

# PROTECTION OF WATER RESOURCES BY USING ENVIRONMENTALLY-FRIENDLY BIOADSORBENTS

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## Abstract

*The current study built and characterized modified sorbents and then tested their ability to absorb the waste products in a lab setting. This work investigated the physicochemical properties and structure of enhanced environmentally friendly sorbents based on alginates, bentonite, and nanoparticles using spectroscopic techniques (SEM, FTIR, X-ray diffraction, and XRD analytical methods). Because the alginate core contains active COOH and OH groups, it may be chemically and physically changed and used in a range of phosphate anion adsorption techniques. We determined the sorption efficiency of a modified Fe<sub>3</sub>O<sub>4</sub>NPs@AlgBT. Using biofilters to lessen nutrient loading is an easy substitute for this. Thus, in a lab setting, the capacity of the Fe<sub>3</sub>O<sub>4</sub>NPs@AlgBT (biosorbent) to absorb nutrients and heavy metals at various starting concentrations and contact times was examined. It has also undergone testing for uses of nutrients other than growth in wastewater. Fe<sub>3</sub>O<sub>4</sub>NPs@AlgBT conducted a nutrient uptake experiment that revealed substantial nutrient uptake in all time intervals (7, 13, 19, and 25 hours) sustained at various pH levels (3–11). From all of these, the maximum amount of nutrients removed was demonstrated by 25-hour biosorption at pH 7,5. A pH of 7,5 and 25 hours later showed the maximum zinc absorption, with an ideal in vitro seaweed content of 0.5 g. The enhanced capacity of Fe<sub>3</sub>O<sub>4</sub>NPs@AlgBT to absorb nutrients and consequently stimulate development was demonstrated in an experimental investigation conducted using wastewater.*

**Keywords:** alginate, bentonite, nanoparticles, adsorbents, waste products

## I. Introduction

The excessive rise in nutrient content in water bodies, particularly in nitrogen and phosphorus, is a result of aquaculture's quick expansion. The standard method for obtaining these nutrients is to fertilize the pond with food and animal metabolic waste from raised animals. Thus, creating ecologically friendly plans that reduce these activities' detrimental effects has been the major problem [1-4]. The most pragmatic and economical method of lowering aquaculture nutrient concentrations is to treat wastewater before to its discharge into the ocean. Biological wastewater treatment with macroalgae for nutrient removal is a possibly workable substitute. It has been stated that heavy metals including Fe, Zn, Ca, and Mg have biological importance in humans and can be taken on a regular basis for medical purposes [5-7]

Even for those of biological importance, food intake must be maintained within regulatory limits, as excess will result in poisoning or toxicity, as evidenced by some reported drug symptoms that are clinically pronounced. Methods for removing metal ions from aqueous solutions mainly consist of physical, chemical and biological technologies. The advantages and disadvantages of traditional metal removal technologies are summarized. In recent years, the application of biotechnology for the control and removal of metal pollution has received much attention and is gradually becoming a hot topic in the world. Areas of metal pollution control due to its potential applications [8-12].

An alternative process is biosorption, which uses various natural materials of biological origin, including bacteria, fungi, yeast, algae, etc. These biosorbents have the property of binding metals and can be used to reduce the concentration of heavy metal ions in solution. It can effectively and quickly isolate dissolved metal ions from dilute complex solutions, so it is an ideal candidate for treating complex wastewaters of large volume and low concentration [13-15].

## II. Methods

**Preparation of biosorbent** - Laminariaceae algae samples from several locations in the Caspian Sea were gathered in order to prepare alginates. The alginate extraction method includes numerous phases. Alginate that is water-soluble is created by first converting the alginic acid ions in the algae into pure alginic acid, which is subsequently reduced by sodium carbonate/hydroxide. In order to recover the soluble alginate, calcium chloride precipitation is used to create calcium alginate, which is then processed with sodium carbonate to create sodium alginate. Bentonite – is obtained from a clay deposit located in the village of Dash Salakhly, Gazakh region of the Republic of Azerbaijan (AzRosPromInvest LLC). This deposit is one of the highest quality natural deposits in the world. Nanoparticles of iron oxide  $\text{Fe}_3\text{O}_4$  with superparamagnetic properties were obtained by chemical coprecipitation from aqueous solutions of ferrous and ferric salts in an alkaline medium created with  $\text{NH}_4\text{OH}$  in a nitrogen gas atmosphere. Following separation using a permanent NdFeB magnet, the resultant  $\text{Fe}_3\text{O}_4$  nanoparticles (NPs) were periodically rinsed with distilled water before being disseminated in ethanol. An ethanolic solution of  $\text{Fe}_3\text{O}_4$  nanoparticles was added to an ethanolic solution of the macro heterocycle taken in excess with vigorous stirring. After stirring for 8 hours at ambient temperature, the resulting nanostructures were isolated by applying a constant magnetic field and washed repeatedly with distilled water [16].

A particular amount of bentonite was dissolved in 30 mL of a 2% (v/v) acetic acid solution for 50 minutes. Addition of 0.03 g of  $\text{Fe}_3\text{O}_4$  to the bentonite solution and three hours of stirring produced the same mixture. After adding a certain quantity of bentonite clay to the homogenous mixture, the combination was stirred for 60 minutes at 65 °C before alginate was added. The  $\text{Fe}_3\text{O}_4@AIBT$  mixture was, in the end, washed with 100% ethanol and dried at 50 °C in a furnace.

XRD - Using a Rigaku Mini Flex 600 XRD diffractometer at room temperature, XRD (X-ray diffraction) examination was carried out.  $\text{Cu K } \alpha$  radiation from a Cu X-ray tube operating at 15 mA and 30 kV was utilized in each example. The samples underwent scanning within the 20–70 ° Bragg angle 2 h range.

FT-IR - (FTIR) spectroscopy, were investigated. Using a Varian 3600 FTIR spectrophotometer, FTIR spectra were captured in KBr tablets. At room temperature, the spectra was recorded in the 4000-400  $\text{cm}^{-1}$  range.

Analysis using the Energy-Dispersive Spectrum (EDS) and a scanning electron microscope (SEM)- Prepared samples were subjected to SEM and EDS examination using a Field Emission Scanning Electron Microscope (JEOL JSM-7600F) operating in the SEI domain at an accelerating voltage of 15.0 kV [18].

## III. Results

Using spectroscopic techniques (SEM, FTIR, X-ray diffraction, and XRD analytical methods), researchers examined the physicochemical characteristics and structure of enhanced ecologically friendly sorbents based on alginates, bentonite, and nanoparticles [17].

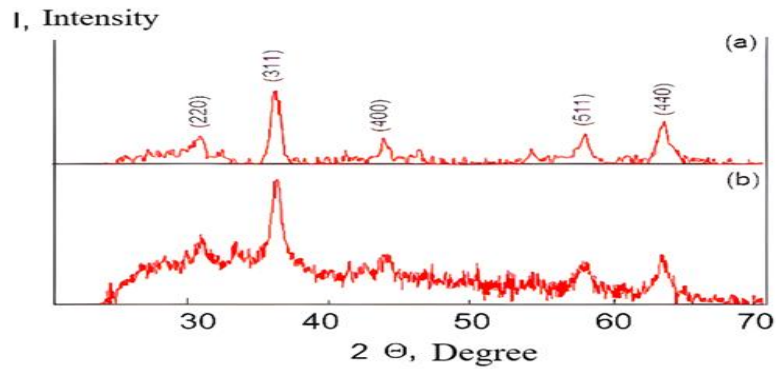


Figure 1: XRD-Pattern of the obtained nanosized samples

Data from the X-ray examination of samples of MC@Fe<sub>3</sub>O<sub>4</sub> NPs are shown. Visualization of all the diffraction peaks of the acquired samples indicates that they are cubic-shaped Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

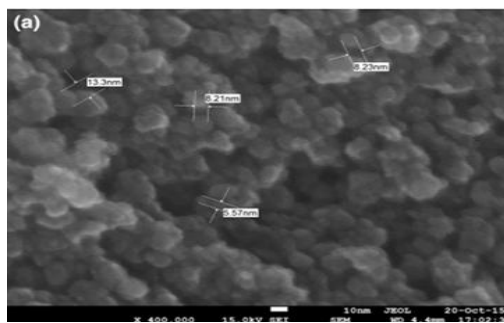


Figure 2: Scanning electron microscope image of Fe<sub>3</sub>O<sub>4</sub> NPs sample

According to the SEM analysis it was investigated that the resulting nanostructures have a homogeneous structure and they are nanosized.

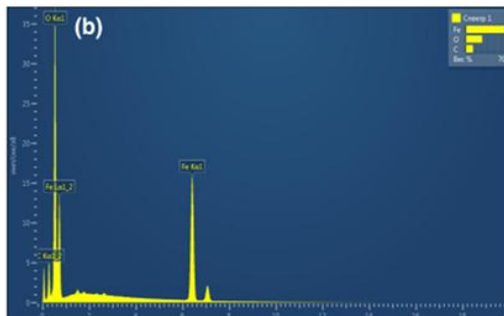


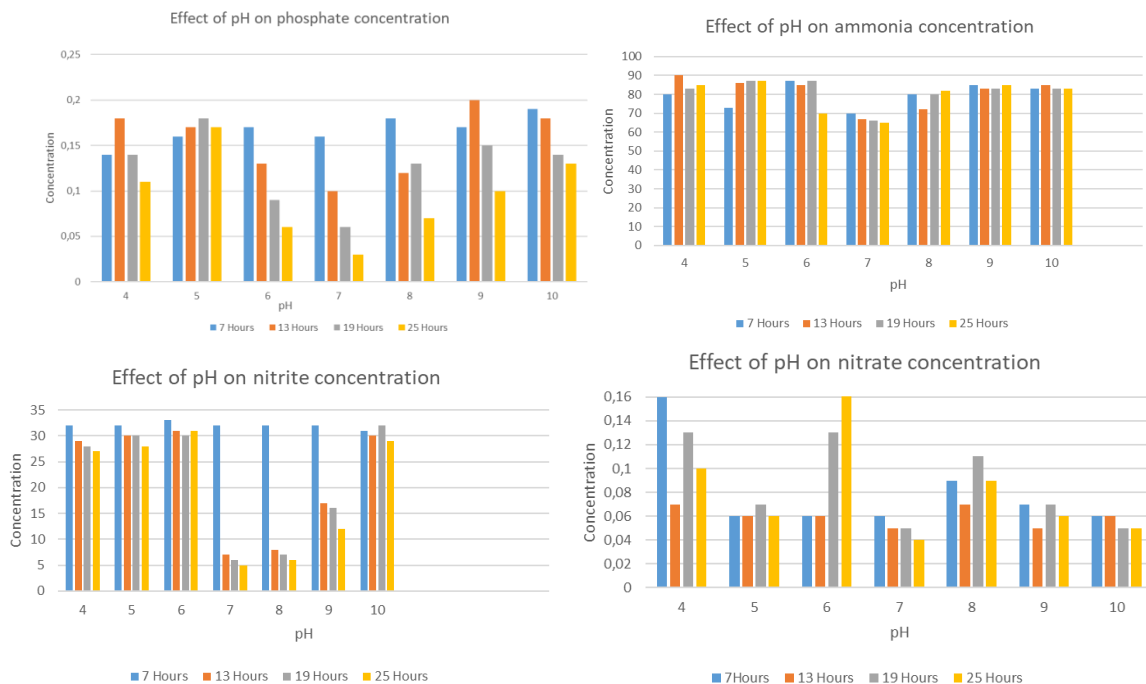
Figure 3: Electron dispersion spectrum of the Fe<sub>3</sub>O<sub>4</sub> NPs sample

The samples indicate EDS analysis verifies the synthesis of magnetite nanoparticles by identifying Fe and O as the primary components present in the sample composition of the produced nanostructures.

### Effect of pH and Time on Nutrient Absorption

In this study, maximum phosphate removal was achieved at pH 7,5, with an initial phosphate concentration of 0.5  $\mu\text{mol/L}$  eventually decreasing to 0.05  $\mu\text{mol/L}$  over 25 hours and a final value of 0.08  $\mu\text{mol/L}$  at pH 7 was the second best (Figure 4). ), pH 6 had the lowest phosphate removal at 25 hours at 0.18  $\mu\text{mol/L}$ . Ammonia concentration decreased significantly in the pH range 3-11. The lowest ammonia removal (88.83  $\mu\text{mol/L}$ ) was recorded at pH 4 after 12 hours; the highest removal was recorded (67.55  $\mu\text{mol/L}$ ) at pH 7,5 and duration 25 h. Nitrate concentrations decreased

significantly at pH 3 and 13. The lowest nitrate removal occurred at pH 6 - 0.07  $\mu\text{mol/L}$ , and at pH 11 - 0.06  $\mu\text{mol/L}$ . The greatest nitrate removal was recorded at pH 7,5, where it decreased from 0.07  $\mu\text{mol/L}$  to 0.05  $\mu\text{mol/L}$ . Nitrite concentration decreased markedly at pH 3 and pH 11. A gradual decrease in nitrite concentration was observed at all pH values. The maximum nitrite removal was 4.88  $\mu\text{mol/L}$  at pH 7,5, while the lowest nitrite removal of 28.30  $\mu\text{mol/L}$  was observed at pH 5. From the results presented, it is clear that pH has a significant effect on the reduction of nutrient concentrations. A pH of 7,5 was found to be at which nutrient concentrations were significantly reduced, although significant nutrient removal was also observed at both acidic and basic pH concentrations. Stirring the nutrient solution also improved nutrient adsorption by the seaweed. Similarly, increasing the duration of the experiment was found to enhance the adsorption process. This is evident from the fact that maximum nutrient removal was achieved after 24 hours.



**Figure 4:** Effect of pH and time on nutrient removal

The effect of pH of aqueous solution is a key controlling parameter for the biosorption of heavy metals. pH levels ranging from 3 to 11 have been tested for the uptake of heavy metals by seaweed. The results showed that the removal of heavy metals was directly proportional to pH (Fig. 4). This experiment was carried out at three different concentrations at two different time intervals. The maximum removal (17.4  $\mu\text{g/L}$ ) of zinc was observed at a concentration of 0.1 g of seaweed at pH 10 in 24 hours, and the minimum removal (87  $\mu\text{g/L}$ ) at pH 6 in 13 hours. At pH 11, maximum zinc removal was achieved at a seaweed concentration of 0.5 g in 24 hours, the zinc concentration was 0.4  $\mu\text{g/L}$ . 0.5  $\mu\text{g/L}$  was the second best maximum zinc removal rate at the same seaweed concentration observed after 13 hours. 1 g concentration of seaweed significantly reduces zinc content. Minimal zinc removal was observed after 13 hours at pH 3 (73.66  $\mu\text{g/L}$ ). Maximum zinc removal was observed at pH 11 at 24 hours (3.4  $\mu\text{g/L}$ ). Metal uptake increased with increasing pH. A gradual increase in the biosorption of heavy metals was observed as the pH transitioned from acidic to basic. Although heavy metal biosorption was recorded at both acidic and basic pH, heavy metal removal was unsatisfactory under acidic conditions. Thus, it is clear from the present study that pH above neutral conditions is capable of improving the removal of heavy metals. This may be due to the presence of more free binding sites on the biomass that absorb heavy metals from solution at these pH concentrations. In the phenomenon of biosorption, the pH value affects two aspects: the solubility of metal ions and the overall charge of the biosorbent, since protons can be adsorbed or released. This behavior will depend on the functional groups present on the algal cell wall, which in turn determine the acidity constant.

The increase in the level of biosorption with increasing pH can be explained by the influence of the number of negative charges, which depends on the dissociation of functional groups. At low pH values, the concentration of hydrogen protons in the solution significantly exceeds the concentration of zinc ions and, therefore, the protons compete with metal ions to form bonds with active sites (functional groups) on the surface of the algae, leaving metal ions free in the solution. These bound active sites subsequently become saturated and inaccessible to other cations. As pH increased, the competing influence of hydrogen protons decreased.

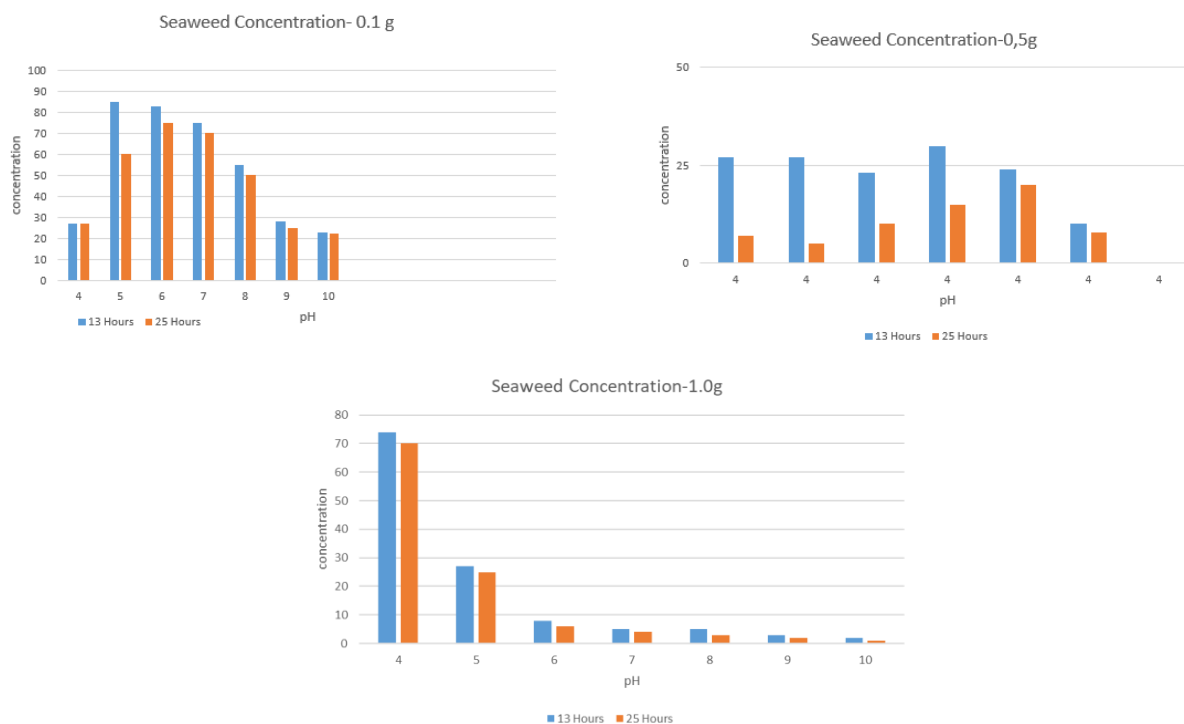


Figure 5: Effect of pH, time and concentration of seaweed on the adsorption of heavy metals

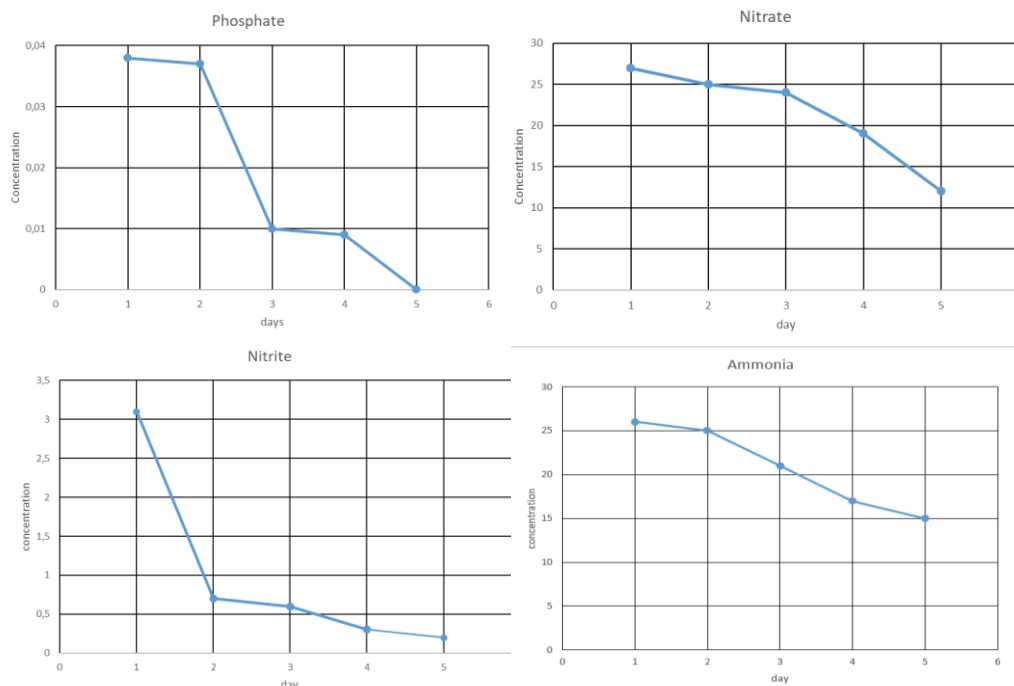
Therefore, an increase in sorption capacity or removal efficiency can be observed. Contact time is also rated as one of the most important factors affecting biosorption efficiency. The efficiency of biosorption increases with increasing contact time. As a result of these experiments, it was found that the efficiency of biomass biosorption reaches a maximum after 24 hours.

Biomass concentration is another important variable during metal uptake. The effect of biomass concentration on the biosorption of zinc ions was studied using different dosage ranges (0.1, 0.5 and 1 g), respectively. High concentrations of biomass can have a sheathing effect, protecting active sites from metal occupation. But the uptake of metals can also decrease with increasing biosorbent dosage, which may be due to the complex interaction of several factors. This may be due to partial cell aggregation, which occurs at high biosorbent concentrations and leads to a decrease in the number of active sites; we also observed this trend in our biosorption experiments. It has been suggested that electrostatic interactions between cells may be a significant factor in the relationship between biomass concentration and metal sorption. Because of this, for a given metal concentration, the lower the biomass concentration in the suspension, the higher will be the metal/biosorbent ratio and the metal retained by the sorbent unit until the biomass reaches saturation.

### Concentrations of the four nutrients tested

The concentrations of the four nutrients tested (NO<sub>2</sub>-N, PO<sub>4</sub>-P, NO<sub>3</sub>-N, and NH<sub>3</sub>-N) decreased significantly during the experimental period indicating that adsorbents have a strong ability to remove nutrients (Figure 6). PO<sub>4</sub><sup>3-</sup> concentrations decreased from 0.038 μmol/L to 0.003 μmol/L, corresponding to approximately 95.6% of the nutrients being eliminated over the five days of the

study. A significant reduction in  $\text{NO}_3$  concentration was observed in the present study. The greatest reduction occurred from the fourth (20.585  $\mu\text{mol/L}$ ) to the fifth days (13.392  $\mu\text{mol/L}$ ), corresponding to the removal of approximately 49% of nutrients.



**Figure 6:** Rate of removal of nutrients from wastewater

The nutrient removal capacity for the entire period was approximately 55.55%. At the end of the experiment (fifth day), most of the  $\text{NO}_2$  was absorbed, which is consistent. Removal efficiency 93.4%. There was also significant. Removal of  $\text{NH}_3^+$  (43%) during the experiment. Significant decrease in  $\text{NO}_3$  (13.392  $\mu\text{mol/L}$ ) during the culture period. This decrease may be due to the mineralization of organic matter. Previous studies have also shown that seaweed is capable of removing high concentrations of  $\text{PO}_4^{3-}$ . However, only the studies carried out found higher than in our present study. Removal of  $\text{NH}_4^+$  from wastewater by seaweed occurred gradually between the beginning and end of the experiment (27.123–15.976  $\mu\text{mol/L}$ ). The biofiltration capacity of  $\text{NO}_3$  obtained in this experiment was significantly higher. Because nitrate has a secondary source in nitrification processes. In addition, all other aspects must be taken into account changes in seaweed removal efficiency.

#### IV. Conclusion

In conclusion, ecologically friendly  $\text{Fe}_3\text{O}_4\text{NPs@AlgBT}$  sorbents have been obtained and has huge adsorption capacity in the incorporation of layered double hydroxides and the alginate matrix significantly improved the adsorption capacity of the developed toward water treatment.

The study showed that  $\text{Fe}_3\text{O}_4\text{@AlgBT}$  showed significant removal of nutrients and heavy metals. Therefore, it is considered for bioremediation of domestic and industrial wastewater that may cause environmental pollution.

It was concluded that  $\text{Fe}_3\text{O}_4\text{@AlgBT}$  can be used as a bioremediant in wastewater treatment plants to preserve nature and natural resources.

In addition, waste from cultivated seaweed can be used as feedstock to produce biofuels, biofertilizers and animal feed additives, reducing the cost of the wastewater treatment process.

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