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Research Note

Removal and Recovery of Cu^{+2}, Cr^{+3} and Ni^{+2} by Using Dried Biomass of Sargassum Algae in a Batch System

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Algae are a group of living organisms that play an important role in heavy metal removal from polluted wastes. Their usage is rather economical, especially if the waste is not heavily polluted. Since the use of live algae creates some problems, products of their dried mass were used in this study. The sargassum species was collected from the Persian Gulf, dried, cut in pieces and then used as the biomass. The adsorption process, with influencing factors such as initial concentrations, retention time, pH and temperature, were considered. In dilute wastewater (less than 25 mg/l), this method can reduce the concentration of remaining heavy metals after 10 min retention time at a suitable level, for discharging into the environment. pH and temperature did not have an effect on the results. Absorption equations for the metals in question have been developed and the economical evaluation was compared using statistical methods. To recover metals and regenerate the biomass, EDTA and HCl were examined. It was found that using EDTA (4 mM) and HCl (pH = 2) after 90 min had an efficiency of about %85 and %75 and EDTA is more efficient than HCl. It should also be mentioned that recovery has cost benefit if the metal of interest is noble and valuable. After 5 consequent cycles of adsorption and recovery using HCl and EDTA, the biomass lessened by 30% and 16%, respectively. The remaining heavy metal in the algae is increased gradually until we have 90% reduction in recovery using HCl and 65% using EDTA, because the active cell wall group of algae is damaged by HCl. During the first cycle, most of the metals were recovered. The primary and annual recovery costs were about 90 and 350 times more than the value of recovered heavy metal.

INTRODUCTION

Protection of the environment is a major concern of human communities. Development and various related activities release lots of poisonous materials into the environment, and heavy metals are the most dangerous of all. These metals come from different sources, such as: Soil erosion, volcanic eruption, leakages of land fill, city sewage, industrial wastes, electroplating, tannery and many others. Some metals are necessary for human and animal health as micronutrients, though the same compounds at higher doses are poisonous and cause adverse health effects. Some risks of heavy metals are as follows:

1. They do not decompose or decay .They penetrate surfaces, such as ground water or soil;
2. They create a vast range of effects within biological environments, from allergic reaction to death;
3. Some of them, due to their affinity with amines and sulfidril, are enzyme inhibitors;
4. Many of them are carcinogenic and/or mutagenic;
5. Some edible plants absorb these compounds via their roots which accumulate and become part of the food chain, directly or indirectly;
6. In aqueous environments they become more poisonous;
7. Two or more metal species have synergistic effects.

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Referring to health effects, the importance of wastewater treatments on metal elements becomes more evident. There are several removal methods, which are physico-chemical and biological. Each of these methods consists of chemical sedimentation, ion exchange, adsorption, membrane, electrical techniques, and evaporation etc. Experiment showed that most of the conventional methods produce some complexes with other compounds and create problems in treatment plants. Therefore, some special precautions regarding conditions, such as temperature, light, pH, etc. [1-3], should be taken.

Biosorption is important from two points, the elimination of poisonous metals and the recovery of precious elements. Biological absorption by metabolism is only possible by using living organisms, which is done slowly and includes adsorptions and intercellular absorption [4].

The adsorption mechanism of Cu, Cr, and Ni, using the dried algae biomass of the sargassum species is independent of metabolisms. Absorption is accomplished by the exchange of metal cations with active groups of cellular walls. Most absorption is done by a carboxily group of algenic acids. That produces dentate compounds. Another path of absorption is due to sulfate groups of cellular walls [5-7]. The desorption of adsorbed metals is also possible for destructive and non-destructive recovery.

For a selection of the best recovery processes, factors such as simplicity and the value of organisms and of the products to be recovered, should be considered. If a non-destructive method of recovery is employed, then, the biomass could be regenerated and reused. In the case of a destructive method, acid and alkalic compound are used and the biomass is not reusable [8,9].

METHODS AND MATERIALS

Adsorbing Biomass

Sargassum, a brown macro algae collected from the Persian Gulf on Queshm Island, was used as the biomass. The algae was dried in the sun, transferred to the lab, cut in pieces ($d = 0.50 - 0.84$ mm), washed with doubled distillated water to wash out any mineral contaminants and then dried at 60°C to the fixed weight. A part of this biomass was examined for a sign of the metals in question, to be used as blank.

Reagents

Waste was prepared in the laboratory as follows:
Heavy metal solutions with different initial concentrations were prepared by dissolving: %99.5 Cu $(NO_3)_2.3H_2O$, %98 Cr $(NO_3)_3.9H_2O$, %97 Ni $(NO_3)_2.6H_2O$ in doubled distillated water.

All glasses and other instruments were washed to be free from any precontamination.

Analytical Methods

The samples (1 mL) were removed at experiment, filtered using Millipore membrane filters of 0.45 μm pore size and analyzed for heavy metals by atomic absorption. An atomic absorption spectrometer [10] (Varian Spectra-200 AA) was used for analyses of the artificial waste before and after exposure to algaes.

Effects of Retention Time and Initial Concentration

Experiments to determine the optimum contact time required to reach equilibrium were performed in Erlenmeyer flasks, using 200 mL of metal solution and approximately 5 grams of biomass (dry matter) at constant pH and temperature. Samples (1 mL) were removed at different time intervals (10, 20, 30, 45 and 60 min) and analyzed for heavy metals concentration by atomic absorption.

Effects of pH

These experiments were done at pH of 2, 4, 6, 8, 10 and 12 in 30 min retention time and at a constant temperature. Solutions of NaOH and H_2SO_4 were used to adjust the pH. Samples (1 mL) were removed, filtered and analyzed for heavy metals concentration by atomic absorption.

Effects of Temperature

These experiments were done at temperatures 0, 15, 25, 35 and 45°C with an initial concentration of 50 mg/l and retention time of 30 min. Samples (1 mL) were removed, filtered and analyzed for heavy metals concentration by atomic absorption.

Data Analysis

The SPSS program computed special adsorption equations and the results were drawn by leaner regression.

Recovery

To determine the recovery reducing reagent, the time and efficiency of HCl and EDTA were examined as follows:

0.1 g of sargassum saturated with the metals in question was examined as a batch system. HCl with pH of 2, 3, 4, 5 and 6 and EDTA of 0.2, 0.5, 1, 2, 3 and

4 mM, at a retention time of 10, 30, 45, 60 and 90 mins, were examined. Samples (1 mL) were removed, filtered and analyzed for heavy metals by atomic absorption.

Experimental recovery at 5 consecutive cycles of absorption and recovery were followed as the above recovery experiment by HCl (at pH = 2) and EDTA (using 4mM), with a 90 min retention time (in this condition, the role of recovery was maximum).

RESULTS

The results of the different experiments appear in Figures 1 to 7 for the effect of the variables involved in metal removal. The effect of retention time on the removal of metals with different concentrations is shown in Figure 1. This method had about 90% efficiency for heavy metals removal and is completely feasible for reducing heavy metal concentrations to levels as low as required by environmental legislation, with an initial concentration of 25 mg/l; however, this method for concentrated wastes could be used as a complete method. The adsorption experiments of heavy metals (Cu, Cr, Ni) showed that by reducing the initial concentration and increasing retention time, the remained concentration of heavy metals in the solution was reduced. 10 min retention time for removing the metal was enough. However, after more than 10 min, the concentration of remaining heavy metals was not very much changed. The use of a retention time of more than 10 min was not, therefore, found to be economical. The affinity of algae mass for adsorbing heavy metals was found to be as follows: Cr^{+3} >Cu^{+2} >Ni^{+2} and, for recovery, was the opposite of adsorbing. By increasing the electrical charge and atomic mass, the adsorption affinity of algae was increased.

The effect of different pH and initial concentration on the removal of heavy metals by a dried mass of sargassum is shown in Figure 2. At the pH = 12 for Cu and Ni and pH = 8 for Cr, the maximum rate of sedimentation was reached. Since Cr has an amphoteric property, the maximum adsorption was reached at pH > 8.

The effect of different temperature on the removal of heavy metals by a dried mass of sargassum is shown in Figure 3, which shows that temperature is not effective in heavy metal removal.

The results of the recovery experiments of 0.5 mM adsorbed heavy metals (Cu, Cr and Ni) using 0.1 g dried mass of sargassum and different concentrations of HCl and EDTA at different retention times, is shown in Figures 4 to 6 . The recovery experiments showed that with increasing the rate of concentration and consumption of reagents (HCl, EDTA) and retention time, the efficiency of recovery was increased. It was

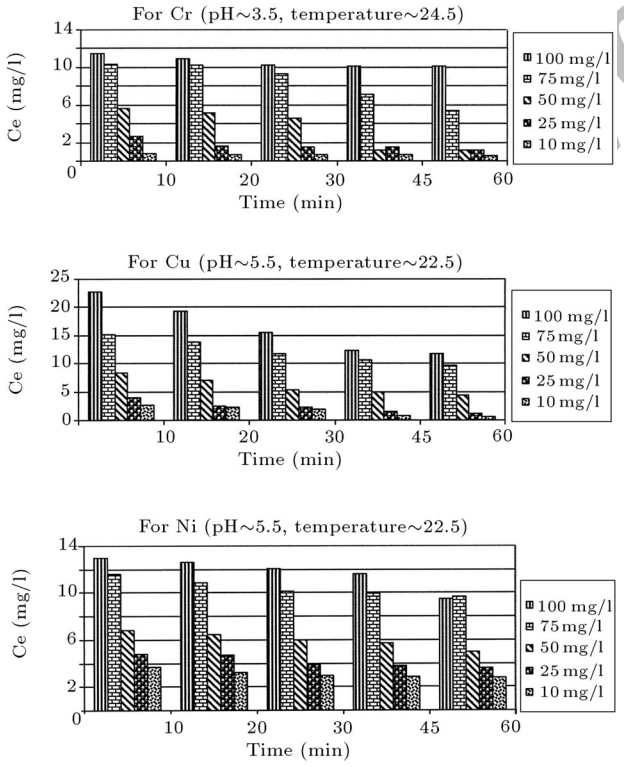

Figure 1. Effect of retention time and initial concentration on heavy metal adsorption by dry mass of sargassum.

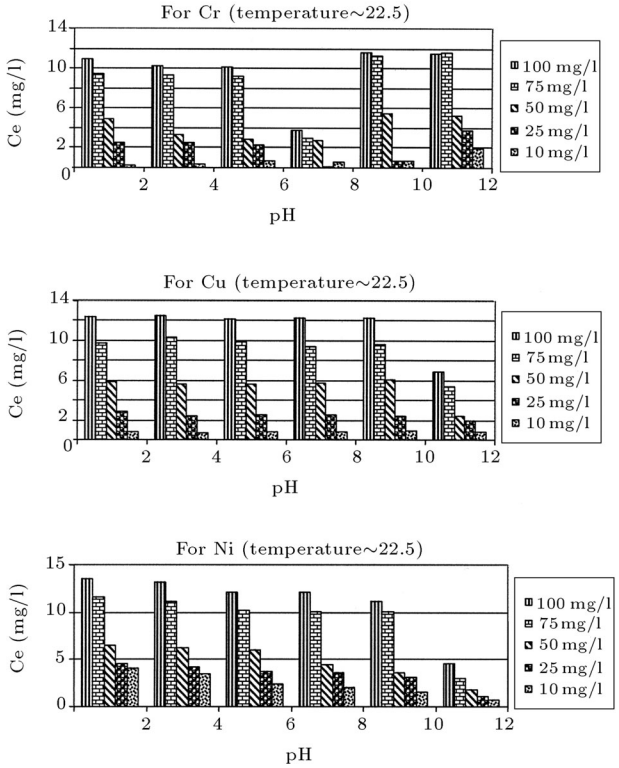

Figure 2. Effect of pH and initial concentration on heavy metal adsorption by dry mass of sargassum (retention time = 30 min).

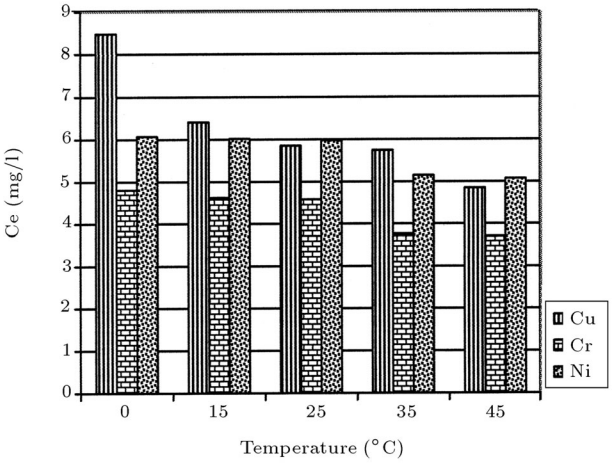

Figure 3. Effect of temperature on heavy metal adsorption by dry mass of sargassum (retention time =30 min and initial concentration= 50 mg/l).

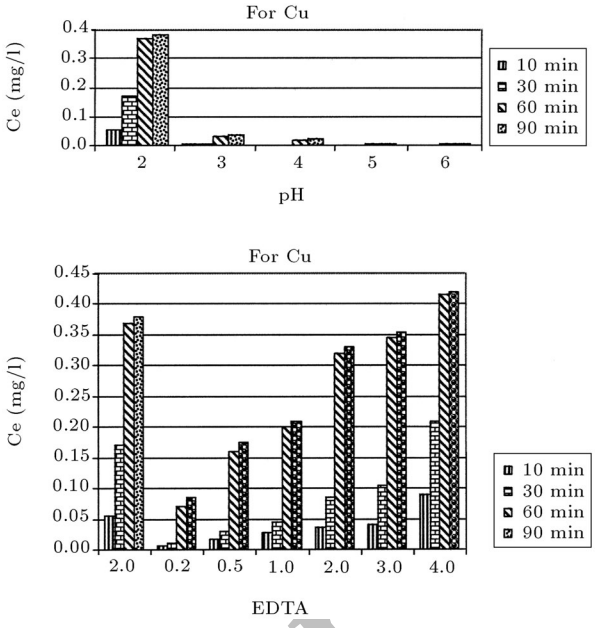

Figure 4. Recovery result of 0.5 mM adsorbed copper with 0.1 g sargassum at different retention times.

found that using EDTA (4 mM) and HCl (pH = 2) after 90 min had an efficiency of about 85% and 75% and that EDTA was more efficient than HCl because of the heavy metals affinity to EDTA.

The maximum recovery of heavy metals was at 90 min retention time, but, 60 min retention time was enough for recovery. At more than 60 min, the concentration of heavy metals recovery was not noticeable and using more than 60 min was not economical.

The result of 5 consecutive cycles of absorption and the recovery of 0.5 mM heavy metals (Cu, Cr, Ni) by HCl (at pH = 2) and EDTA (with a usage of 4 mM) at 90 min retention time (in this condition, the role of recovery is maximum) and 0.1 g exposed sargassum,

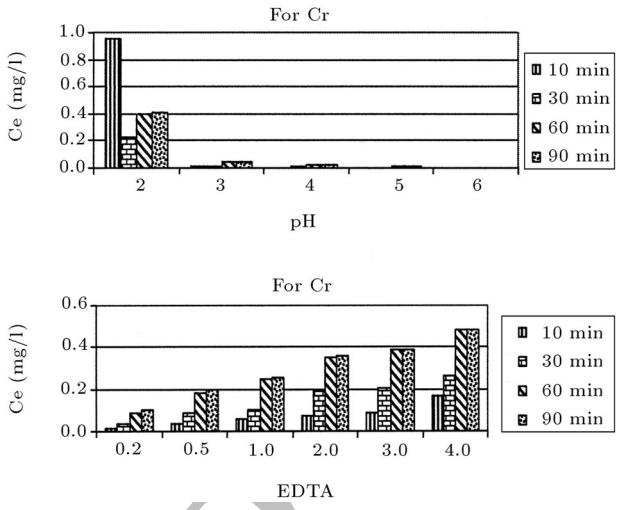

Figure 5. Recovery result of 0.5 mM adsorbed chromium with 0.1 g sargassum at different retention times.

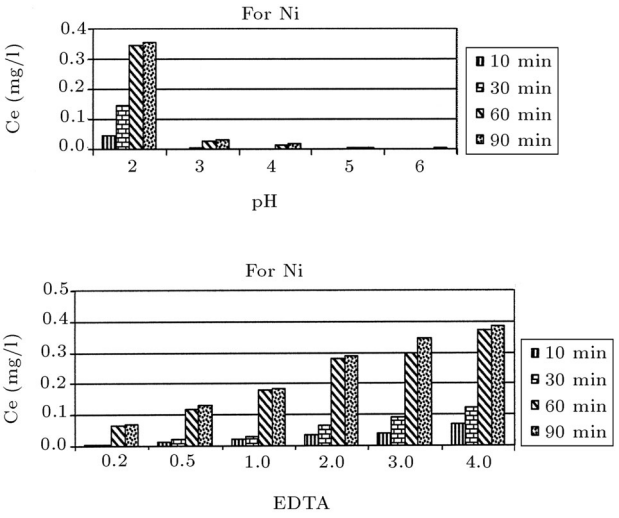

Figure 6. Recovery result of 0.5 mM adsorbed Nickel with 0.1 g sargassum at different retention times.

is shown in Figure 7. The remaining heavy metal in the metal in the algae is increased little by little and 90% reduction in recovery efficiency by HCl and 65% by EDTA are found, because the active cell wall group of algae was damaged by HCl and the biomass was lost by 30% and 16%, respectively.

To formulize the findings, special adsorption formulas were developed by drawing linear regression with experimental adsorption data in a batch system, which are presented in Figures 1 to 3. All obtained figures are linear, which is significant for prediction of the simultaneous effects of different parameters for a removal relation. Results and coefficients were shown in Table 1.

The effects of all parameters (retention time, pH, initial concentration and temperature that were shown by x_1, x_2, x_3 and x_4), on the remaining concentration

Table 1. Coefficient and significant parameters that were obtained by linear regression of SPSS.

Metal	Model	Coefficient	Std Error.	Sig.
Cu	Constant	4.874	1.666	0.005
	Retention time	-9.540E-02	0.022	0.000
	pH	-0.232	0.100	0.024
	Initial concentration	0.159	0.008	0.000
	Temperature	-7.854E-02	0.056	0.165
Cr	Constant	0.905	1.443	0.533
	Retention time	-5.072E-02	0.019	0.011
	pH	5.691E-02	0.076	0.457
	Initial concentration	0.112	0.007	0.000
	Temperature	-1.920E-02	0.048	0.689
Ni	Constant	5.796	1.062	0.000
	Retention time	-3.332E-02	0.014	0.020
	pH	-0.501	0.064	0.000
	Initial concentration	0.104	0.005	0.000
	Temperature	-2.039E-02	0.035	0.562

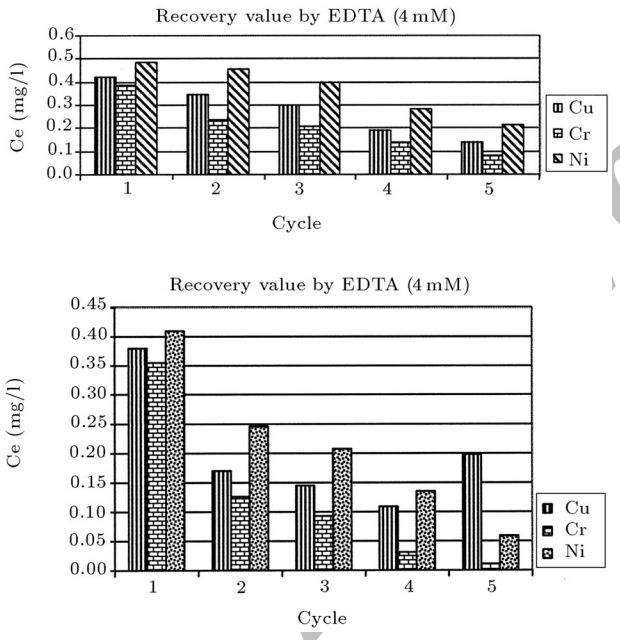

Figure 7. The result of 5 consequent cycles of recovery and adsorption of 0.5 mM heavy metals by HCL (pH = 2) and EDTA (4 mM) in 90 minutes by sargassum algae.

of heavy metal, were calculated as follows:

$$\text{Cu}: y = -9.540^{*}10^{-2}x_1 - 0.232x_2 + 0.159x_3 - 7.854^{*}10^{-2}x_4 + 4.874,$$

$$\text{Cr}: y = -5.072^{*}10^{-2}x_1 + 5.691^{*}10^{-2}x_2 + 0.112x_3 - 1.920x_4 + 0.905,$$

$$\text{Ni}: y = -3.33^{*}10^{-2}x_1 - 0.501x_2 + 0.104x_3 - 2.039^{*}10^{-2}x_4 + 5.796.$$

For the Cu formula, the range of pH is 1-11 and the initial concentration is 50-100 mg/l. For the Cr formula, the range of pH is 1-7, 9-11 and the initial concentration is 25-100 mg/l. For the Ni formula, the range of pH of 1-11 and the initial concentration of 25-100 mg/l were acceptable.

CONCLUSION

The cost of construction and the equipment for a batch adsorbing system was 1660 rials ($2.0) for each liter of wastewater. The annual cost for the repairing and maintenance of the system, including material utilities, disposal of used algae and operation was estimated at 8479.7 rials ($10.5) for each liter of wastewater. The cost of investment and annual wear was 32.7 rials ($0.4) for each liter of wastewater.

The cost of construction and the equipment for the recovery system was 567.2 rials ($0.7) for each gram of biomass and the annual cost for the repairing and maintenance of the system, material utilities, disposal of used algae and operation was 1987.7 rials ($2.4) for each gram of biomass. The cost of investment and annual wear was 111.7 rials ($0.1) for each gram of biomass.

In the first cycle, where the highest amount of recovered metal exists, the primary cost of recovery was about 90 times and annual recovery cost about 350

times more than the value of the heavy metal recovered. By increasing the number of recovery cycles, the cost of recovery, in comparison with recovered metal, was increased. The using of biomass and the recovery of heavy metals (Cu, Cr and Ni) with regard to the cost of sargassum biomass (that is, cheap), was not economical.

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