C., Azebalo I.A., Casas I., Martinez M., Miralles N. and Florido A., Modelling of the Ni(II) removal from aqueous solutions onto grape stalk wastes in fixed-bed column. J. Haz. Mat. 174 (20100144-150.

[11] Shukla S.S., Yu LJ., Dorris KL., Shukla A., Removal of nickel from aqueous solution by sawdust. J. of Hazardous Materials, 2015, 121(1-3) (2015) 243-246.

[12] Sciban M., Klasnja M., Skrbic B., Adsorption of copper ions from water by modified agricultural by-products. Desalination, vol. 229, iss. 1-3 (2008)170-180.

[13] Sivolobova N.O., Gracheva N.V., Zhashueva K.A., Sikorskaia A.V., Adsorption materials

on the basis of sunflower husk. Engineering bulletin of Don,, 1 (2017) 2-8 (in Russian).

[14] Asubiojo O.I., Ajelabi O.B. Removal of heavy metals from industrial waste water using natural adsorbents, J. Toxicological and Environmental chemistry, 2009, vol. 91, iss. 5 (2009) 883-890.

[15] Abdelfatah I., Sayed F.E., Almedolab A. Removal of Heavy Metals from Waste Water using Corn Cob. Sustation Case Study, 2016.

[16] Machado R., Santos C., Correla M.J.N., Carvalho J.R., Biosorption of copper by grape stalks and pine bark biomasses. The European J. of Mineral Processing and Environmental Protection, vol. 3, no. 1 (2003) 108-118.

[17] Florido A., Valderrama C., Azevalo I.A., Casa S.I., Martinez M., Miralles N., Application of two sites non-equilibrium sorption model for the removal of Co(II) onto grape stalk wastes a fixed-bed column. Chemical Engineering J., vol. 156, №2 (2010) 298-304.

[18] Willaescusa I., Fiol N., Martinez M., Removal of copper and nickel ions from aqueous solutions by grape stalks wastes. Water Res., 38 (2004) 992 – 1002.

[19] Farin N.V., Matos G.D. and Arruda M.A.Z. Grape bagasse as a potential bio-sorbent of metals in effluent treatments. Bioresour. Technol., 98 (2007) 1940-1946.

[20] Farin N.V., Matos G.D., Lehmann E. and Arruda M.A.Z., Grape bagasse as an alternative natural adsorbent of cadmium and lead for effluent treatment. J. Hazard. Mater., 154 (2008) 1007-1012.

[21] Love the Team. What diseases are treated with oak bark, useful properties of the bark of oak 2001.

[22] Fenglian Fu, Qi Wang., Removal of heavy metals ions from waste waters. Preview. J. of Environmental Management, 92 (2011) 407-418.

[23] Yusupova A.I., Treatment of Waste Waters Containing Heavy Metal Ions by the Sorbents and Extracts from Tannin-Containing waste. The thesis work, Kazan, 2015 (in Russian).

[24] Kalabegashvili N.G., Ioseliani D.K., Balarjishvili G.I., Samkharadze L.O., Tsiskarishvili R.P., Dolidze A.V., Waste water purification from heavy metals with the use of local clays and mineral Brucite. Proceedings of the Georgian National Academy of Sciences, v. 43, №2, (2017) 162-164.

[25] Ioseliani D.K., Balarjishvili G.I., Kalabegashvili N.G., Samkharadze L.O., Mikadze I.I., Purification of waters polluted with heavy metals using adsorption method. World Science, 2018, №4 (32), vol. 1 (2018) 64-66.

[26] G.Tsitsishvili.Adsorbtio Process.Tbilisi,1959.

[27] The order N15/N "sanitary rulesofwater sampling " (Article 15 and 23) of Ministry of labor, health and social protection.22/01/2004, Tbilisi.

[28] Zhang Yu B., Shukva ASS Y., Dorris KL., The removal of heavy metal from aqueous solutions by sawdust adsorption-removal of copper. J. Hazard Mater. 80(1-3) (2000) 33-42.

[29] Shaikhiev I.G., Bagauva A.I., Removal of iron (III) ions by extracts of oak bark and leaves and study of morphology and kinetics of waste sedimentation. Water, chemistry and ecology, 3 (20140 70-84 (in Russian).

[30] Wells A.F., Structural inorganic chemistry, 5th ed., Clarendon Press, Oxford, 1984, p. 1288 (metallic radii for 12-coordination); Shannon R.D. Acta Crystallogr., Sect. A: Found. Crystallogr. 32, (1976) 751- 759.