BIMETALLIC NANOPARTICLES AND METAL OXIDE NANOPARTICLES SUPPORTED GRAPHENE OXIDE (GOH AND GOK), FOR TREATMENT OF TEXTILE INDUSTRIAL WASTE WATER

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Abstract - In this work, we have synthesized the bimetallic nano-particles, metal oxide nano-particles, graphene oxide and graphene oxide-metal oxide nano-composites by the given methodology. The dye solution of the fixed concentration was prepared. The observations were noted down visually as well as by the UV spectroscopy. In the further extension of the work only two dyes were selected methylene blue and Eriochrome black T. Eight samples of the graphenes prepared by us using various methods were selected for the dye degradation experiments. The observations were noted. Thus it was concluded that bimetallic nano-particles are better adsorbent for both florescent and non-florescent dyes than graphene oxide. Similarly, copper oxide-graphene oxide nano-composite was a better adsorbent than the metal oxide nano-particles.

Keywords - Dye Degradation, Bimetallic Nanoparticles, Metal Oxide Nanoparticles, Graphene Oxide, UV Spectroscopy, TGA.

I. INTRODUCTION

s are the natural or synthetic substances which are used to add or change the color. Dye is used in various industries like leather, textile materials, cosmetics, paper, paint, plastic etc. Dye structure is made up of an auxo-chrome and a chromo-phore. Dyes are important in industries as it is used for decorative, aesthetic and artistic purposes even though discharge of large amount of dyes in water leads to water pollution. The emission of dyes into environment generates coloration of natural water, toxicity causing pollution.

The cleaning of waste water is most serious environmental problem also it is of severe public health concern as synthetic dyes cause serious side effects. Dying process discharges many chemicals through polluted water and these chemicals may result in the death of aquatic life. Azo dyes are the largest group of colorant which contain 60% to 70% organic dyes produced in the world. Use of synthetic dye has an adverse effect on all forms of the life. In present, dyes contain sulphur, napthol, vat dyes, nitrates, acetic acid, soaps, enzymes, chromium compounds and heavy metals like Cu, As, Pb, Hg, Ni and Co collectively make the textile effluent highly toxic. The textile dying industries have created huge pollution in water, it also affects BOD and COD level of water. It also hinders with self purification process of water and also results in the loss of soil productivity. Azo dyes widely used in textiles industries mainly lead to carcinogenic problems. Most of the dyes characterized by complicated constitution and high chemical stability lead to retard photosynthetic activity, inhibit the growth of aquatic biota by blocking sunlight. Green synthesized nano-particles were found to have the ability to degrade toxic dyes. In general the photo-degradation process supported by catalyst depends on various factors such as the type and pH, illumination power and time and initial concentration of the dye.

II. DETAILS of EXPERIMENT

2.1 Materials and Procedures

All chemicals were purchased from Sigma Aldrich. Zinc Acetate, sodium selenite, graphite, Copper Acetate, sodium hydroxide, sodium nitrite, hydrogen peroxide and dyes listed in table no.1.all solutions prepared in deionized water. All the dyes Eriochome black T, Bromothymol blue, Alizarin Red, Titan Yellow, Solo-chrome black, solochrome dark black, Methyl Orange, methyl red, malachite green, Indigo Carmine, Brilliant Yellow, Florescence, Eosin B, Eosin Y, Rose red, Congo red were purchased from Sigma-Aldrich.

2.2 Methodology:

The catalysts used for the dye degradation were graphene oxide prepared by modified Hummers method (GOh) and Graphene oxide prepared using potassium dioxide(GOk), different metal oxides (copper oxide and magnesium oxide) nanoparticles prepared by biological route, bimetallic nanoparticles like zinc-selenium and copper–zinc bimetallic nano-particles.

2.2.1 Synthesis of Graphene Oxide (GOh) by Modified Hummers Method:

46 ml of cold concentrated sulphuric acid was added into a mixture of 2g of graphite powder mixed thoroughly with sodium nitrate. $KMnO_4$ (6 g) is added gradually with stirring and cooling in an ice bath, so that the temperature of the mixture was

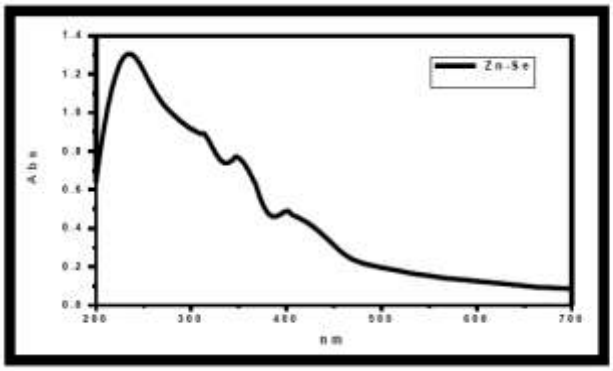
maintained below 20°C. The mixture is again stirred at 35 °C for 30 min, and distilled water (75 ml) is added slowly which causes violent effervescence and the temperature is increased to 85-90oC. After 1hour, the reaction is terminated by the addition of distilled water (100 ml) and 30% H2O2 solution (20 ml), after which the color of the suspension changes to bright yellow. The suspension is then washed with 5% HCl solution three times for removal of metal ions followed by washing with deionized water. The compound formed is graphitic oxide. It is followed by sonication for further exfoliation and the formation of graphene oxide. Then it is filtered with Whatman filter paper using a vacuum filter pump. The paste collected from the filter paper is then dried at 60°C. This is the graphene oxide, abbreviated as GOh henceforth in the thesis.

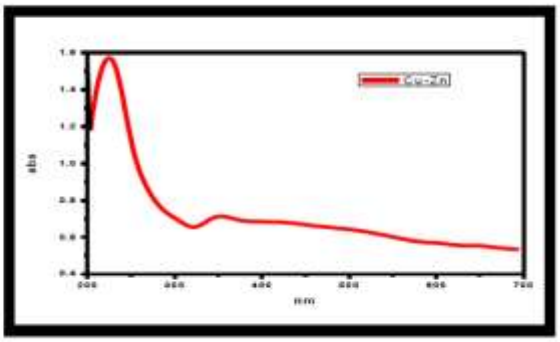
2.2.2 Synthesis of GOk Using Potassium Dioxide:
In the method the reagent hydrogen peroxide, used for quenching the oxidation reaction is replaced by potassium dioxide. The product formed is named as GOk by us.

2.2.3Synthesis of Zn-Se Bimetallic Catalyst :
70ml of 0.2 M solution of each of the Zinc Acetate($Zn(OAc)_2$)and sodium selenite (Na_2SeO_3) were prepared in distilled water and transferred into 250ml round bottom flask. Followed by addition of hydrazine hydrate in ethylene glycol in 1:1 ratio. Then 0.1gm polyvinyl pyrrolidone was added drop wise into the above solution and the solution was stirred for 8 hrs. This gave yellowish precipitate of zinc-selenium which was washed with ethanol several times and dried at 70^0C in oven for 2 hrs. (22)

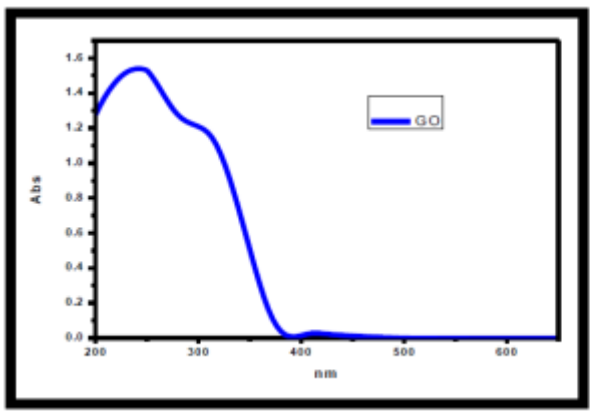
Synthesis of Copper-zinc Bimetallic Catalyst:
70ml of 0.2 M solution of each of the Copper Chloride ($CuCl_2$)and Zinc Acetate ($Zn(OAc)_2$) and sodium selenite(Na_2SeO_3) were prepared in distilled water and transferred into 250 ml round bottom flask. Followed by addition of hydrazine hydrate in ethylene glycol in 1:1 ratio. Then 0.1gm polyvinyl pyrrolidone was added drop wise into the above solution and the solution was stirred for 8 hrs. This gave greenish precipitate of copper-zinc which was washed with ethanol several times and dried at 70^0C in oven for 2 hrs. (22)

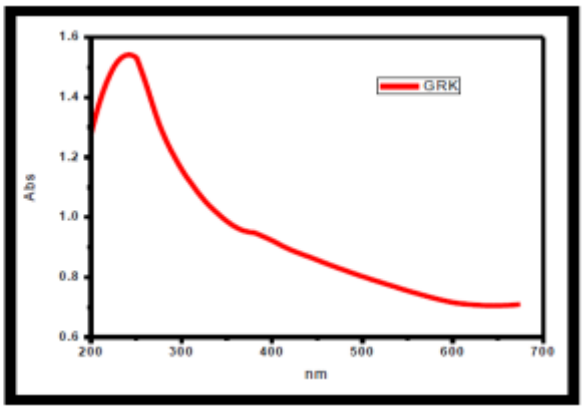
Result for the Analysis of the catalysts :
All the catalysts, graphene oxides, metal oxide(CuO, MgO) nanoparticles and the bimetallic (Zn-Se, Cu-Zn) nanoparticles were characterized for their properties by the techniques like Ultraviolet-Visible Spectroscopy, powdered X-ray diffraction, Cyclic Voltametry, Thermogravimetric Analysis.
Ultraviolet-Visible–Spectroscopy:
UV-visible spectra of all samples and their absorption maxima were analysed at wavelength 200-800nm.



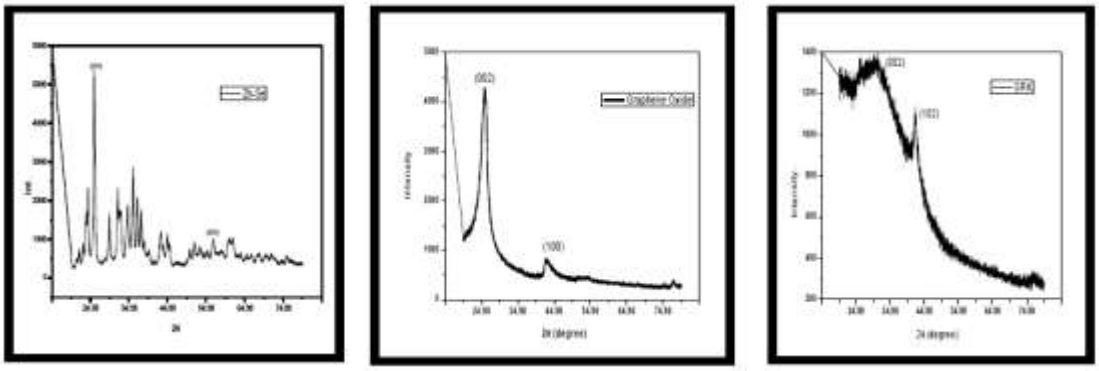


Powdered X-Ray Diffraction analysis of Synthesized Nanoparticles

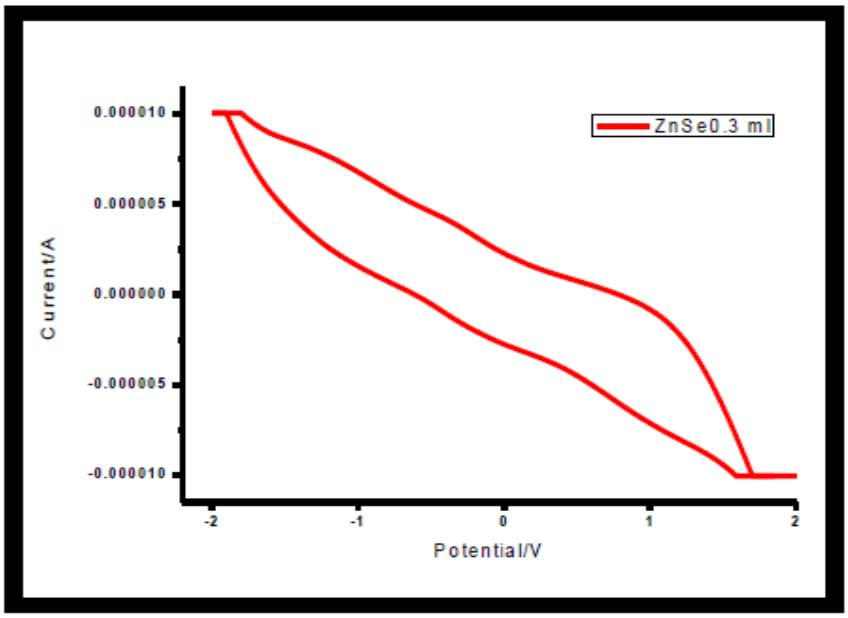




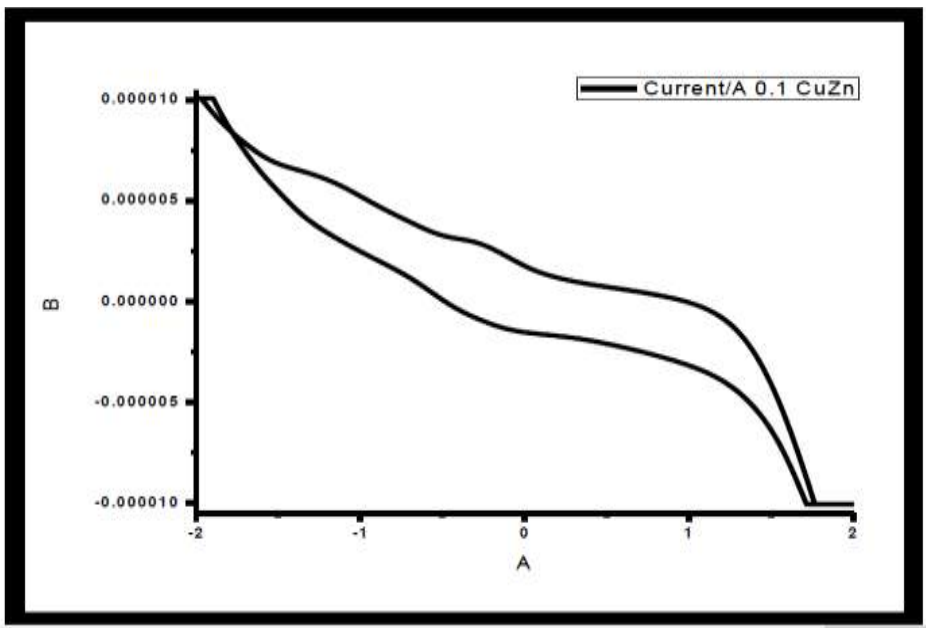
Powdered X-Ray Diffraction analysis of Synthesized Nanoparticles



Cyclic Voltametry

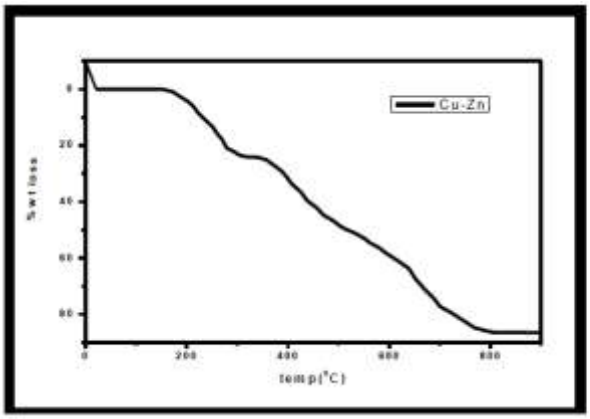


Plot of Cyclic Voltametry Zn-Se nps at diff. conc.current flow

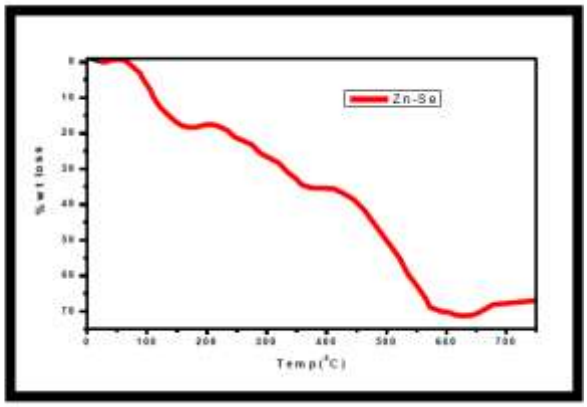


Plot of Cyclic Voltametry of Cu-Zn nps at diff. conc and conc and current flow

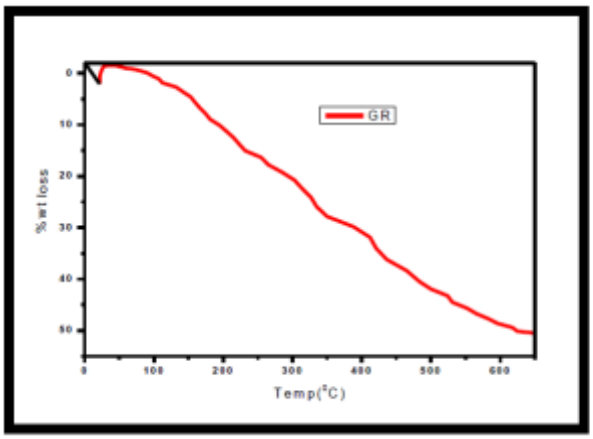
Thermogravimetric Analysis Spectra of Nanocatalysts



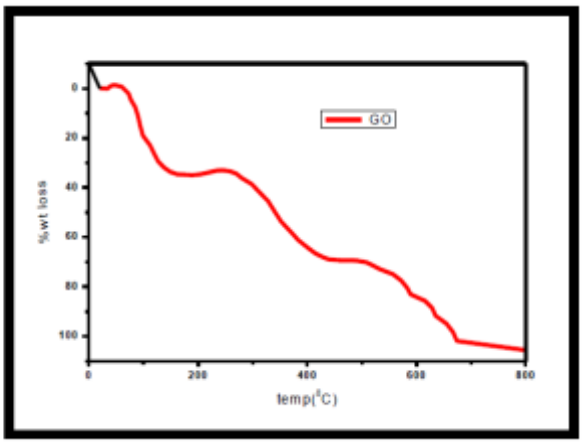
Thermal decomposition of Cu-Znnpsby TGA



Thermal decomposition of Zn-Se nps by TGA



Thermal decomposition of GOk by TGA



Thermal decomposition of GOh nps by TGA

Dye Degradation by the Synthesized particles

Dye Degradation by Metal oxide nanoparticles, Bimetallic Nanoparticles and graphene oxide :
10ppm(10mg/1000ml) dye solution of different fluorescent and non-fluorescent dyes is prepared using deionized water. 20ml dye solution of 10ppm concentration of each of the dyes was taken in 55ml hard glass test tube. 20mg of each of the catalysts was added in each of the test tube. Then sonicate above solution for half hour. After sonication place the above solution in presence of light (200 watt). Observe the color change of the solution after every 15 minutes. Collect 1ml solution and observe the color change by Ultraviolet- visible Spectrophotometer analysis.

Procedure for Mixed Dyes Degradation:
1ml of 10ppm of each dye solution (total volume 10ml) was taken in hard glass tube. Into this 20mg of each catalyst was added in each of the test tube. Above mixture was sonicated for 15 minutes and then kept in light and the color change was observed with the time.



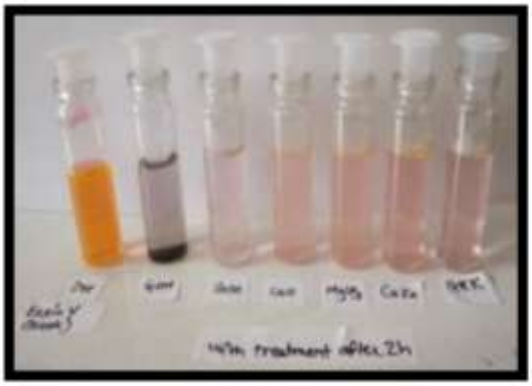
dyes before addition of catalyst



dyes after addition of catalyst



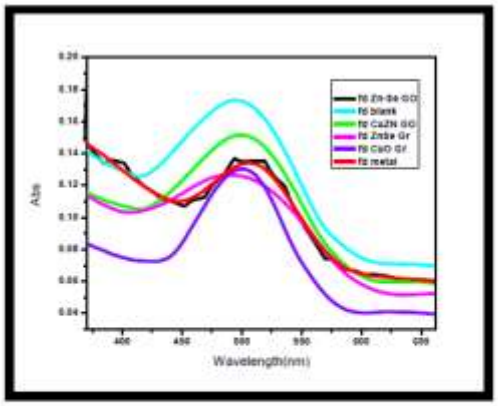
fluroscin dye with catalyst

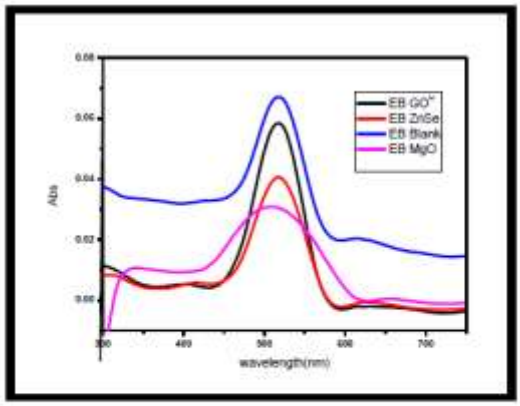


Eosin Y dye with catalyst



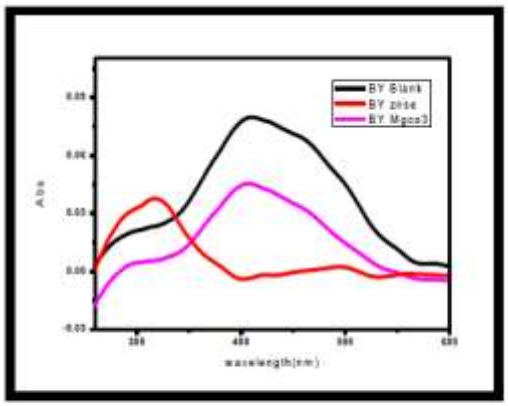
Rose red dye with catalyst

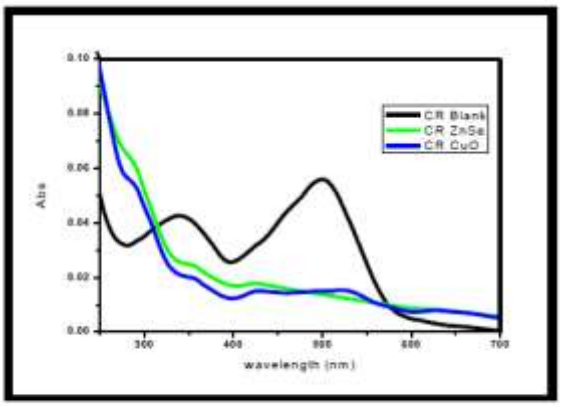




Fluorescent dye degradation by mixed catalysts

Eosin B dye degradtion





Brilliant Yellow Dye

Congo red dye degradation

III. RESULTS AND DISCUSSION

Discussion of the dye degradation :

Zinc-selenide bimetallic nanoparticles were found to be better adsorbent for all the dyes for both fluorescent and non-flourescent dyes when time is considered. For mixed dyes solution copper-zinc bimetallic nanoparticles were found to be better adsorbent and time required for degradation of dyes is only 30 minutes. Amongst the graphitic materials graphene oxide produced by using potassium dioxide is found to be better adsorbent.

For the Non Flourescent dyes degradation with mixture of catalyst CuO-GOh and CuO-GOk were found to be better adsorbents. Similarly for the Flourescent dyes degradation with mixture of catalyst

Cu-Zn GOh and Cu-Zn GOk were found better for dye degradation.

IV. CONCLUSIONS

Zinc-selenide bimetallic nanoparticles were found to be better adsorbent for all the dyes for both types of fluorescent and non-flourescent dyes when time is considered. For mixed dyes solution copper-zinc bimetallic nanoparticles were found to be better adsorbent and time required for degradation of dyes is only 30 minutes. Amongst the graphitic materials graphene oxide produced by using potassium dioxide is found to be better adsorbent. For the Non-Flourescent dyes degradation witha mixture of catalyst CuO-GOh and CuO-GOk were found to be better adsorbents. Similarly for the Flourescent dyes degradationwith mixture of catalyst Cu-Zn GOh and Cu-Zn GOk were found better for dye degradation.
Thus it can be concluded that bimetallic nanoparticles are better adsorbent for both florescent and non-florescent dyes than graphene oxide. Similarly, copper oxide graphene oxide nanocomposite was a better adsorbent than the metal oxide nanoparticles.

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