



Sequestering heavy metals from wastewater using cow dung



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ABSTRACT

The presence of heavy metals (e.g., Zn, Cu, Pb, Ni, Cd, etc.) in aqueous solutions constitutes a major environmental problem. The present work represents a review of the recently published literature discussing the use of cow dung as adsorbent for the removal of metal ions from aqueous solution using batch experiments. The potential health and environmental hazards of metal ions in addition to the kinetic and isothermal models usually assessed to fit the biosorption experimental data were also reviewed. Conclusively, it was established that the use of cow dung is a promising adsorbent in the removal of heavy metals from waste waters and environment.

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1. Introduction

The presence of inorganic pollutants such as metal ions in the ecosystem cause a major environmental problem. Toxic metal compounds coming to the earth's surface not only contaminate earth's water (seas, lakes, ponds and reservoirs), but can also contaminate underground water in trace amounts by leaking from the soil after rain and snow [1]. There are numerous metals which

are significantly toxic to human beings and ecological environments, they include chromium (Cr), copper (Cu), lead (Pb), cadmium (Cd), mercury (Hg), zinc (Zn), manganese (Mn), nickel (Ni), etc [2]. Heavy metals constitute an important part of environmental pollutants and source of poisoning [3]. They are present (in various forms) in the soil, natural water and air and may become contaminants in food and drinking water [4]. Some of them are constituents of pesticides, paints and fertilizers application.

Due to the hazards associated with the contamination of water, there had been the development of various technologies for water purification such as filtration and ion-exchange, precipitation with carbonate or hydroxide [5].

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Concentration of metal beyond the tolerance level may be regarded as toxic if it affects the growth or metabolism of cells [6]. The lethal toxicity mechanism of a high concentration of heavy metal during a short term exposure disrupts the respiratory surface while during long term exposure; the metal gets accumulated in the internal organs [7]. Due to various advancements in industrial activities, the levels of discharge of these heavy metals have increased. Some of these toxic pollutants like Pb, Cr, Cd get processed into food through various ways [8].

Due to the numerous threats posed by heavy metals in the environment, it is very important to reduce the presence of these toxic metals in environment. Some of the methods which have been employed till date are electrolytic deposition, electro dialysis, electrochemical, evaporation, precipitation, ion exchange, reduction, reverse osmosis. [9]. However, most of these methods are associated with high instrumental and operational costs [10]. Thus, employing remediation biologically can be very cost effective and highly efficient. For this purpose, plants, microbes or biodegradable waste (e.g. dead leaves, vegetable peels) can be employed.

Several researchers have reported the potential use of agricultural by-products as good adsorbents for the removal of metal ions from aqueous solutions and wastewaters. This process attempts to put into use the principle of using waste to treat waste and become even more efficient because these agricultural by-products are readily available and often pose waste disposal problems. Hence, since they are waste products, they are more cost-effective when compared with the conventional adsorbents like activated carbon. Also, the use of agricultural by-products for wastewater treatment does not involve complicated regeneration process [11].

Many attempts to convert carbonaceous materials into activated carbon for heavy metals removal have been reported in the literature [12]. These include pecan shell [13], apricot stone [14], coconut shell [15], peanut shell [16], wheat bran [17], coconut and seed shells of palm tree [18], rubber wood sawdust [19], rice husk [20] and corncob [21]. Activating agents comprise steam, CO₂, ZnCl₂, H₂SO₄ and H₃PO₄, KOH and NaOH [12]. It has been reported that activation using ZnCl₂ demonstrate a small weight loss during the carbonization process [22]. A few researchers also utilize animal waste for the same reason [23]. The aim of the present review work is to investigate the use of cow dung as an adsorbent for removing heavy metals from aqueous solutions.

2. Effects of heavy metals

Water polluted with heavy metals from various industries has been a serious environmental problem for many years. Heavy metals are not biodegradable and hence accumulate in water bodies and aquatic creatures therein. They can easily enter the food chain because of their high solubility in water. Excessive consumption of these sources can cause a number of illnesses such as diarrhea, nausea, brain disorders, liver and renal dysfunctions, and cancers [24]. Thus, it is essential to remedy metal-contaminated effluents before they are discharged into the environment.

Metal ions are reported as priority pollutants, due to their mobility in natural water ecosystems and their toxicity [25]. The problem associated with metal ions pollution is that they are not biodegradable and are highly persistent in the environment. Thus, they can be accumulated in living tissues, causing various diseases and disorders [26]. Heavy metal toxicity can result in damage to or reduced mental and central nervous functions, lower energy levels and damage to blood composition, lungs, kidneys, liver and other vital organs [27]. The potential health hazards of some metal ions

Table 1
List of some heavy metals and their health hazards [28]

| Contaminants | Potential health effects from long-term exposure above the maximum contamination level |
|---------------------|--|
| Antimony | Increase in blood cholesterol; decrease in blood sugar |
| Arsenic | Skin damage or problems with circulatory systems, and may have increased risk of getting cancer |
| Barium | Increase in blood pressure |
| Cadmium | Kidney damage |
| Chromium (total) | Allergic dermatitis |
| Copper | Short term exposure: Gastrointestinal distress. Long term exposure: Liver or kidney damage |
| Lead | Infants and children: Delays in physical or mental development; children could show slight deficits in attention span and learning abilities Adults: Kidney problems; high blood pressure |
| Mercury (inorganic) | Kidney damage |
| Selenium | Hair or fingernail loss; numbness in fingers or toes; circulatory problems |

as given by the EPA [28] are summarized in Table 1.

3. Source of exposure

Heavy metals are released into the environment from many sources. Arsenic is introduced in water through natural and anthropogenic sources: release from mineral ores, probably due to long-term geochemical changes and from various industrial effluents like metallurgical industries, ceramic industries, dye and pesticides manufacturing industries and wood preservatives [29].

The major sources of antimony released into the environment through wastewater streams are industries such as lead-storage batteries, soldering, bearing and power transmission equipment, sheet and pipe metals,ammunition, flame retardants, ceramics, casting, pewter, enamels, and paints [30].

Wastewaters such as those generated during dyes and pigments production, film and photography, galvanometry, metal cleaning, plating and electroplating, leather and mining may contain undesirable amounts of chromium (VI) anions [31].

Cobalt, which is widely used in alloys (especially magnetic steels and stainless steels), electronics, porcelain and radioisotope therapy, is now commonly found in contaminated water [32].

Manganese is released into the environment by industries such as those involved in the production of fertilizer, petrochemicals, electroplating, tanneries, metal processing, and mining [33].

Mercury can be found in wastewater discharged from chlor alkali, paper and pulp, oil refinery, paint, fossil fuel burning, metallurgical processes, pharmaceutical and battery manufacturing [34].

Effluents from production of batteries, gasoline additives, pigments, alloys and sheets etc. Often contain high concentrations of lead ions [35].

Mining and metallurgy of nickel, stainless steel, aircraft industries, nickel electroplating, battery and manufacturing, pigments and wastewaters from ceramic industries contain high amounts of nickel ions [36].

Zinc can be found in wastewater from metallurgical processes, galvanizing plants, stabilizers, thermoplastics, pigment formation, alloys and battery manufacturing in addition to the discharges of municipal wastewater treatment plants [34].

Industrial wastewaters are a major source of pollution in the environment. They discharge toxic heavy metals into the environment and cause health problems among animals [37,38,39]. The discharge of toxic metal effluents by various industries resulted in both land and water pollution and the destruction of

mainly water flora and fauna due to intense toxicity [40]. These metals gain access to the food chain through bioaccumulation from contaminated water, soil and air thereby posing a serious threat a serious threat due to its toxicity and non degradable properties [41].

Industrial activities and mining operations have exposed man to these toxic metals [42]. Man's exposure to heavy metals comes from industrial activities such as mining, smelting, refining and manufacturing processes [43]. Heavy metals constitute an important part of environmental pollutants and source of poisoning [3].

Metal-rich mine tailings, metal smelting, electroplating, gas exhausts, energy and fuel production, down wash from power lines, intensive agriculture and sludge dumping are the most important human activities that contaminate soils with large quantities of toxic metals [44,45]. An increased use of metals and chemicals in these process industries has resulted in the generation of higher concentration of these metals, thereby creating serious environmental disposal problems [46,47].

4. Adsorption as a method of heavy metals removal

Adsorption is a mass transfer process by which a desired substance (adsorbate) is transferred from the liquid phase to the surface of a solid (adsorbent), and becomes bound by a physical or chemical attraction [48]. Adsorption has become a preferred choice than other techniques of heavy metal remediation due to its simplicity, cheap, easy to scale-up and most importantly ability to remove pollutants at low concentration even at part per million levels with high efficiency [48,49].

The benefits of other physico-chemical processes are outweighed by a number of drawbacks. Significant disadvantage of chemical precipitation, includes the production of sludge containing high concentration of heavy metals, which must be treated prior to disposal to prevent heavy metals from leaking back to the environment [49]. Limitations of other physico-chemical treatments are given in Table 2 below [49].

Adsorption of metal ions onto activated carbon is mainly influenced by its physical and chemical characteristics like surface area, pore volume and surface functionalities. Research findings indicate that metal ions can bind to the surface of activated carbon through a number of mechanisms, such as ion exchange [50–52], surface-complex formation [51–53], π -cation interactions [50,54] and coordination to functional groups [55,16].

5. Cow dung as adsorbent for heavy metal removal

Cowdung ash is an eco-friendly and low cost adsorbent. It is a bio-organic waste that contains 12.48% calcium oxide, 0.9% magnesium oxide, 0.312% calcium sulphate, 20% aluminium oxide, 20% iron oxide and 61% silica [56]. The presence of maximum percentage of silica makes it to exhibits considerable affinity

for metal ions. Advantage of utilizing cow dung as activated carbon is not only revolving around its low economic value, but also can stop other environmental problems of foul odor resulting from it [57].

Cow dung has many important properties which have been in use since ages. It is combined with soil bedding and urine which is used as manure for agricultural purpose. It is also used in the production of biogas which is used to generate electricity and heat. It can also be used to repel mosquitoes and as cheap thermal insulator. Cow dung is also an optional ingredient in the manufacture of adobe mud brick housing [58].

6. Factors affecting heavy metal adsorption

6.1. Effect of pH

The pH value affects two phenomenon in biosorption namely: metal ion solubility and biosorbent total charge, since protons can be adsorbed or released [59]. The acidity of the medium affects the competition ability of hydrogen ions with metal ions to active sites on the biosorption surface [60].

According to Romera et al. [59] the pH value of the medium affects the system's equilibrium state, it can be represented by the following equations:



$$K_a = \frac{[B^-][H^+]}{[B-H]} \quad (2)$$

$$pK_a - pH = \log \left(\frac{[B-H]}{[B^-]} \right) \quad (3)$$

For pH values lower than pK_a , equilibrium shifts to the left, consuming protons and increasing pH until its value equals pK_a . When the pH of the medium is higher than pK_a , the opposite will happen [60].

It has been generally reported that in highly acidic medium ($pH \approx 2$) the removal of metal ions is almost negligible and it increases by increasing the solution pH up to a certain limit.

According to Elaigwu et al., [61] the adsorption of Pb(II) from aqueous solution by activated carbon prepared from cowdung was pH-dependent. The highest percentage removal of Pb^{2+} was observed at pH of 2.0. This later decreased when the pH was increased to 3.0. It was also observed that there was a steady increase between pH 4.0 and pH 8.0. This trend is with what Kobya et al., [14] reported, that the optimum pH for the removal of Cr(VI) is 1 while that for other metals is between 3–6. To some extent, binding behavior may suggest that COOH groups maybe responsible for the binding of the Pb^{2+} , since the ionization constant for a number of COOH groups range between 4.0 and 6.0, Horsfall and Spiff [62].

At lower pH the COOH groups retain their protons. This reduces the probability of binding a positively charged ion. At $pH > 4$, the ionized COO⁻ ligands attract the positively charged Pb^{2+} ions thus leading to binding. It could thus be concluded that binding follows an ion-exchange mechanism that involves electrostatic interaction

Table 2

Physicochemical treatments for heavy metals-contaminated water [49].

| Methods of treatment | Disadvantages |
|----------------------------|--|
| Chemical precipitation | Slow process, poor settling, sludge production, high operating and handling costs for chemicals used and sludge treatment prior to disposal. |
| Coagulation-flocculation | Sludge generation, high operational costs due to high chemicals consumption and sludge disposal. |
| Dissolved air flotation | High operating cost, imperfect removal performance. |
| Membrane filtration | Membrane fouling, high operating and maintenance costs, high energy consumption. |
| Ion-exchange | Low surface area, high capital cost, varying metal removal ability of different resins, difficult to scale-up. |
| Electrochemical treatments | High operational cost, need periodic maintenance, high energy consumption. |

Table 3
Effect of pH on the adsorption of Chromium.

| pH | % removal of Cr |
|----|-----------------|
| 1 | 73.884 |
| 3 | 72.076 |
| 5 | 69.342 |
| 7 | 67.344 |
| 9 | 64.648 |
| 11 | 63.474 |

between the negatively charged groups in the walls of the substrate and metallic cations.

Lekshmi and Divanshu [63] observed that the pH of the solution also played a significant role in the adsorption capacity of the adsorbent. It was observed that as the pH increased, the adsorption capacity of the adsorbent decreased. The maximum adsorption capacity of Cr occurred at pH of 1. The effect of pH on the adsorption of Cr is shown in Table 3.

6.2. Effect of contact time

In adsorption systems, contact time plays a vital role irrespective of other experimental parameters affecting the adsorption kinetics. The determination of the optimum contact time needed to achieve the highest removal of metal ions is very important in batch biosorption experiments. It is important in selecting a wastewater treatment system [64].

Elaigwu et al. [61] observed that as the contact time was increased, the amount of metal ions removed also increased. This trend was consistent between 40 and 30 minutes contact time when equilibrium was attained. Further increase of contact time beyond 80 minutes resulted in decrease in the adsorption of Pb^{2+} . Mostly, the observable time for maximum adsorption is between 60–100 minutes. Further contact time may be time wasting Shukl and Pai [65].

Lekshmi and Divanshu [63] kept pH and concentration constant in order to understand the effect of time. The pH was kept constant at 1 since maximum adsorption was inferred at this pH. As shown in Table 4, it was observed that there was an increment in the adsorption from 52% to 74% as the time was increasing. Thus, showing that time is directly proportional on the adsorption of Cr.

Also, Mullai et al. [66] varied the contact time and found that the adsorption of Cr (VI) increased with increase in contact time irrespective of initial concentration of hexavalent chromium. The equilibrium was attained at the end of three hours. The metal was removed due to adsorption by 20 g of cow dung ash. Similar results were made by Viswanadham et al. [67] and Hameed et al. [68] in their work on removal of zinc and nickel ions using a biopolymer, chitin and 2,4 D pesticide on activated carbon derived from date stones. However, Monser and Adhoum [69] reported that a large fraction of tartrazine was removed in 20 minutes.

Table 4
Effect of time on adsorption of Chromium.

| Time (in h) | % removal of Cr |
|-------------|-----------------|
| 0.5 | 51.698 |
| 1 | 64.10 |
| 2 | 69.282 |
| 3 | 71.108 |
| 4.5 | 72.73 |
| 6 | 73.884 |

Table 5
Effect of adsorbate concentration on amount of Pb^{2+} sorbed.

| Concentration of adsorbate (mg/l) | Initial concentration of Pb^{2+} (mg/l) | Lead concentration (mg/l) at equilibrium | Amount adsorbed (mg/g) | % sorbed (Q_e) |
|-----------------------------------|---|--|------------------------|--------------------|
| 20 | 12.51 | 0.42 | 12.09 | 96.62 |
| 30 | 18.76 | 0.44 | 18.32 | 97.64 |
| 40 | 25.02 | 0.51 | 24.51 | 97.95 |
| 50 | 31.27 | 0.16 | 31.11 | 99.48 |
| 60 | 37.52 | 0.17 | 37.35 | 99.54 |

6.3. Effect of adsorbate concentration

Table 5 shows the effect of adsorbate dosage on the adsorption experiment carried out by Elaigwu et al. [61]. It is generally expected that as the concentration of the adsorbate increases, the metal ions removed should increase according to Okeimen et al. [3]. The trend in the table is in agreement with the expected phenomenon. It is believed that increase in concentration of the adsorbate brought about increase in competition of adsorbate molecules for few available binding sites on the surface of the adsorbent hence increase in the amount of metal ions removed. This trend could also suggest that increase in adsorbate concentration resulted in increase in number of available molecules per binding site of the adsorbent thus bringing about a higher probability of binding of molecules to the adsorbent.

Mullai et al. [66] in their experiments used five different initial concentrations of synthetic chromium effluent such as 500, 600, 800, 900 and 1000 mg/L, the metal removal efficiencies were 100, 83.33, 88.09, 94.3 and 96.72% respectively, using 20 g of cow dung ash at the end of three hours. The metal removal efficiency was 100% for 500 mg/L due to low concentration of effluent. The amount of chromium adsorbed per unit weight was maximum at lower concentration and minimum for higher concentrations [70]. Similar observations were also made by Vasantha Kumar and Bhagavanalu [56] in their work on adsorption of basic dye from its aqueous solution on bio-organic waste.

To know the effect of concentration of Cr, Lekshmi and Divanshu used 3 test samples in which the concentration of Cr were 50, 75 and 100 ppm respectively at a constant pH of 1 and temperature. Readings were taken after different intervals of time. It was observed that on changing the initial concentration from 50 to 100 ppm, the amount adsorbed increased from 36.942 to 72.770. This shows that with increase in the initial concentration of Cr, the amount of Cr removed increases while the percentage Cr removed remains the same.

6.4. Effect of adsorbent dosage

The adsorbent provides binding sites for the sorption of metal ions. Its concentration thus strongly affects the sorption of metal ions from solution [71]. The amount of biosorbent used for the treatment studies is an important parameter, which determines the potential of bio-sorbent in removing metal ions at a given initial concentration [72]. For a fixed metal initial concentration, increase in the dosage of the adsorbent provides greater surface area and availability of more active sites, thus leading to the enhancement of metal ion uptake [71]. At low biomass dosage, the amount of ions adsorbed per unit adsorbent weight is high. Adsorption capacity is reduced when the biomass dosage increases as a result of lower adsorbate to binding site ratio where the ions are distributed onto larger amount of biomass binding sites.

However, at higher dosage, the ions adsorbed are higher due to the availability of more vacant binding sites as compared to lower dosage which has less binding sites to adsorb the same amount of metal ions in the adsorbate solution [73].

Table 6
Effect of adsorbate dosage on amount of Pb²⁺ sorbed.

| Adsorbent (g) | Initial concentration of Pb ²⁺ (mg/l) | Lead concentration (mg/l) at equilibrium | Amount adsorbed (mg/g) | % sorbed (Q _e) |
|---------------|--|--|------------------------|----------------------------|
| 1 | 625.4 | 0.15 | 625.25 | 99.98 |
| 2 | 625.4 | 0.16 | 625.24 | 99.97 |
| 3 | 625.4 | 0.08 | 625.32 | 99.99 |
| 4 | 625.4 | 0.17 | 625.23 | 99.97 |
| 5 | 625.4 | 0.14 | 625.26 | 99.98 |

Elaigwu et al. [61] investigated the effect of the adsorbent dosage on the removal of Pb²⁺ from aqueous solution by varying the dosage of the adsorbent from 1.0–5.0 g. It is expected that an increase in the dosage of adsorbent should yield a corresponding increase in the amount of metal ion adsorbed onto the surface of the adsorbent since there will be more sites for the adsorbate to be adsorbed. Therefore competition for bonding sites between molecules of the adsorbate should decrease with increase in dosage of the adsorbent. Table 6 showed that this trend was inconsistent and therefore suggests that the use of modified cow dung as adsorbent partly depend on its dosage in aqueous solution.

To determine the effect of adsorbent dosage on adsorption process, Mullai et al. [66] used different dosage values of cow dung ash such as 5, 10, 15 and 20 g for the initial chromium concentration of 500 mg/L. The equilibrium metal removal efficiency values at the end of three hours were 83.33, 88.88, 94.11 and 100% respectively. An increase in adsorption of metals with increase in adsorbent dosages was observed and could be ascribed to availability of more active adsorbing sites. Similar results were reported by Nirmala et al. [74] and Akhtar et al. [75] in their work on the removal of hexavalent chromium using industrial waste biomass and organophosphorus pesticides onto chickpea husk respectively.

6.5. Effect of temperature

The effect of temperature on the removal of Pb(II) from aqueous solution was investigated by Elaigwu et al. [61]. It was done by varying the temperature of adsorption between 40 °C and 80 °C. It was observed that Pb²⁺ removal from aqueous solution increased initially until equilibrium was attained and then decreased. The decrease in the sorption process might be due to the weakening of the attractive forces between the adsorbent and the adsorbate ions. An increase in temperature between 70 °C and 80 °C caused a proportional decrease in the amount of metal ion adsorbed onto the surface of the adsorbent. At high temperature, the thickness of the boundary layer was expected to decrease due to the increased tendency of the metal ion to escape from the surface of the adsorbent to the solution phase hence there was bound to be weak adsorption interactions between the adsorbent and the adsorbate.

7. Equilibrium study

Analysing the equilibrium data is an important step in developing an equation describing the process.

For equilibrium modeling of the adsorption systems, the equilibrium data obtained by Mullai et al. in their experiment was fitted with Langmuir and Freundlich models, using their linearized forms.

The Langmuir isotherm model is expressed as:

$$q_e = \frac{QbC}{1 + bC}$$

Where:

q_e (mg/g) and C (mg/L) are the amount of metal ion per unit weight of adsorbent and unadsorbed metal ion in solution at equilibrium, respectively.

Q (mg/g) is the maximum amount of the metal ion per unit weight of adsorbent to form a complete monolayer on the surface.

b (L /mg) is a constant related to the affinity of the binding sites.

The Freundlich isotherm which is based on the heterogeneous surface is expressed as:

$$q_e = K_F C^{1/n}$$

Where K_F and n are indicators of adsorption capacity and adsorption intensity respectively.

The authors observed that the experimental data were found to fit with the Langmuir and Freundlich isotherms. The isotherm constant values of Q , b , K_F and n were 29.1 (mg/g), 0.4582 (L/mg), 0.005 (L/g) and 1.001, respectively. Q (mg/g) is important to identify the highest uptake and the value of b implies the strong bonding of Cr (VI) to cow dung ash at the experimental conditions employed [76].

The separation factor is used to describe the essential characteristics of Langmuir isotherm [77]. It is defined by:

$$R_L = \frac{1}{1 + bCi}$$

According to Treybal [78], the values $n > 1$ represent favourable Freundlich isotherm adsorption condition and the same was obtained by Mullai et al. [66]. Furthermore, the higher correlation coefficients showed that both the Freundlich and Langmuir models were very suitable in describing the adsorption equilibrium of the metal by cowdung ash in the range of concentration used. Similar results were obtained by Iftikhar et al. [79] and Barkat et al. [80] during their studies on adsorption of Cu (II) and Cr (III) using rose waste biomass and Cr (VI) ions using activated carbon respectively.

The adsorption experiment carried out by Lekshmi and Divanshu [63] followed the Langmuir adsorption isotherm process where adsorption and desorption were simultaneous processes occurring in the presence of each other and this gave a mono layer adsorption graph.

8. Future prospects

Many researchers have reported numerous naturally occurring materials for the trapping of heavy metal ions; however, little efforts have been made to use cow dung as adsorbent for the removal of heavy metals from aqueous solutions. This aspect needs to be investigated further in order to promote large-scale use of the adsorbent. Also, further investigations are needed for desorption studies, economically feasible regeneration studies of the adsorbent and application of the adsorbent for real industrial wastewater.

9. Conclusion

In the present work, recently published studies concerning the use of cow dung for metal ions removal from aqueous solutions were reviewed and the following deductions were made:

- Cow dung could be developed onto costly effective and

environmental friendly biosorbents for metal ions removal from aqueous solutions.

- Several experimental operating parameters have been found to influence the biosorption process including the solution pH, contact time, biosorbent dose and metal ion concentration.
- The pH of the solution was proven to be one of the most important factors affecting metal ions biosorption. The solution pH affects metal ion solubility as well as biosorbent total charge.
- It has been generally found that the biosorption capacity increases as the initial metal ion concentration in the solution increases and on the other hand it is reduced when the adsorbent dosage increases.
- The isothermal models including the Langmuir and Freundlich have been widely employed for modeling the biosorption process.

It can thus be concluded that the use of cow dung as adsorbent offers a great opportunity for a clean, cheap, and high effective process for metal ions removal from polluted water.

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