ADSORPTION OF MANGANESE (II) IONS FROM AQUEOUS SOLUTION ON TO VOLCANIC ASHE AND GEOPOLYMER BASED VOLCANIC ASHE

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ABSTRACT

The retention of Mn^{2+} ions in a batch system was carried-out on untreated volcanic ashes (R) and three geopolymers $(R_{0812}, R_{1612} R_{2412})$ synthesized from this volcanic ashes. The influences in contact time, of pH and of initial concentration in Mn^{2+} ions were observed. The characteristics of the adsorption equilibriums were best described by the Langmuir, Freundlich and Temkin adsorption isotherms. The kinetics adsorption studies were carried-out on the experimental results obtained, by using the following kinetic models: first, second, Elovich and intraparticle models. From these studies, it was concluded that maximum adsorption was obtained when 0.1 g of the geopolymer, R_{0812} is in contact with a solution of Mn^{2+} ion of initial concentration of 1100 mg/L, of which the pH is equal to 6.3 for 30 minutes at room temperature. The second order kinetic model best describe these studies for the geopolymers, whereas the Elovich more or less explains the retention of Mn^{2+} ion by the untreated volcanic ashes (R). These experimental results are in agreement with the Langmuir adsorption isotherm and the maximum adsorption capacities obtained with these adsorbents are 192; 111; 84 and 30 mg/g respectively for R_{0812} , R_{1612} R_{2412} and R. Thus, these geopolymers R_{0812} , R_{1612} R_{2412} are excellent materials for the retention of Mn^{2+} ions in aqueous solution.

Key Words: Adsorption, Manganese (II) Ions, Volcani Ashes, Geopolymers

INTRODUCTION

Water and soil pollution by certain chemical Product of industrial origin (heavy metals, colorants, pesticides, fertilizer etc.) constitute a source of degradation of the environment and actually requires a particular interest on the international scale.

Heavy metals (lead, copper, cobalt, manganese etc.) are generally presents like pollutants in a variety of industrial effluents, surface and underground waters. These are the fractions that are highly toxic, usually out of certain concentration norms. They would be present in very high concentrations all along the food chain and would accumulate in very large quantity in certain organs of the human body. These microscopic inorganic pollutants are of major concern because they are non-biodegradables and are very toxic (Cimino *et al.*, 2000). It is therefore, indispensable to normalize the quantity of metal ions presents in industrial effluents and portable/drinking water destine for human consumption.

Mining and industrial activities, are the origin of water pollution by heavy metals, and present an important source of pollution and contribute in a way very certain to the deterioration of theenvironment and to human health. In Gabon, these activities that generally cause pollution include the following areas: mining, petroleum exploitation, energy production etc.

Water is one of the resources the more and more polluted by industrial activities. According to the World Health Organization (W.H.O.), three to four million people die each year in poor countries of sickness linked to bad water quality. Furthermore, 20 % of certain aqua species have disappeared these last years and others are in the process of disappearing (Underwood, 1977).

Research Article

We are interested in the chemical pollution of portable water, in particularly potable drinking water contaminated by excess manganese (II) ions.

Manganese is an oligo-element necessary for human survival but becomes toxic when the concentration becomes too high in the human body. According to W.H.O., the maximum concentration of manganese admissible in drinking water is 0.05 mg/L (Who, 2011). Excess manganese in portable water can cause problems in the nervous system and in the respiratory system and hinders the intellectual development and normal growth of infants. Manganese cans also provoque the illness of Parkinson decease, pulmonary disorder and bronchitis. The exposure of humans to manganese for a long period can render him impotent (ATSDR, 2000; Barceloux, 1999; Collipp *et al.*, 1983). It is therefore, necessary to proceed with the treatment of water contaminated by excess manganese so as to reduce their impact on the environment and to human health.

In this sense, several procedures have been used: coagulation-flocculation (Kacha *et al.*, 1997), adsorption on activated carbon (Ketcha *et al.*, 2009), electro coagulation (Shin and Lee. 2006) ions exchange, inverse osmosis and extreme filtration, etc.

These devolution techniques, amongst others, have shown high efficiency, but in many cases, are also very erroneous. Research has therefore, been oriented towards treatment methods using natural materials like clays, agricultural waste (wood saw dust, activated carbon, etc.), and volcanic ashes. Amongst these materials and from diverse studies carried-out, the volcanic ashes have shown that they can be of excellent adsorbents and catalysts (Esparaza *et al.*, 2011). These volcanic ashes are characterized by their important capacity of adsorption and their abundance in volcanic zones (Esparaza st al., 2011).

Numerous scientific work has already been carried-out on the adsorption of manganese (II) ions by different adsorbents: calcium silicate (El-Heleceles, 2012), clays (Yavuz *et al.*, 2002) activated carbon (Mengistie *et al.*, 2012) nut shells of *Tamarindus indica* (Suguna *et al.*, 2010) etc. On the contrary, no researcher has been interested in the adsorption of manganese (II) ions by volcanic ashes. Several questions can therefore be asked:

-what are the optimal adsorption conditions (pH, temperature, initial concentration of the adsorbant, C_o, contact time, t, etc.) that are necessary to achieve manganese (II) ions from aqueous solution by volcanic ash non-treated and geopolymeres synthesized from volcanic ashes?

-can the non-treated volcanic ashes also be efficient in the adsorption of manganese (II) ions like the treated volcanic ashes?

-compared to clays, activated carbon and the other adsorbents, are the volcanic ashes efficient?

-the type of adsorption that occur on them what kinetic order do they obeys?

-which of the adsorption isotherms explains better the adsorption process?

It is in trying to answer some of these questions that this work has been formulated.

The scientific process adopted consists of using the experience obtained from batch adsorption experiments of firstly, the preparation of manganese (II) ions from pure manganese sulphate monohydrated obtained from Riedel-Germany. Then, we carried-out kinetics and equilibrium studies of the affects of certain important parameters influencing the retention of manganese (II) ions by non-treated and treated volcanic ashes. The following reaction conditions were particularly taken into consideration: agitation time, t, pH of the reaction medium, the quantity of adsorbent used, m, temperature, T, $^{\circ}C$ and initial concentration of the manganese (II) ions solution, C_0 . The results obtained from these studies were applied to the following adsorption models: Langmuir, Freundlich and Tempkin.

After having optimized the operating parameters in this study of the adsorption of manganese (II) ions on the volcanic ashes, we now attempted to see the effect of the influence of the different chemical composition of the different volcanic ashes used, so as to finally contribute to a better knowledge of the

Research Article

adsorption of manganese (II) ions by both the non-treated volcanic ash and the geopolymers synthesized from the volcanic ashes.

MATERIALS AND METHODS

Adsorbent

The volcanic ashes used in this work are from Galim in Babountos, a locality in the West Region of Cameroon (Kamdem *et al.*, 2002). These are materials of particles with very weak density and of varied forms. The crude samples collected were washed with distilled water, dried at 105 °C for 72 hours, grind and sieved at 80 µm to obtain a gray colored powder, R (the brute volcanic ashe).

An alkaline solution was used to prepare the geopolymer, which is a mixture of sodium hydroxide aqueous solution (12M) and sodium silicate of density of 1370 Kg/m³. The sodium hydroxide solution is obtained by dissolving in distill water crystals of sodium hydroxide with purity equal to 99%. The mass composition of the solution of sodium silicate used is 28 % SiO₂; 8.9 % Na₂O and 62.8 % H₂O. In order to determine the quantity of the alkaline solution used to synthesize the geopolymers (treated volcanic ashes), three mixtures, having each the mass ratio $Na_2OSiO_2/NaOH$ equal to 0.8 : 1.6 and 2.4, were prepared. Before use of these alkaline solutions prepared, they are allowed to stand at room temperature (24 \pm 3 °C) for at least 24 hours (Jaarsveld *et al.*, 2003). These samples are noted as R_{0812} , R_{1612} and R_{2412} , for the geopolymer obtained.

Adsorption of Mn2⁺ ions in a Batch system

We prepared a mother solution of Mn^{2+} ions of 2000 mg/L by dissolving 2 g of manganese sulphate monohydrate in 1 L distilled water. From this solution, we prepared by a series of dilution 200 mL of several daughter solutions with concentrations varying from 300 to 1500 mg/L. In order to adjust the pH of the adsorbate solution, we prepared a 100 mL of a dilute solution of sodium hydroxide of 0.1 N and hydrochloric acid of 0.1 N solutions.

The batch experiments were carried-out by bringing into contact varying quantities of (0.1 to 0.5 g) the adsorbents together with a 20 mL of the solution of Mn^{2+} ions with initial concentrations ranging from 300 to 1500 mg/L. We varied the pH from 2 to 8. The residual Mn^{2+} ion concentration was determined by complexometric titration of the solution with EDTA of concentration of 1000mg/L. The EDTA solution was obtained by dissolving 1 g in 1 L distilled water. The adsorption studies were carried-out at different time intervals, varying from 10 to 50 minutes, then titrated. The quantity, Q_t (mg/g) adsorbed at time t (minutes) and the percent removal $%$) of the Mn²⁺ ions was obtained by using the following equations (Limoussin, 2007).

 $Q_t = (C_i - C_t)$. V/m

Percent removal $= (C_i - C_t)$. 100/C_i

Where,

 Q_t : quantity adsorbed (mg/g);

 C_i : initial concentration of the adsorbate Mn²⁺ ion (mg/L);

 C_t : concentration of the adsorbate at the instant t ($C_t = C_e$ at equilibrium);

 C_e : concentration of the adsorbate at equilibrium (mg/L);

V: volume of the solution (L);

m: mass of the adsorbent (g).

Titration of the Manganese Sulfate Solution

A complexometric method of titration was used to determine the amount of Mn^{2+} ions in solution by using EDTA in the presence of Erichrome Black T (NET) as indicator. The procedure used was as follows:

Procedure

A 50 mL burette was filled with EDTA solution. In a 250 mL erlenmeyer flask, was introduced 10.0 mL solution of the manganese (II) ion and about 40 mL of distilled water. This was followed by adding about 7 mL of an aqueous solution of 0.5 mol/L of hydroxylamine chlorhydrate to avoid the oxidation of the

Research Article

 Mn^{2+} ions and 10 mL aqueous solution of triethanolamine. This is to prevent the precipitation of manganese hydroxide. A spatula of ammonium chloride and NET are also added. This solution should be rose at this point or a few drops of an aqueous solution of ammonia should be added until the color of the solution appears rose. This solution is then titrated by using EDTA to obtain a clear blue color at the endpoint without traces of violet color. This exercise is concordantly carried-out twice.

RESULTS AND DISCUSSION

Characteristics of volcanic ashes

The values mentioned in Table 1 corresponds to the precursor/brute volcanic ashe used to synthesize geopolymers and are in agreement with those reported by Davidovits, 1994 and Palomo *et al.*, 1999. It has been reported that the percent calcium oxide had a significant influence on the properties of the geopolymers (Jaarsveld *et al.*, 2003; Xu *et al.*, 2004). This percentage is 7.88 % with the brute volcanic ashe, R.

Oxides	$(\%)$
SiO ₂	41.36
Al_2O_3	15.41
Fe ₂ O ₃	12.82
CaO	7.88
MgO	6.45
MnO	0.2
Na ₂ O	2.22
K_2O	0.90
P_2O_5	0.48
Cr_2O_3	0.03
TiO ₂	3.04
SO ₃	Trace
LOI	9.31
$SiO2/Al2O3$	2.89

Table1: Chemical Composition of Brute Volcanic Ashes (R)

The lost of ignition, LOI is 9.31 % and the amorphous phase occupies 64.8 % of the structure of the material. It is evident that the presence of an important amount of the amorphous phase in the aluminosilicate favors the synthesis of geopolymers (Jaarsveld *et al.*, 2003; Williams). The size of the particles varies between 0.23 and 80 μ m and the average diameter of the particles (d₅₀) is of 10.68 μ m. The specific surface area is $15.7 \text{m}^2/\text{g}$. The particle size is an important physical parameter having an impact on the synthesis of aluminosilicate geopolymers and on the resulting product because a significant part of the takes place at the liquid-solid interface (Diaz *et al.*, 2010).

Characteristics of Treated Volcanic Ashes (Geopolymers)

Infrared Spectroscopy

Figure 1 show the IR spectra of the precursor volcanic ash and the geopolymers used in this work. These spectra expose two principal domain of absorption. The first absorption band is a sharp peak at 2360 cm^{-1} and represensent the geopolymers. This peak is characteristic of –OH vibration under the force of H bonding (Lee *et al.*, 2002), which put in evidence the absorption of water molecule by the geopolymers. The second type of absorption bands shows two bands; one at 1650 cm^{-1} and the other at 1540 cm^{-1} . These two bands are characteristic of H-O-H vibration in water molecule. The third region of the important absorption bands around $950-1000$ cm⁻¹ has been attributed to an extended asymmetric vibration band of Si-O-Si (Villa *et al.*, 2010). The intensity of this peak important enough for the precursor volcanic ash (Figure 5a) but manifestively reduces with increased $Na₂O.SiO₂/NaOH$ mass ratio

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Figure 1: IR Spectral of Adsorbents used (a=R, b=R0812, c=R1612, d=R2412)

Figure 2: X-ray Diffractogramme Geopolymers (a=R0812, b=R1612, c=R2412)

Research Article

equal to 0.8 ; 1.6 and 2.4, of the alkaline solution used to synthesize the geopolymers (Figures 5 b-c-d). This result is indicative of the reality of the formation of Si-O-Si groups as the synthesis of geopolymers is in progress.

The weak intensity of the peak around 600 cm^{-1} is attributed to extended asymmetric vibration bands of some groups of Si-O-Si and SI-O-Al of the geopolymers (Cheng and chiu *et al.*, 2003).

Influence of Some Adsorption Parameters

Influence of Time of Agitation

The equilibrium time is a very important parameter in the study of surface phenomenon because it permits us to know the duration in which adsorption is optimal. The adsorption of Mn^{2+} ions by 0.1 g adsorbent (R, R0812, R1612, R2412) has been studied by varying the time from 10 to 50 minutes. We used for each adsorbent, an initial concentration of a solution of manganese sulphate distinct from one to the other. The results obtained are represented in Figure 3. Figure 3 shows that the quantity of Mn^{2+} ions adsorbed by the different adsorbents increases gradually the first 30 minutes. After this time, this quantity stays quasy constant for the rest of the adsorption process. The increase in the quantity could be explained by the presence of active sites on the surface of the adsorbents. After which the Mn^{2+} ions having reacted with the quasitotality of the active sites on the adsorbent, obstruct the pores of which the sizes are particularly small, prevent further the reaction of other Mn^{2+} ions. Thus, the concentration gradient of the Mn^{2+} ions reduces considerably because the quantity in solution is weak. Therefore, the retention process of Mn^{2+} ions is maximum and the rate of the reaction becomes saturated: the adsorption equilibrium is reached. From these plots, the precursor volcanic ash and the treated volcanic ashes–geopolymers behave in the same manner, except the R0812 adsorbent whose quantity adsorbed is less as a function with time. For the four adsorbents (R, R_{0812} , R_{1612} , R_{2412}) used, the equilibrium adsorption is reached after 30 minutes. Giving the fact that we have used a given initial solute concentration for each adsorbent, we can retain that the equilibrium time is: independent of the initial concentration in solute.

In a previous work realized with the adsorption of Mn^{2+} ions on activated carbon [13], the equilibrium was reach after 2 hours of agitation. One can conclude that the adsorption of Mn^{2+} ions on the precursor volcanic ash (R) and the treated volcanic ashes–geopolymers (R_{0812} , R_{1612} , R_{2412}) is fast.

Figure 3: Influence of Adsorption Time of Some Mn2+ Ions

Influence of the Mass of Adsorbent Used

In order to determine the mass of adsorbent for which maximum adsorption occurs, we varied the masses of the non-treated and treated volcanic ashes from 0.1 to 0.4 g. The time of agitation was fixed at 30 minutes at room temperature. The results obtained are shown Figure 4.

From this figure it is observed that quantity adsorbed gets from9.336 to 0.247 mg/g respectively for the mass 0.1 to 0.2 g for the volcanic ashes used. This mass varies very little for the masses of adsorbents varying from 0.2 to 0.4 g. We had maximum adsorption for 0.1 g volcanic ashes used.

Influence of the Initial concentration Percentage Removal of Mn^{2+} ions

Figure 5, represents the percent adsorption of Mn^{2+} ions by the four adsorbents used in this work. We have shown that the percent retention of Mn^{2+} ions by the geopolymers (R_{0812} , R_{1612} , R_{2412}) and the precursor volcanic ashes (R), reduces with increasing solute concentration. However, one observes an increase in the percent retention, for R, R_{0812} , R_{1612} , at the solute concentration equal to 700 mg/L before reducing progressively again from 900 mg/L. This slight increase in adsorption can be explain as due to the creation of new adsorption sites on the surface of the adsorbents concerned.

As for the geopolymer R_{2412} , the percent retention decreases in a manner that is constant. It gets from 67.06 % (300 mg/L) to 25.55 % (1500 mg/L). This monotony could be explained as the progressive occupation of sites on the surface of the adsorbent.

The maximum percent removal of Mn^{2+} ions by R_{0812} is 88.27 % (300 mg/L). It reduces gradually with increasing initial concentrations (55.85 % at 1500 mg/L). As for the R_{1612} geopolymer, it strongly retains Mn^{2+} ions at very weak solute concentrations (88.27 % at 300 mg/L). Its percent retention reduces considerablely at very high solute concentrations (32.2 % at 1500 mg/L). Amongst the four adsorbents

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used for the adsorption of Mn^{2+} ions in aqueous solution, the geopolymers are more effective than the precursor volcanic ash.

Figure 6 represents the quantity of Mn^{2+} ions adsorbed by each adsorbent as a function of initialsolute concentration. From this figure, it can be shown that the treated volcanic ashes (geopolymers) adsorb much more than the precursor volcanic ash. The maximum quantity adsorbed by R_{0812} is about 167.54 mg/g. This value is largely superior to 96.65; 76.65 and 9.336 mg/L, quantities adsorbed respectively by R_{1612} , R_{2412} and R. It is necessary to indicate here that maximum adsorption has been obtained for initial concentrations, in solute, superior or equal to1100 mg/L.

The very small quantity of \mathbf{Mn}^{2+} ions adsorbed by the precursor volcanic ash can be explain by the very poor fixation sites on the surface of this material, the average particle size big enough (10.68 µm) and its weak specific surface area $(15.7 \text{ m}^2/\text{g})$. In fact, the IR spectra of the non-treated volcanic ash reveal to us the absence of OH, Si-O-Al, Si-O-Si groups – and the presence of traces of water molecules on the surface of the adsorbent. Furthermore, the X-ray diffraction patterns of the R shows that there is an abundance of diopside (CaMgSi₂O₆), of anorthoclase (KAlSi₃O₈ + NaAlSi₃O₃), of maghemite (Fe₂O₃, γ Fe₂O₃) and of hematite (Fe₂O₃) at the surface of the adsorbent. We remark also here the basicity due to diopside, anorthoclase and Si-O-Si which tend to be neutralized by maghemite and hématite which are Lewis acids. As seen from their chemical composition, only the bases SiO_2 and Al_2O_3 constitute susceptible sites on which the Mn^{2+} ions can fix it. Therefore, the insufficient nucleophiles sites (bases de Lewis) present on the surface of R could justify why the very small quantity of the adsorption of Mn^{2+} ions by these volcanic ashes.

As for the geopolymer, the quantity of the Mn^{2+} ions adsorbed depend on the ratio in mass of Na₂SiO₃/NaOH utilized for their preparation. This quantity reduces with an increase of this ratio. The presence of nucleophiles groups –OH, and Si-O-Al (Figure 2) at the surface of these geopolymers justifies their efficiency as compared to the non-treated volcanic ash. These surface groups being basic constitute active sites for the fixation of Mn^{2+} ions. We also noted from the IR spectra in Figure 1 that the ratio in mass of Na₂SiO₃/NaOH increases, the more these groups –OH, H-O-H, and Si-O-Al become abundant at the surface of the adsorbent. Furthermore, the X-ray diffraction pattern of the geopolymers in Figure 2 indicates to us that the R_{0812} geopolymer contains a quantity of anorthoclase and some diopside. These

Research Article

compounds are importantly much more basic in nature than the geopolymers R_{1612} and R_{2412} . Again, the efficiency of the R_{0812} geopolymer with respect to R_{1612} and R_{2412} geopolymers could be explained not only by the abundance of some nucleophiles sites $(CaMgSi₂O₆$ et KAl $Si₃O₈ + NaAlSi₃O₃$) on the surface of R₀₈₁₂ geopolymer, but also the fact that the addition of the alkaline solution of Na₂O.SiO₂ in the geopolymers results in the progressive creation of undesirable sites for the Mn^{2+} ions at the surface of the R_{1612} and R_{2412} geopolymers.

Table 2: Adsorption Equilibrium

From Table 2, the values of the linear correlation coefficient (R^2) of the geopolymers are close to 1, especially in the case of the modelisation of the results obtained with the Langmuir isotherm.

Figure 7: Capacity of Maximum Adsorption of Mn2+ Ions by Geopolymers.

From the equilibrium studies, it shows that the Langmuir isotherm describes better the adsorption process of Mn^{2+} ions on the geopolymers. Furthermore, the peak intensities in Figure 7 together with the correlation coefficients obtained show that adsorption is very favorable for all the geopolymers and unfavorable for the precursor volcanic ash. The adsorption process is endothermic and there is ion exchange.

Kinetic Studies Adsorption

Research Article

From these kinetic studies, we can conclude that the pseudo second order kinetic model best describe the adsorption of Mn^{2+} ions onto the geopolymers R_{0812} , R_{1612} , R2412 and involves a chemisorptions reaction. As for the other kinetic model, the Elovich kinetic model more or less explains the adsorption of Mn^{2+} ions on the non treated volcanic ash better. This is justified from the linear correlation coefficient value (0.9186) obtained for this model. The pseudo first order kinetic model does not correlate well with the results obtained because the value of R^2 is far from unity.

Conclusion

This present study was on the adsorption of manganese (II) ions in aqueous solution on precursor volcanic ash, obtained from a locality in Galim - Cameroun, and the synthesized geopolymers from this precursor. From this study, it is noted that adsorption isotherms are of type I in Langmuir classification of adsorption isotherms. The capacity of adsorption is influenced by the time of agitation, the mass of the adsorbent used, the pH of the solution of the solute adsorbed, the initial concentration of the adsorbate, the structure of the adsorbent and the ratio in mass of the $Na_2O.SiO_2/NaOH$ utilized to prepare the geopolymers.

The pseudo second order kinetic model describes perfectly the adsorption of Mn^{2+} ions on the geopolymers R_{0812} , R_{1612} , R_{2412} whereas that of the adsorption of these ions on R follows more or less the Elovich model with respect with the other model. These experimental results are in agreement with the Langmuir isotherm and the maximum quantity that can be absorbed by the different adsorbents used are 192; 111; 84 et 30 mg/g respectively for R_{0812} , R_{1612} , R_{2412} and R.

Compared to clays, activated carbon and other adsorbents used for the retention of Mn^{2+} ions, one notes that the precursor volcanic ash and the geopolymers which are obtained from these precursor materials are efficient. These treated volcanic ashes (geopolymers) are adsorbing Mn^{2+} ions much better than the non-treated volcanic ash.

The adsorption energy obtained by applying the Temkin model has permitted us to confirm the adsorption of manganese (II) ions on the different adsorbents utilized as an endothermic reaction. The optimal condition of adsorption of Mn^{2+} ions on the treated and non-treated volcanic ashes, are those of using 0.1 g of the geopolymers R_{0812} in an initial solution of concentration of 1100 mg/L of Mn²⁺ ions of which the pH is equal to 6.3 at room temperature.

As further work, we propose to carry-out more research to include parameters such as adsorption temperature, stirring speed of the batch reaction, specific surface area of the synthesized geopolymers, dispersion of metal on the surface of the adsorbents, the pH of the reaction medium and to reduce not only the mass of the adsorbent used, but also the mass of the ratio of $\text{Na}_2\text{O}.\text{SiO}_2/\text{NaOH}$ utilized to preparation to the geopolymers. We intend to characterize the entire structure and texture of the geopolymers that we will use in this work by using well known surface techniques. The specific surface area will be determined by using the B.E.T. liquid N_2 adsorption method at 77 0K ; the complete physico-chimical properties, X-ray diffraction, X-ray Fluorescence and the Scanning Electron Microscopy will be determined .The Transform Fourier Infrared Spectroscopy will be used to determine the surface properties of the geopolymers.

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