

Sorption Study of Co (II), Cu(II) and Pb(II) ions Removal from Aqueous Solution by Adsorption on Flamboyant Flower (*Delonix Regia*)

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Abstract The ability of *Delonix regia* (Flamboyant) flower to remove Co(II), Cu(II) and Pb(II) ions from aqueous solutions through biosorption was investigated in multimetal batch experiments at 32°C. The metal ions concentration was determined by atomic absorption spectroscopic (AAS) method. The influence of pH, Contact time, adsorbent dosage and initial metal ion concentration were investigated. The study revealed that maximum removal of Co(II), Cu(II) Pb(II) ion from aqueous solution occurred at pH of 5. The contact time for the adsorption process was found to be at 60 minutes. The amount of metal ions adsorbed increases with increase in adsorbent dosage and initial metal ion concentration. The biosorption of Pb(II) and Co(II) ions exhibited pseudo-second-order kinetics models whereas Cu(II) ion followed for both pseudo first order and second order kinetics model. This study shows that *Delonix regia* flower is a viable agricultural waste for the removal of Co(II), Pb(II) and Cu(II) ions from aqueous solution.

Keywords Sorption, Flamboyant Flower, Aqueous Solution

1. Introduction

The contamination of water by toxic heavy metals is a worldwide problem [1]. This fear has been heightened in recent times due to advancement in technology coupled with increasing industrial activities, both contributed to release of heavy metals into the environment [1-3]. Heavy metals like cobalt, lead, copper, cadmium are present in the environment. They do not degrade or destroy and so, pollute the environment [4]. Uncontrollable discharge of these heavy metals to the environment can be detrimental to humans, animals and plants [5]. These heavy metal ions cause major effects like headache, dizziness, nausea and vomiting, chest pain, tightness of chest, dry cough, shortness of breathe, rapid respiration, nephritis and extreme weakness when their concentration is above the recommended limit [6].

However, several methods have been developed to remove heavy metals from industrial waste water before discharge into the water bodies. These methods include reduction, precipitation, ion exchange, reverse osmosis, dialysis and adsorption by coated carbon [7]. Activated carbon was also used and found to be an effective adsorbent though it suffers from the disadvantage of possessing high cost.

Several adsorbents like discarded automotive tyres, human hair, starch, xanthate, etc has been successfully tried but were not easily and widely available [1] they also have limited application as they cannot remove metal ions at low concentration within the range of 1-100mg/L [7]. Biosorption of heavy metals from aqueous solution is a relatively new technology for the treatment of industrial waste water [8]. The main advantage of using biosorption technology is due to its cost effectiveness, affordability, availability and environmental friendliness [9]. These materials could be an alternative for expensive waste water treatment process [9]. Very recently, [10] utilized flamboyant tree pod to sorb Hg (II) ion from water and found out that adsorption process follows the pseudo-second kinetic model and the equilibrium data fitted well to both Freundlich and Redlich-Peterson isotherm model.

More so, dynamic biosorption of Zn (II) and Cu (II) ions using pre-treated red rose (*Rosa gruss*) was investigated by [11]. The studies of the removal of copper ions from aqueous solution using dried sun flower as an adsorbent was carried out by [12]. [13] narrated the potential of Nile Rose Plant as an adsorbent to remove metal ions like (Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺) from wastewater within various experimental conditions. Equally,[14] reported that Okra wastes from food canning processes could serve as a potential adsorption of lead removal from various aqueous solutions.

Delonix regia (Flamboyant) tree plantation is grown around the world for ornamental reasons, preserving the soil

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and also conserving the environment. Apart from these benefits, the tree produces flowers in large quantities and at times litters the environment. Developing nations like Nigeria faces solid waste disposal problem, this necessitate the need for the conversion of this waste to useful, value-added products for the removal of metal ions from aqueous solution which would be of benefit to the environment as well as the scientific community in the search for cheaper adsorbent materials.

The objectives of this study is to determine the adsorptive capability of *Delonix regia* flower and establish the adsorption kinetics using pseudo-first and pseudo-second order models for the removal of lead, cobalt and copper ions from aqueous solution.

2. Materials and Methods

2.1. Sample collection

The *Delonix regia* (flamboyant) flowers were collected from different point at the Federal University of Technology, Minna, Bosso campus and also at Bahago secondary school in Minna, Niger state in Nigeria. A composite sample was made from where representative samples were taken for sorption studies.

2.2. Sample pre-treatment

The waste flowers were thoroughly washed with de-ionised water to remove debris. The fresh flowers were sun dried and were grounded using mortar and pestle, it was washed several times with de-ionised water to remove the colour in the substrates. Furthermore, the washed sample was once again dried, ground to fine powder by mortar and pestle then it was then sieved with a mesh size of 300 μ m to obtain a very fine powder and was kept in an airtight container for further sorption studies.

2.3. Preparation of aqueous solution

A multimetal aqueous stock solution of Pb(II), Cu(II) and Co(II) ions were prepared with their respective salts by carefully weighing out 1.6g of Pb(NO₃)₂, 3.8g of CuCl₂ and 13.04g of CoCl₂ and was dissolved together in a 1000 cm³ volumetric flask and diluted with de-ionised water to the mark, which gave a concentration of 1000 mg/L. Successive dilutions was made, first, by preparing concentration of 100 mg/L from the 1000 mg/L stock solution, by pipetting 10cm³ of the solution into a 100 cm³ volumetric flask and making up to the mark with de-ionised water. Successive dilution of the 100ppm was used to prepare other concentrations of 5, 10, 15, 20, 25 and 30 mg/L respectively.

2.4. Multimetal Batch sorption experiments

2.4.1. Effect of contact time

30cm³ of the prepared aqueous solution was measured into a conical flask and mixed with 0.5g of the substrate, well corked and the mixture was constantly shaken in a rotary

shaker at 420rpm, with time intervals of 20, 40, 60, 80, 100 and 120 minutes. After each contact time, the mixture was filtered using Whatman filter paper (No. 42) and the concentration of each was determine using Flame Atomic Absorption spectrometer (model, PerkinElmer; Analyst 200).

2.4.2. Effect of pH

30 cm³ of the prepared aqueous solution was measured using a measuring cylinder, followed by the addition of 0.5 g of the sample in a conical flask. The pH was varied from 1 to 10. 0.1 M HCl or 0.1 M NaOH was used to adjust the pH of the metal ion solutions to the desired value of interest. The metal solutions containing the biosorbent in the conical flask were well corked and shake using Gallenkamp flask shaker for 60minutes and thereafter the mixture was filtered, and then the concentration of each metal ions removed was determined using Flame Atomic Absorption Spectrometer, (model, PerkinElmer; Analyst 200).

2.4.3. Effect of initial metal ions concentration

30 cm³ of (10, 15, 20, 25 and 30 mg/L) aqueous solution was measured from the prepared 100 mg/L and was mixed with 0.5g of the sample, corked and the mixture was constantly shaken in a shaker at 420rpm for 60 minutes. After constant time intervals, the mixture was filtered using Whatman filter paper (No. 42) and the concentration of each metal ion was determined using Flame Atomic Absorption spectrometer.

2.4.4. Effect of Dosage

30 cm³ of the prepared aqueous solution was measured into different conical flasks, followed by the addition of varying masses of the sample (0.5, 1.0, 1.5, 2.0, and 2.5 g) and was well corked. Thereafter it was shaken using Gallenkamp flask shaker for 60minutes, filtered, and then the concentration of each metal ions bound was determined once again using Flame Atomic Absorption Spectrometer.

2.4.5. Calculation of Metal Uptake

This was used to determine the amount of metal absorbed by the biosorbent.

$$q = \frac{(C - C_e)V}{M}$$

Where, q is the amount of metal ion adsorbed in mg/g; C is the initial metal ion concentration in mg/L; C_e is the final concentration in mg/L; V is the volume of metal ion solution in liters; M is the mass of *Delonix regia* flower used in gram.

The percentage Removal of the metal ion was also determined using;

$$X\% = \frac{C - C_e}{C} \times 100.$$

Where, X% is the percentage of metal removed.

Kinetics study analysis

Pseudo-First-Order Kinetics.

The rate law is shown below:

$$dq_t / dt = k_1 (q_e - q_t)$$

Where, q_e and q_t are the amount of each of Co(II), Pb(II)

and Cu(II) absorbed at equilibrium and time t , respectively. k_1 is the rate constant for the pseudo first order biosorption. The integrated law then becomes:

$$\text{Log}(q_e - q_t) = \text{log } q_e - k_1 t / 2.303$$

A plot of $\text{Log}(q_e - q_t)$ against time t , was made and values of k_1 and q_e were obtained from the slope and intercept, respectively.

Pseudo-second order Kinetics

Applicability of the second order kinetics is tested with the rate equation:

$$(dq_t / dt) = k_2 (q_e - q_t)^2$$

Where k_2 is rate law for pseudo second order biosorption.

On integrating between the boundary condition of $t=0, q_t=0$ and $t=t, q_t=q_t$, the following expression was obtained:

$$qt / (q_e - q_t) = k_2 t^2$$

On linearizing,

$$t / q_t = 1 / k_2 q_e^2 + t / q_e$$

A plot of (t/q_t) against t gives $(1/q_e)$ as slope and $(1/k_2 q_e^2)$ as intercept from which k_2 can be obtained. Both models tested for suitability using their correlation of coefficient, R^2 (Ho and McKay, 2000, Oyebamiji *et al.*, 2009)

3. Results

3.1. Discussion

3.1.2. Influence of pH

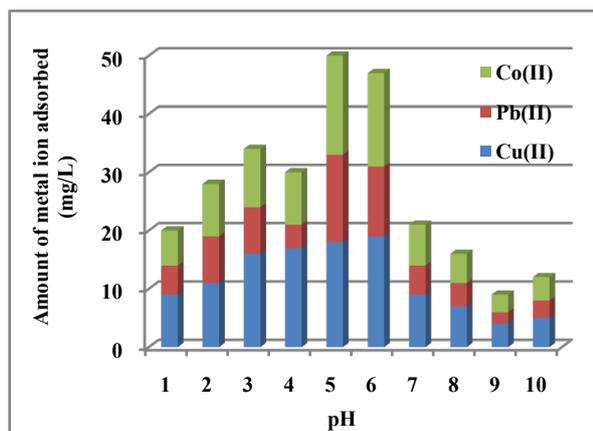


Figure 1. Effect of pH for the Sorption of Co(II), Pb(II) and Cu(II) ions by *Delonix regia*

Metal sorption is critically linked with pH and the effect of pH of a solution is an important controlling factor in the sorption experiment. For this, the role of hydrogen ion was investigated at different pH and so the amount of metal ions removed was determined and results for the adsorption of Co(II), Pb(II) and Cu(II) ions is shown in the figure 1 above. The amount of metal ions removed by the substrate at low pH of 1, 2, and 3 were low compared to pH of 4 and 5. This may be due to increase in competition between the hydrogen ion and the metal ions, because at this pH value, the concentration of hydrogen ion is high[15]. As such hydrogen ions were being removed by the substrate, instead of the metal ions. It would be plausible to suggest that at lower pH

value, the surface of the adsorbent is surrounded by hydroxonium ions (H_3O^+), thereby preventing the metal ions from approaching the binding sites of the sorbent[16,17]. This means that at higher H^+ concentration, the biosorbent surface becomes more positively charged such that the attraction between biomass and metal cation is reduced[18]. As the pH increases from 4 to 6, more negatively adsorption sites became available thus facilitates increase in amount of metal ions sorbed. Maximum adsorption for Cu (II), Pb (II) and Co (II) ions occurred at pH 5. The plausible reason for the better adsorption observed at pH 5 and pH 6 may be attributed to the larger number of H^+ ions present, which in turn neutralize the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion of organics at higher pH. At higher pH, the capacity of the adsorbent recessed. The reduction in adsorption may be possible due to the abundance of OH^- ions, causing increased hindrance to diffusion of organics contributing to metal ions. Further increase in pH from 7 to 10 resulted to decrease in adsorption of the metal ions. This may be ascribed to the fact that during adsorption the degree of protonation of the adsorbent functional group decreased gradually and as a consequent removal was decreased. A close relationship between the surface basicity of the substrate and the anions was evident[19] and similar to other findings where the electrostatic interactions between the anions and the protonated sites of the adsorbent are the main adsorption mechanism[11,20].

3.1.3. Effect of contact time

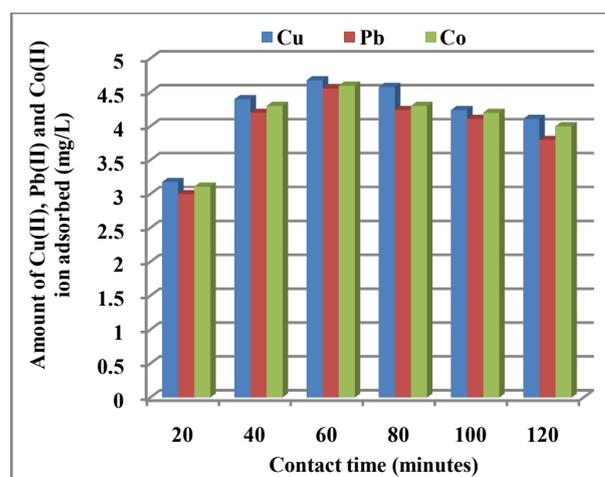


Figure 2. Contact time for the sorption Co(II), Pb(II) and Cu(II) ions by *Delonix regia* flowers

The result of contact time for the adsorption of Co (II), Pb (II) and Cu(II) ions by *Delonix regia* is shown in figure 2. For an initial metal ion concentration of 5 mg/L, it was observed that the amount of Co (II), Pb (II) and Cu (II) ions absorbed increased with increase in agitation time up to 60 minutes. This may be attributed to effective contact and availability of active sites, after the equilibrium was attained at 60 minutes it was followed by a progressive reduction in the metal uptake. Figure 2 also shows that the kinetic of Cu biosorption was faster than that of Co and Pb. This may be

ascribed to the fact ion with smaller ionic radii diffuse faster than ion with larger ionic radii[16,18]. The trend of adsorption was Cu (II)> Co (II)>Pb(II) ion. This result is inline with what was reported by[13] who studied the possibility of using Nile rose as an alternative substrate to remove metal ions like Cu(II), Zn(II), Cd(II) and Pb (II) from wastewater within various experimental conditions.

3.1.4. Effect of adsorbent dosage

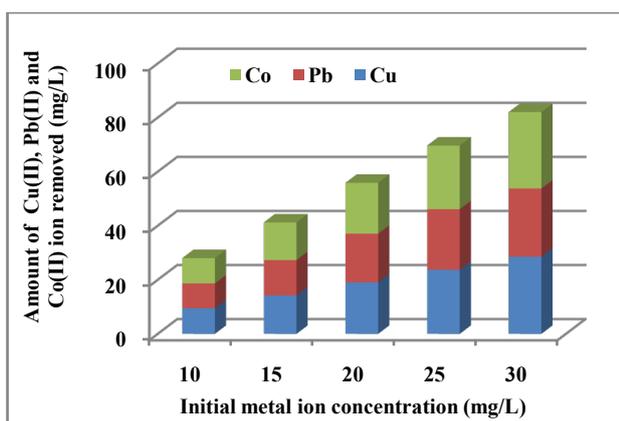


Figure 3. Initial Metal ion concentration for the sorption of Co (II), Pb(II) and Cu(II) ions by *Delonix regia*

The figure 3 shows that the amount of Cu (II), Pb(II) and Co(II) ion removed as dosing mass was increased. The increase in metal uptake with increase in dose of adsorbent from 1.0 – 2.5 g was due to the increase in surface area and number of active sites for the adsorption of Co(II), Pb(II) and Cu(II) ions, although more of Cu(II) ion were removed than Co(II) and Pb(II) ion. The trend could be explained in terms of progressive increase in the electrostatic interaction between the adsorbent and metal ions. The higher the electrostatic interaction, the more the amount of metal ions sorbed. Moreover, more adsorption sites were being covered as the dose of the adsorbent increased [19]. This finding corroborated several other researchers [14,16-18,21].

3.1.5. Effect of initial metal ions concentration

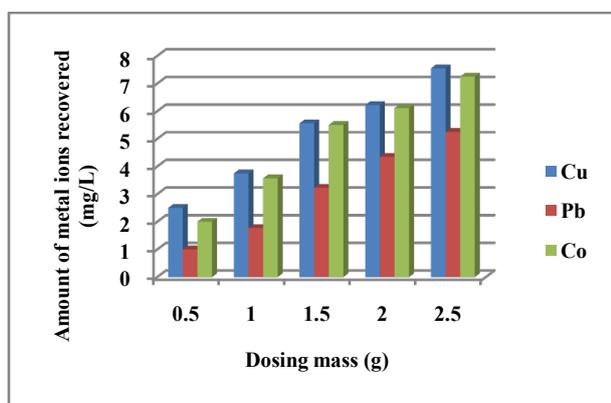


Figure 4. Effect of dosage on sorption of Co(II), Pb(II), and Cu(II) ions by *Delonix regia* flower

The effect of initial metal ions concentration on Co(II),

Pb(II) and Cu(II) ions is illustrated in figure 4 above. The amount of metal ions adsorbed for Co(II), Pb(II) and Cu(II) ions, increases with increase in concentration. The gradual increase in the rate of adsorption of Co(II), Pb(II) and Cu(II) ions at equilibrium of 60 minutes indicates that the adsorption occurs through a smooth continuous formation of adsorption layer till saturation[22]. The trend observed for the various metal ions under the same experimental conditions revealed that the pattern of adsorption was a function of the substrate as well as that of the metal ions followed by ion exchange [17, 18]. Also the adsorbent removed heavy metals ions (Cu>Co>Pb) efficiently from aqueous solutions and adsorption of metal increased with increasing atomic weight and ionic radii. Adsorption of metal ions increased with increase in initial metal concentration.

3.1.6. Adsorption Kinetics

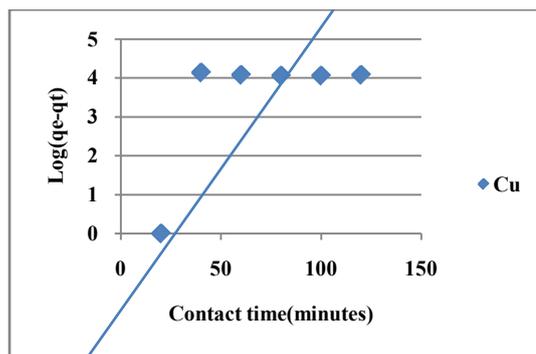


Figure 5. Pseudo-first order for sorption of Cu(II) ions by *Delonix regia*

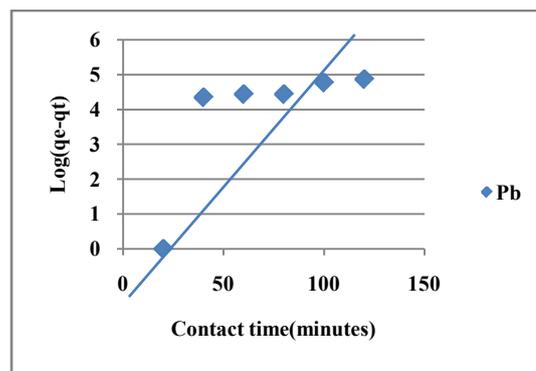


Figure 6. Pseudo-first order for sorption of Pb(II) ions by *Delonix regia*

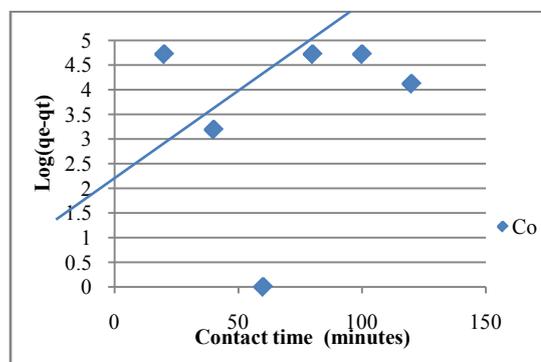


Figure 7. Pseudo-first order for sorption of Co(II) ions by *Delonix regia*

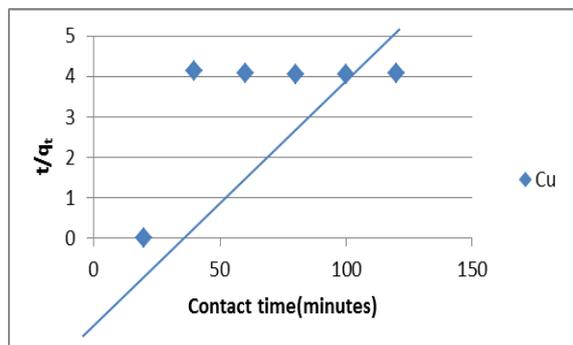


Figure 8. Pseudo-Second Order for Sorption of Cu(II) ions by *Delonix regia*.

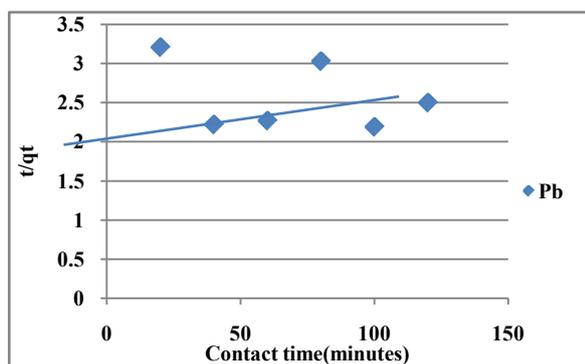


Figure 9. Pseudo-Second Order for Sorption of Pb(II) ions by *Delonix regia*.

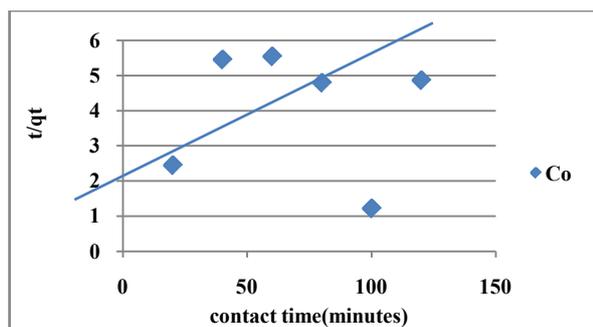


Figure 10. Pseudo-Second Order for sorption of Co(II) ions by *Delonix regia*.

The mechanism of the adsorption of Co (II), Pb(II) and Cu(II) was tested using pseudo first-order and second order kinetic models [15,16,23]. The adsorption kinetic of the heavy metals removed from aqueous solution was studied using the experimental data obtained from sorption time investigation. Figure 5 – 10 shows the plots of pseudo-first order and pseudo-second order models for the sorption of Co(II), Pb(II) and Cu(II) ions by *Delonix regia*. The kinetics investigation indicated that the sorption of Co(II) and Pb(II) ions could be well explained using the pseudo-second order while the sorption of Cu(II) ions could best be explained using both models. This might be ascribed to the fact that Cu (II) ion has smaller ionic radii (0.73Å) which tends to diffuse through the adsorbent pores or cell wall faster than Co (II) (0.74Å) and Pb (II) (1.20Å) ions with larger ionic radii [24].

In order words, the data showed good compliance with the

pseudo-second order model. As a consequent of this correlation of the experimental results with the pseudo-second order model, it is plausible to suggest that the main adsorption mechanism was chemisorption reaction [25].

Table 1. Pseudo-First-Order constants for the Biosorption of Co(II) and Pb(II) and Cu(II) ions by *Delonix regia* Flower

Metal	K_1	$q_e(\text{calc})$	R^2
Co	0.009	2.947	0.001
Pb	0.036	1.250	0.234
Cu	0.028	1.389	0.9993

Table 2. Pseudo-Second-Order constants for the Biosorption of Co(II) and Pb(II) and Cu(II) ions by *Delonix regia* Flower

Metal	K_2	$q_e(\text{calc})$	R^2
Co	0.954	500	0.9998
Pb	0.559	250	0.9997
Cu	0.564	35.7	0.9999

4. Conclusions

The following conclusion can be drawn from this study,

1. The biosorption process was pH, Contact time, dosage and metal ion concentration dependent.

2. Contact time of adsorption was found to occur at 60 minutes for all three metal ions.

3. Pseudo-First and Second order kinetic model can be used to describe the binding of Cu ions to *Delonix regia* flower with $R^2=0.416$. However, pseudo-first order can be used to describe the kinetics for the biosorption of Pb and Co ions. That Flamboyant flower could be used an alternative to highly expensive activated carbon to remove the selected metal ions.

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