



## Evaluation of the Degradation Potential of New inorganic cation Exchanger towards Crystal Violet: A UV/Vis DRS study

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### Abstract

Efficiency for the removal of crystal violet (CV), one of the earliest synthetic dyes, on novel inorganic cation exchanger were studied using UV/Vis DRS. Cerium(IV) arsenomolybdate, a heteropoly acid based cation exchanger were synthesized and characterized using FTIR, XRD, TGA, SEM-EDS techniques. Its composition was found to be Ce: As: Mo; 1.8:1:1.4 and it is quite chemically stable. CeAsMo shows enhanced catalytic activities towards degradation of CV. The oxidizing power of heteropoly acid units and electron exchange character of Ce are credited to the degradation efficiency of the exchanger. The effects of catalyst dosage, pH of the medium, concentration of dye solution, shaking time as well as temperature were ascertained, and the favorable conditions for maximum degradation were determined. CV was degraded more than 95% in the presence of new exchanger within 2 hours. The reproducibility of exchanger's behavior as catalyst showed at least a three-cycle of degradation process. The degradation of CV in binary dye-metal mixtures has also been considered since dye effluents usually contain many metal ions. Whole studies disclose that the CeAsMo showed higher efficiency towards the removal of Crystal violet dye and can apply them to the target applications of environmental remediation and catalysis.

**Keywords:** Crystal violet, degradation, UV/ Vis DRS, arseno molybdate, heteropoly acids.

### Introduction

Interest in the application of inorganic cation exchangers in different fields has increased rapidly in recent years. They have been used as ion-exchange membrane<sup>1,2</sup>, ion selective electrode<sup>3,4</sup>, catalyst<sup>5</sup>, sorbent in chemical refining process for metal ion recovery, regeneration of decontaminants, removal of the hazardous chemicals from aqueous effluents<sup>6-8</sup> etc. Heteropoly acid salts are most striking due to their distinctive properties such as Bronsted acidity, chance to modify their acid-base and redox properties by altering their chemical composition, ability to accept and release electrons, high proton mobility<sup>9,10</sup> etc. Cerium based materials got great interest due to their redox properties, because of conversion between Ce (III) to Ce (IV) valence states under oxidation and reduction conditions. Cerium containing catalysts are broadly used as efficient oxidation systems due to their special properties such as redox, oxygen release and storage abilities<sup>11,12</sup>. Cerium based ion exchangers are reported having enhanced applications like decolourisation of water by adsorption or degradation of organic dyes<sup>13,14</sup>.

Textile, pulp and paper manufacturing and plastics industry wastewater is seriously charged with unconsumed dyes, and sometimes traces of metals. These effluents can be a source of serious damage to the environment and consequently many environmental remediation techniques such as analytical, biochemical and physicochemical methods are used for characterization and elimination of hazardous dyes from water. But each conventional method has its shortcomings because the dyes molecules are very stable to light and oxidizing agents, and

are resistant to aerobic digestion<sup>15,16</sup>. Among various dyes, Crystal Violet is a potent carcinogenic, which is responsible for promoting tumor growth in some species of fish. There are many reports regarding the degradation of CV. Unfortunately, most of these experiments were carried out under UV/Vis light irradiation<sup>17,18</sup>. In the present challenge the catalytic activity of new inorganic cation exchanger, CeAsMo was evaluated by degrading CV in different conditions without any irradiation and external catalytic agent. The degradation efficiency in binary dye - metal mixtures was also studied since dye effluents usually contain many metal ions. The UV/Vis DRS studies reveal that CeAsMo showed higher efficiency towards the removal of Crystal violet dye and can apply them to the target applications of environmental remediation and catalysis.

### Material and Methods

**Apparatus and instruments:** FTIR spectrometer model Thermo Nicolet Avtar370 for IR studies, X-ray diffractometer BrukerAXS D8 Advance for diffraction studies, Perkin Elmer Diamond TG/DTA Analysis system for thermal analysis and an electric shaking machine for shaking. Chemical composition was determined using EDS. ELICO LI613 pH meter was used for pH measurement and an electric thermostat oven was used for heating the sample at various temperatures. UV/Vis spectrophotometer model JASCO V660 was used for spectrophotometric measurements.

**Synthesis and characterisation of ion exchange material:** The CeAsMo was prepared by precipitation method as follows: 0.1 M Ammonium ceric(IV) nitrate (E.Merck) was added under

vigorous stirring to a mixture of 0.05M sodium arsenate (Loba Chemie, India) solution and 0.05M sodium molybdate (E.Merck) solution, in 1:3:2 volume ratio keeping the pH at 1.0. After that it was filtered, washed with deionised water and dried. The ion exchange material was then converted in to the H<sup>+</sup> form by treating with 1.0 M nitric acid for 24h with occasional shaking and intermittent shifting of acid. It was then washed with deionised water to remove the excess acid, dried and sieved to obtain particles of 60-100mesh.

The chemical stability of the exchanger was assessed in mineral acid like HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>, bases like NaOH and KOH and organic solvents like acetic acid, acetone, ethanol and diethyl ether. Properties like ion exchange capacity (IEC), pH titration studies, distribution studies and effect of temperature on IEC etc were studied in order to examine its utility as competent inorganic cation exchanger and we reported earlier<sup>19</sup>.

**Degradation of CV using CeAsMo:** The degradation of CV was studied in the presence of CeAsMo cation exchanger. 30ppm solution of crystal violet dye was prepared in deionised water and was diluted as and when required. The catalytic degradation was observed upon addition of 0.30 g of CeAsMo to the dye solution at room temperature. To find out the percentage of dye degradation, the sample were collected at regular intervals and the absorbance of the sample at  $\lambda_{\text{max}} = 590$  nm was measured using a UV/Vis DRS. The absorbance of dye solutions at an initial ( $A_0$ ) and after a definite time ( $A_t$ ) was used in Beer's Law to evaluate the degradation efficiency of the material: Degradation =  $[1 - (C_t/C_0)] = [1 - (A_t/A_0)]$

The effects of catalyst dosage, initial concentration of dye solution, pH, temperature and time of contact of dye solution

with the catalyst etc were considered to calculate the favorable conditions of dye degradation catalysed by CeAsMo. The effect of inorganic cations like Pb<sup>2+</sup>, Cu<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> in dye solution was also considered for the catalytic activity of CeAsMo in the CV degradation reaction. Controlled experiments were also carried out to confirm that reaction is not a result of photo catalytic reaction.

## Results and Discussion

FTIR (figure-1a) shows broad band in the region ~3341cm<sup>-1</sup> attributed to symmetric and asymmetric -OH stretching,<sup>20</sup> whereas band at ~1622cm<sup>-1</sup> is due to H-O-H bending. A peak in the region 809cm<sup>-1</sup> is attributed to metal oxygen vibrations<sup>21</sup>. A band at 1310 cm<sup>-1</sup> is due to the presence of (AsO<sub>4</sub>)<sup>3-</sup> and the sharp intense peak around ~1384 cm<sup>-1</sup> may be due to the presence of  $\delta$  (AsOH).

The X-ray diffraction spectrum (figure-1b) of cation exchanger cerium (IV) arsenomolybdate shows a number of peaks at different 2 $\theta$  values. The analysis of these signal peaks supports towards its semi crystalline nature<sup>22</sup>. SEM image of CeAsMo (figure-1c) reveals that the particles having an irregular and porous shape.

The TG of CeAsMo (figure-1d) shows a sharp weight loss up to 170°C, attributed to the loss of moisture and hydrated water and the weight loss observed from 260-345°C due to condensation of exchangeable hydroxyl groups which is the usual behavior of inorganic ion exchangers<sup>23, 24</sup> and a continuous weight loss in the temperature range 465-800°C is due to decomposition of the material to the corresponding oxide.

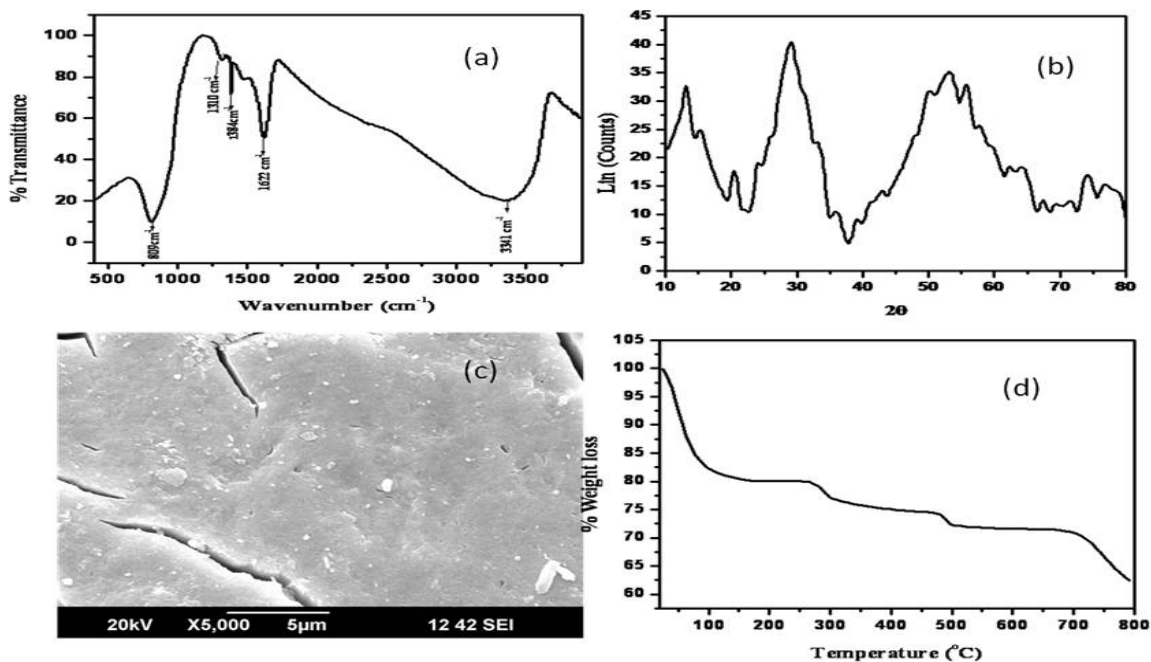
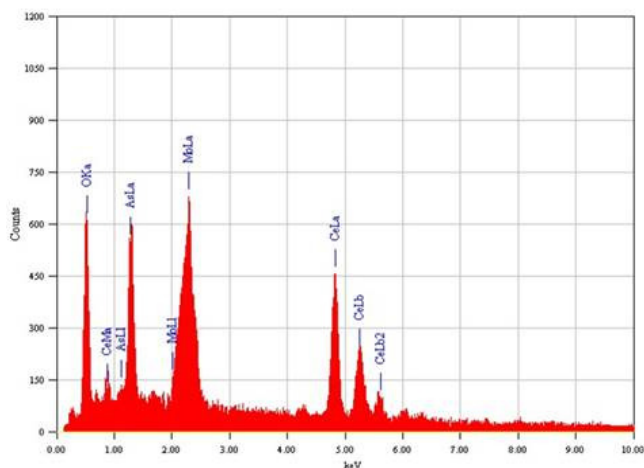


Figure-1 (a) FTIR Spectrum, (b): XRD, (c): SEM image and (d): TGA of BiTeW

The energy dispersive spectrometry (EDS) was used to recognize the elements exist in the prepared sample by taking a selective portion of SEM image in the form of peaks of spectrum. The elemental composition of the prepared catalyst is listed in the table-1 in percentage weight as well as percentage of atomic elements in the sample and its spectral images are given in figure-2.

**Table-1**  
**Composition of elements in CeAsMo**

Element	Mass%	Atom%
O	10.62	45.13
As	15.41	13.99
Mo	22.23	15.76
Ce	51.75	25.12
Totals	100	100



**Figure-2**  
**EDS spectrum of CeAsMo**

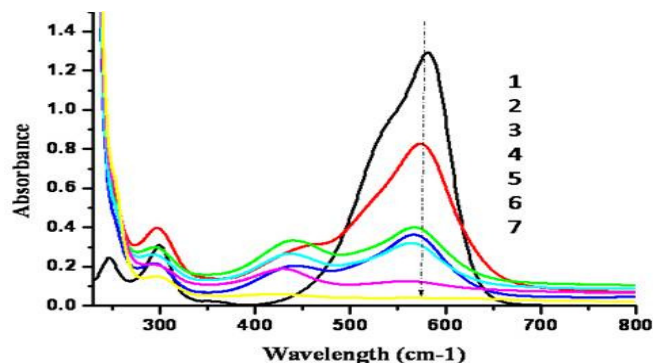
**Catalytic activity of CeAsMo - degradation of Crystal violet:**

In a controlled experiment, 20 ml of 30 ppm solution containing crystal violet was taken in three beakers. The first, second and third beakers containing dye and 0.30 g of catalyst were kept in dark, in natural light and exposed to UV light for 6 h respectively. The absorbance of the CV solution of three beakers was measured by UV/Vis DRS. It was noted that the absorbance of solution in each beaker has shown drastic decrease from initial absorbance. When we compared the percentage of decolourisation in each beaker, the interesting aspect noted was that there was no significant change, indicating the degradation reaction is not an outcome of photo catalytic reaction, only the presence of catalyst was required for the reaction to proceed. So here we reported the degradation efficiency of the new ion exchange material at room temperature and the result of experimental parameters like initial dye concentration, catalyst dosage, pH of the solution, time of contact and the effect of temperature since these are vital to attain the higher degradation efficiency of catalyst.

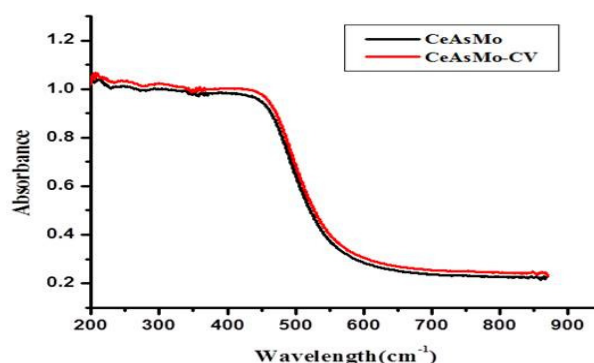
Several species are supposed to be responsible for the

degradation. Yet, the correct mechanism for dye destruction is still in question. Most probably, this degradation proceeds by an adsorption- oxidation- desorption mechanism. Initially, the CV molecules get adsorbed on the surface of the CeAsMo catalyst. After that, the oxidizing species in catalyst having high oxidizing capacity cause destructive oxidation of the dye molecules. Finally, the small molecules as a result of dye degradation are desorbed off the CeAsMo surface and the catalyst is, hence, recovered.

Figure-3 shows the CV absorption spectra during the degradation reaction. The decrease in absorption at 590 nm is due to the destruction of aromatic linkage. The disappearing peaks in the UV/Vis DRS spectra indicate the degradation of dye molecules. Additionally, the DRS of pure CeAsMo and CeAsMo-CV, catalyst retained after degradation of CV show similar absorption pattern (figure-4). This showed that the UV/Vis absorption band wavelength was not shifted and the intensity of absorbance was also having no change for these two samples. The absorption of pure CeAsMo and CeAsMo-CV shows similar bands between 200-380nm and same reflectance in visible region. It confirms that no molecules of the dye were present on the surface of the material, and the decolourisation of solution is due to the degradation of dye molecules.



**Figure-3**  
**UV/Vis DRS spectra of CV during degradation. (1) 0 min; (2) 10 min; (3) 40 min; (4) 60 min; (5) 80 min; (6) 100 min; (7) 120 min**



**Figure-4**  
**UV/Vis DRS spectra of pure samples of CeAsMo and catalyst retained from dye solution after CV degradation**

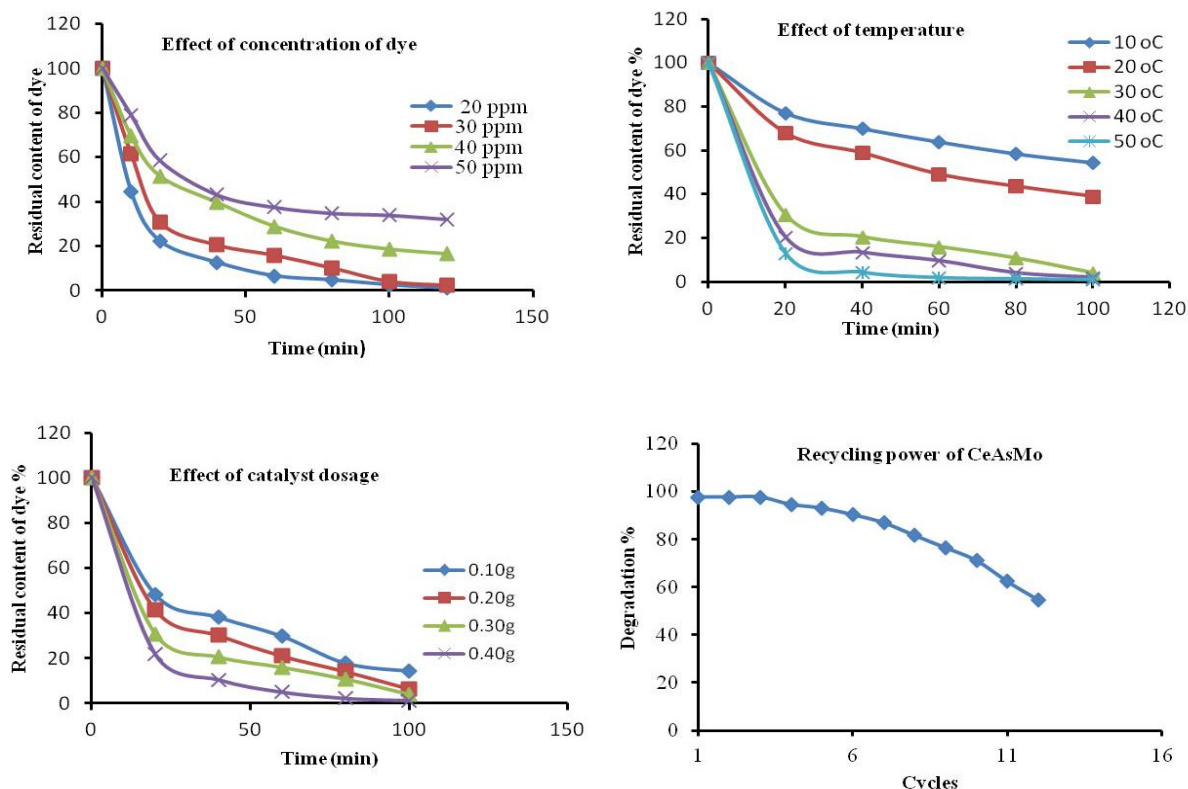
**Effects of various experimental parameters on degradation of CV:** Effects of various parameters such as temperature, amount of catalyst and initial concentration of the dye solution on rate of degradation were studied (figure-5) and it was found that the rate of decolourisation increased with increase in temperature and catalyst dosage and decrease in concentration of solution. The degradation efficiency of the dyes at different concentrations and temperatures were studied by determining their residual concentrations spectrophotometrically. Residual percentage content of dyes was plotted against time.

Residual content of dye =  $C_t/C_0 \times 100$ , where  $C_t$  is concentration of dye solution at time t and  $C_0$  is initial concentration of dye. In high concentrations of the dye solutions the degradation rate decreased due to multi layer formation of the dye molecules on the material. The increase in degradation rate at different catalyst dosages ranging from 0.01 to 0.04 g is due to an increase in the possibility of active sites and accordingly an increase in the number of adsorbed dye molecules on the catalyst surface.

We used CeAsMo catalyst for a number of cycles for the degradation process of CV. Following each cycle, the catalyst was removed from the system, washed with water and dilute  $HNO_3$ , and treated at 40°C over 2h. The repeatability of catalytic

activity within 2h is shown in figure-5. Up to the end of each cycle of the experiments it was found that no molecules of the dye were present on the surface of the material which was confirmed from the UV/ Vis DRS spectrum. CeAsMo show better reproducibility for dye degradation and can use thrice without any loss in its capacity and about 6% reduction in degradation efficiency after 6-cycles of experiments is observed.

The most important factor affecting catalytic degradation is pH since the adsorption capability of dye molecules on catalyst surface is a significant phase during the process. The reason for increase in the rate of molecule decomposition is due the increase in the number of target molecules adsorbed onto catalyst surface. We considered the effect of pH on the catalytic activity of CeAsMo (0.30g) during the CV degradation process with an initial concentration of 30ppm over a pH range of 3.0-10.0. Dye solution pH was adjusted by adding suitable amounts of 0.1M HCl and 0.1M NaOH. The degradation yield in the different pH is shown in figure-6. It is observed that rate of degradation increases with varying pH from 3.0 to 6.0, it may be explained that adsorption process below pH 5 is less probably due to more affinity of the material for  $H_3O^+$  as compared to dyes. If pH is increased further, the rate decreases. This is because of repulsion between excessive  $OH^-$  ions on catalyst surface and electron rich dye surface.



**Figure-5**  
 Effect of various parameters on degradation of CV with CeAsMo

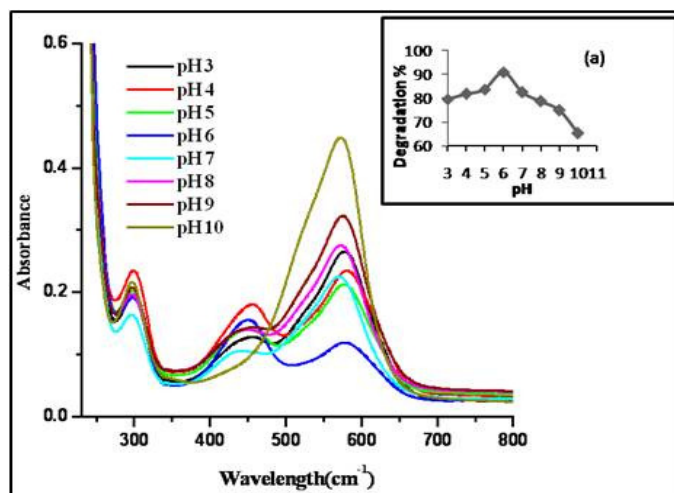


Figure-6

UV/Vis DRS spectra during degradation of CV with variation of pH. Degradation percentage with variation of pH is shown in the inset

**Influence of various inorganic cations on degrading power of CeAsMo:** Dye effluents discharged from different industries often contains various inorganic cations. Different cations prove various effects on dye degradation. The effect of  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Mn^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$  (0.005M,10ml) was investigated on CV (30ppm,30ml) degradation catalyzed by CeAsMo (0.30g) at pH 6. The cations gave the following order for degradation yield:  $Hg^{2+} > Cd^{2+} > Mn^{2+} > Cu^{2+} > Pb^{2+}$  (figure-7) and which was against the order of distribution coefficient. The inhibitory effect is due to the fact that the cations block the active sites on the surface of the catalyst.  $Pb^{2+}$  and  $Cu^{2+}$  shows more affinity towards the exchanger and decrease the area of catalyst surface and hence decreases the catalytic activity of the exchanger.

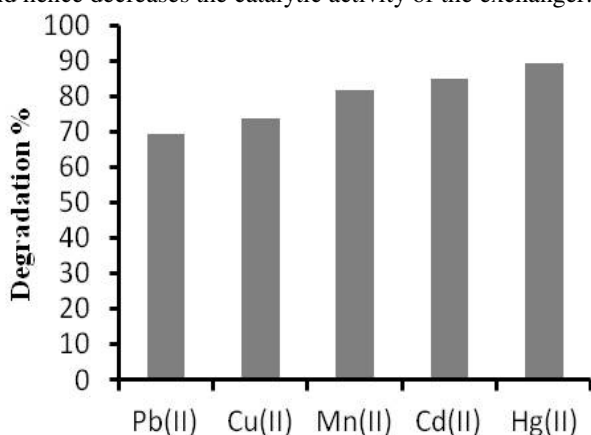


Figure-7

Effect of inorganic cations on the degradation efficiency of CV on CeAsMo within 120min

## Conclusion

The DRS analyses show that CeAsMo can be successfully used

for the degradation of crystal violet dye without any external catalytic agent. The enhanced adsorption and degradation of crystal violet over the catalyst surface is highest at pH 6.0. The rate of degradation can be controlled by temperature variation and catalyst dosage. In addition, the catalyst can be easily recovered and recycled without any loss in its capacity and efficiency. Thus an eco-friendly and environmental protecting process is proposed for the removal of hazardous organic dyes from wastewater.

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