DEVELOPEMENT OF A PROCESS FOR WASTE EGGSHEEL VALORISATION

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Abstract

In this work it was evaluated the adsorption efficiency of calcined eggshell (CES) from the egg-breaking operations in the treatment of wastewaters from different industrial units. It was evaluated the removal of organic material, expressed as chemically oxygen demand (COD), in leachate wastewaters from sanitary landfill (LLWW) and the municipal residual wastewaters (NWW). It was also assessed the efficiency of alkaline metals removal, specifically aluminum, copper, chromium and nickel from effluents of industrial unites from superficial treatments. A detailed study of the eggshell characteristics, before and after the absorption process, was carried out, aiming at investigate the adsorption mechanism underlying the removal of different pollutants. Results demonstrate that adsorption of organic material and metals in the calcined eggshell, achieved 89% of organic material (COD) removal in municipal wastewaters and 81% in landfill leachates wastewaters. It was also verified a removal of 95,4% aluminum from residual wastewaters from anodizing industrial plant and a removal of 88% copper, 95% chromium and 30% nickel, in effluents from superficial treatments produced in Ni/Cr plating plants.

This evidence demonstrates that calcined eggshell-based adsorbent proved to be appropriated to wastewaters treatment with high contents of organic matter and heavy metals, from different aqueous systems or different industries. The application of this adsorbent in this methodology showed good cost-benefits ratio, which proves that it can be an effective alternative to activated carbon.

1- INTRODUCTION

Water is an essential natural resource for the existence and survival of animals, plants and mankind. Therefore the contamination of water by toxic contaminants through the discharge of industrial wastewater is a worldwide environmental problem. Rapid industrialization and the increase in world population have seriously contributed to the degradation of surface and ground water [1,2]. Metals such as copper, nickel, chromium and aluminum have been recognized as hazardous heavy metals. Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders, so they must be removed before discharge [3]. Hence the treatment of industrial wastewaters is essential to the sustainable development of the world. Various methods are available for the removal of toxic pollutants from water and wastewater including: reverse osmosis; ion exchange; precipitation; electro-dialysis and adsorption. Among these, adsorption is by far the most versatile and widely used method for the treatment of wastewater due to its high removal capacity and easy operation at large scale [4].

Adsorption is a physic-chemical technique which involves mass transfer between liquid and solid phase to remove or at least reduce chemical residues from wastewaters. Activated carbon has been the most and widely used adsorbent in wastewater treatment methodology. Despite of its efficiency in adsorption process, this type of adsorbent has a high cost which makes it no longer attractive to be used in small-scale industries [5]. Duo to the problems mentioned previously, in recently years it was been made efforts and research to produce alternative low-cost adsorbents that can substitute activated carbon in wastewater treatment. This type of low-cost adsorbents derives from agriculture waste, industrial by-products or natural materials [6]. Therefore, eggshell from egg-breaking operations constitutes significant waste disposal problems for the food industry, so the development of value-added by products from this waste is to be welcomed. The porous nature of eggshell makes it an attractive material to be employed as an adsorbent [6]. Several researches have been conducted to evaluate the adsorption ability of eggshell as low cost adsorbent, in artificial wastewater with mono or multi components. This studies demonstrated the effectiveness of this adsorbent in the removal of heavy metals [3,7-9], phenolic compounds [10], dyes [11] and pesticides [12]. Arunlertaree *et al* (2003) investigated the removal of lead from manufacturing wastewater by adsorption onto eggshell powder. They have conducted several batch studies at unadjusted pH, reaching the reduction of lead concentration to values below quality standards [13]. Park *et al* (2007) studied the adsorption of chromium, cadmium and lead from a real electroplating wastewater treatment facility [14]. The authors identified calcined eggshell as a good adsorbent for treatment of acidic wastewater with a considerable uptake of heavy metals, as result of eggshell neutralization capacity.

Although many research works have been done recently to evaluate the potential of using eggshell as adsorbent for the treatment of simulated wastewaters, few studies was been realized in industrial effluents. Considering this, the aim of the present work was to evaluate the adsorption capacity of eggshell low-cost adsorbent on real industrial effluents comparing different operating conditions.

2- MATERIALS AND METHODS

Adsorbent

The adsorbent used in the present paper was calcined eggshell powder, collected from a local hatchery waste. Shells were washed successively with distilled water and eggshell membrane was separated by hand. After complete removal of the organic fraction, shell was washed again. Then Eggshell were dried at 105ºC for 24h, milled and calcined at 1000ºC for 2h. The adsorption capacity was calculated by determining the final concentration at equilibrium, according to Eq, 1

$$qt =((C_0\text{-}Ce)*V)/m \quad (1)$$

where qe (mg/g) is the solute adsorption capacity per gram of eggshell, C_0 and Ce (mg/L) are the concentration at initial and equilibrium, respectively, V (L) is the volume and m (g) is the mass of eggshell used.

Characterization of real wastewater effluents

Four different types of wastewater effluents were analysed. Removal of organic matter was assessed in municipal wastewater (NWW) from unit treatment facilities and from landfill leachates wastewater (LLWW), collected from a local landfill plant. Adsorption of aluminium was studied in the wastewater effluent from an aluminium anodizing plant (AWW) and the adsorption of copper (Cu), chromium (Cr) and nickel (Ni) was realized in wastewater effluent from the acid leaching process of galvanic sludges (GLWW). The samples were recovered in proper containers and stored at 4ºC [15]. The concentration of organic matter was determinate by measuring chemical oxygen demand (COD), by closed reflux method. The concentration of aluminium (Al), copper (Cu), chromium (Cr) and nickel (Ni) was determined by atomic absorption spectrometry (AAS) [15].

Adsorption experiments

In order to optimized the operating conditions for pollutants removal in the different wastewater samples used in adsorption experiments, batch studies were carried out with calcined eggshell with agitation and pH control. All batch adsorption studies were conducted at room temperature. To determine the effect of CES concentration in COD removal on LLWW sample, 0.25, 0.5, 0.75, 4, 8, 10, 25, 50, 100, 150 and 200 g/l of CES were added to each set of experiments, at 120 minutes of reaction time with constant agitation. Adsorption experiments in COD removal on MWW samples were carry out using CES in different concentration. For this purpose it was used 5, 10, 25, 50, 100, 150 and 200 g/l of CES for each set of experiments, at 120 minutes of reaction time with constant agitation. For the removal of aluminium in anodizing wastewaters (AWW) it was used CES concentrations varied from 0.75 to 8 g/L, at 120 minutes of reaction time with constant agitation. For copper, chromium and nickel removal from galvanic acid leaching wastewaters (GLWW) it was used CES in 0.01 g/l for each set of experiments at different reactions time, 0 to 4 hours, at constant agitation.

3- RESULTS AND DISCUSSION

Wastewater effluents composition

Table 1 shows the chemical composition of the four effluents used in adsorptions experiments. Results demonstrated that landfill leachate wastewater (LLWW) has a higher content in organic matter, expressed in COD, compared to municipal wastewater (MWW). Anodizing wastewater (AWW) has a high content in aluminium (870 mg/l) which is related to the anodizing industrial process. Regarding to galvanic leaching wastewater (GLWW) it is possible to verify a low content in metals. This type of effluent has a high content in dissolved metals and therefore it was necessary dilute the solution which explain the low metals determination.

	Municipal wastewaters (MWW)	Landfill Leachate wastewaters (LLWW)	Anodizing wastewaters (AWW)	Galvanic acid leaching wastewaters (GLWW)
pH	7.75	8.38	13.04	3,43
CQO [mg/L]	579	5760	-	-
Metals [mg/L]				
Al	-	-	870	-
Cr	-	-	-	6,0
Cu	-	-	-	2,4
Ni	-	-	-	10,7

Table 1: Chemical characterization of the different types of effluents used in the present study.

Organic matter removal by adsorption

Figure 1 shows the adsorption and removal of organic matter, expressed in COD, in landfill leachate wastewaters (LLWW).

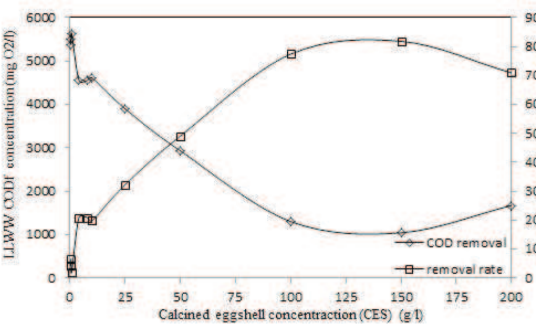

Figure 1: Effect of adsorbent dosage on the adsorption and removal rate of COD on CES in LLWW effluent

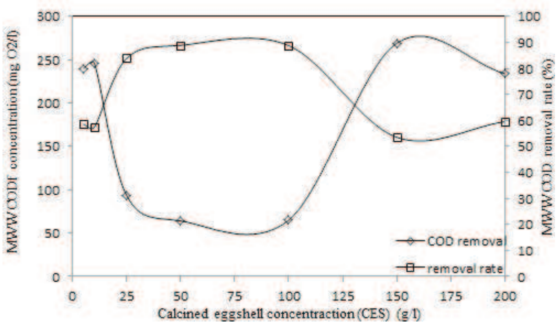

Figure 2: Effect of adsorbent dosage on the adsorption and removal rate of COD on CES in MWW effluent

Removal of organic matter in the landfill leachate wastewaters reached high removal rates with high concentrations of CES, specially with 25-200 g/l. Maximum removal rate (81,8%) was achieved with a concentration of 150 g/l of CES which represents a adsorption capacity (qt) of 31,4 mg effluent/ g adsorbent.

Figure 2 shows the adsorption and removal of organic matter, expressed in COD, in municipal wastewaters (NWW). Results showed that maximum efficiency of adsorption it`s achieved at 50 g/l CES, allowing to remove approximately 89% of COD which represents adsorption capacity (qt) of 10,3 mg $_{COD}$/ g $_{adsorbent}$. It is possible to verify that the affinity of CES in the adsorption of organic matter is superior in high load and is also possible to state that initial concentration of organic matter influence the COD removal and adsorption capacity.

Anodizing wastewater (AWW) treatment by adsorption

Figure 3 shows the adsorption and removal rate of aluminium from AWW varying different concentrations of CES at pH 4.5. This value of pH is justified by the speciation curve of aluminium, because at this value of pH, aluminium is found in soluble form, allowing its removal through adsorption [26]. Results showed that the best adsorption and removal rate of Al is found at 4000 mg/l of CES, allowing obtaining 95,4% of removal rate, which represents an adsorption capacity (qt) of 208 mg effluent/ g adsorbent.

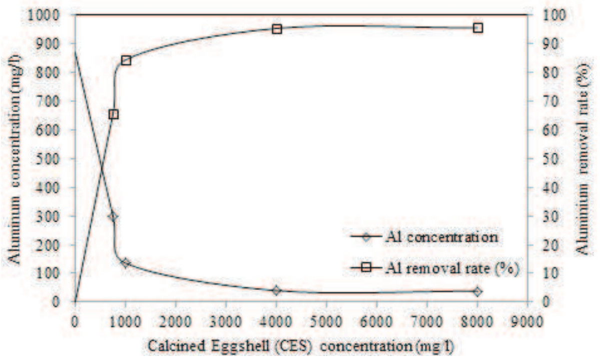

Figure 3: Effect of adsorbent dosage on the adsorption and removal rate of aluminium on CES

Galvanic acid leaching wastewaters (GLWW) treatment by adsorption

Figure 4 shows the removal rate and adsorption capacity of CES in the uptake of copper (Cu), chromium (Cr) and nickel (Ni) from galvanic acid leaching wastewaters (GLWW).

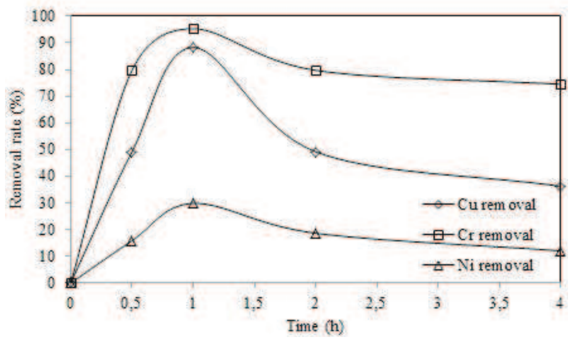

Figure 4: Removal rate of Cu, Cr and Ni according to time reaction with 0,01 g/l of CES without pH adjustment

According to Wang e Qin (2005), the speciation curve of Cu and Cr indicates that above pH 6, these metallic species can precipitate and below this value, these metals are found in soluble form, allowing its removal through adsorption process [16]. In order to optimize the adsorption conditions to this assumption, it was used a small concentration of CES (0,01 g/l). Speciation curve of Ni indicates a larger spectrum, being possible to find a soluble form a pH below 7. Results showed that chromium has the best removal rate, obtained 95% followed by copper with approximately 88% and nickel with 30%. Nickel lowest adsorption and remove rate is possible related to the low pH of solution. The adsorption of these three metals reveals that the uptake mechanism obtained the best results at 1 hour of reaction for both. The adsorption capacity (qt) of CES in the removal of chromium showed a maximum uptake of 90 mg chromium/g adsorbent, which is an expressive result.

4- CONCLUSIONS

The results showed that eggshell by-product may be a promising adsorbent for several types of pollutants present in wastewater effluents. The studies involving real wastewater effluents, illustrated the potential of eggshell as a substitute of traditional adsorbents. Concerning the removal of organic matter, from two specific effluents, with higher and low charge of organic matter, results demonstrated a goods adsorption capacity and removal rates for both cases without requiring a change on the operating conditions. Additionally, the results obtained for the adsorption of aluminium, prove that CES works as an effective adsorbent in wastewater from anodizing plants. It was obtained a 95% removal of Al with an adsorption capacity of 208 mg aluminium/ g adsorbent. The results obtained in the decontamination of an effluent containing Cr, Cu and Ni reveals that CES is an effective adsorbent, especially in the uptake of chromium because it was achieved a 95% removal of Cr with an adsorption capacity of 90 mg chromium/g adsorbent. From the evidences of all the performed experiments, it is possible to conclude that calcined eggshell is a promising adsorbent for the removal of some types of water pollutants.

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