

Kinetics and Adsorption Isotherms Studies of Acridine Orange Dye from Aqueous Solution by Activated Charcoal

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ABSTRACT

The goal of this research is to evaluate the efficiency of charcoal as low cost and effective adsorbent for acridine orange (a cationic dye) from aqueous solution at room temperature. Effect of initial pH (2-8), shaking time (5min. - 1hour), adsorbent dose (0.1gm- 0.9gm) and dye concentration (37mg/30ml-185mg/30ml) were investigated. Results demonstrated that charcoal act as good adsorbent for the removal AO where 99.15% of the dye was adsorbed within 30 minutes. For the maximum dye removal efficiency (100%), optimum conditions were obtained at pH 8 (99.24%), adsorbent dose of 0.9g and dye concentration of 185 mg with charcoal. Kinetics of adsorption was investigated as well as Langmuir and Freundlich isotherms were employed to describe equilibrium studies. The Langmuir adsorption isotherms models and pseudo second order kinetics fitted the experimental data best with high regression coefficient R^2 . The results of the present studies points to the potential of charcoal as an effective adsorbent for the removal of dye from contaminated water sources.

Keywords: Acridine Orange, Charcoal, Isotherms, Langmuir, Freundlich, Kinetics

1. INTRODUCTION

Adsorption of Waste water pollutants onto activated carbon surfaces has been studied widely and a huge literature is available on this progressively important practical problem^{1,2}. Recycling is the major concern for this century; besides the recycling the conversion of the waste materials to less toxic substances is also a major issue therefore Wastewater management is one of the demanding issues in the world. It's of primary concern to make waste water less toxic and less injurious for the nature. The conventional aim of wastewater treatment is to permit wastewater to be disposed safely, without a danger to public health, polluting watercourses or causing other irritation. Increasingly another important aim of wastewater treatment is to recover energy, nutrients, water and other precious resources from waste water³.

Waste products of many industries (e.g. textile, leather, paper, pulp, plastics, food etc.) contain enormous amount of dyes and pigments which are used for coloring their final products⁴. Dyes present in waste water may cause severe environmental pollution problems (e.g. reducing light penetration in water and photosynthesis).

The removal of these toxic materials from water in cost-effective manner, remains an important hitch. Surprisingly there is no handy method to eliminate the color of the dye from the water. The available methods of primary treatments including sedimentation and flotation are not effective for the removal of color without simultaneous chemical treatments. Other Processes such as membrane separation, coagulation and ion exchange are also used for the removal of color from dye waste water, but the cost of the process is the main negative aspect of these techniques⁵. Pollution caused by the textile wastewater is a common problem faced by many industrial countries. Dyes used in the textile industries are particularly difficult to remove by the conventional waste treatment methods because of their stability towards light, oxidizing agents and resistance towards aerobic digestion. Rather than these expensive and difficult techniques Adsorption is an advanced and better technique for water reuse in terms of initial cost and not affected by toxic substances^{6,7}. Adsorption is one of the most promising decolorization techniques in dyeing wastewater treatment. Adsorption techniques for wastewater treatment have become more widespread in recent years owing to their efficiency in the removal of pollutants too stable for biological methods⁸. The main advantage of adsorption in recent times became the use of low-cost materials, which reduces the procedure cost.

Acridine Orange, we briefly denote as AO, is a heterocyclic dye containing nitrogen atoms which is extensively used in the fields of printing, dyeing leather, printing ink, and lithography, it has also been used widely in biological stain. Toxicological investigation shows that amino acridine has mutagenic potential. In literature, there are various ways and techniques that can be used for the removal of organic dyes; among them is the adsorption process^{9,10}.

Activated carbon adsorption treatment has been confirmed to be an effective replacement for the combined biological and chemical treatment. The performance of an activated carbon treatment process depends on the type of carbon and the characteristic of the wastewater in addition to the operating conditions. Activated carbon is relatively modern form of porous carbon materials with a number of significant advantages over the more traditional powder materials. These include high surface area and adsorption capacity as well as adsorption power from the gas and liquid phase¹¹. Surface area, porosity and surface chemistry also affect adsorption process¹². The hydrogen present in active carbon is the residual hydrogen and is spread throughout the surface. The presence of oxygen arises only by the

subsequent oxidation of the carbon during manufacturing and activation. Oxygen and hydrogen combine with the surface carbons and form a variety of surface complexes. The major groups determined on the surface of the active carbons are $-\text{OH}$, $>\text{C}=\text{O}$, $-\text{COOH}$, aromatics, lactones, and heterolytic ether structures^{13, 14}.

2. EXPERIMENTAL

All reagents of pure quality (E-Merk) were used throughout the experiment. Dye stock solution of $1 \times 10^{-3} \text{ mol dm}^{-3}$ was prepared in 250 ml of deionized distilled water. Solution of dye was preserved in polyethylene bottle. Stock solutions of NaOH or HCl of 0.1 mol dm^{-3} was prepared in distilled water and charcoal is used as adsorbent. The effect of agitating time was investigated by 900 mg of adsorbent surface with $1 \times 10^{-4} \text{ mol dm}^{-3}$ and $2 \times 10^{-4} \text{ mol dm}^{-3}$ dye solution for 5, 10, 15, 30, 45 and 60 minutes. The effect of acridine orange concentration was investigated by agitating (37-185) mg concentration of acridine orange with fixed amount of adsorbent. The effect of adsorbent concentration was shaking by a series of known concentration of acridine orange with adsorbent weight ranging from (300-900) mg. The effect of pH on acridine orange adsorption on charcoal was studied by agitating 900mg of charcoal at different pH values. The percent removal of dye from solution was calculated by the following equation:

$$\text{Percentage removal} = \left[\frac{C_0 - C_i}{C_0} \right] \times 100$$

3. RESULTS AND DISCUSSION

In the present work, adsorption of acridine orange with charcoal was examined. The main purpose of this research was to study the adsorption isotherms, adsorption kinetics, and the effect of agitating time, effect of acridine orange concentration, effect of adsorbent concentration and effect of pH.

3.1 Effect of agitating time

The effect of agitating time on dye and adsorbent are shown in Figure 1. Adsorption of acridine orange dye increased with increasing contact time. In adsorption process rapid uptake at the initial stage showed that there were easily accessible sites for molecules of adsorbate. As the experiment proceeds, saturation occurred, resulting in the percentage uptake to be remained almost constant. The data which is noted from the adsorption of acridine orange onto charcoal showed that a contact time of 30 min. was sufficient to achieve equilibrium. The rate of adsorption of dye remained almost constant after this time. This may be due to the deficient in the number of available adsorption sites at the end of the adsorption process.

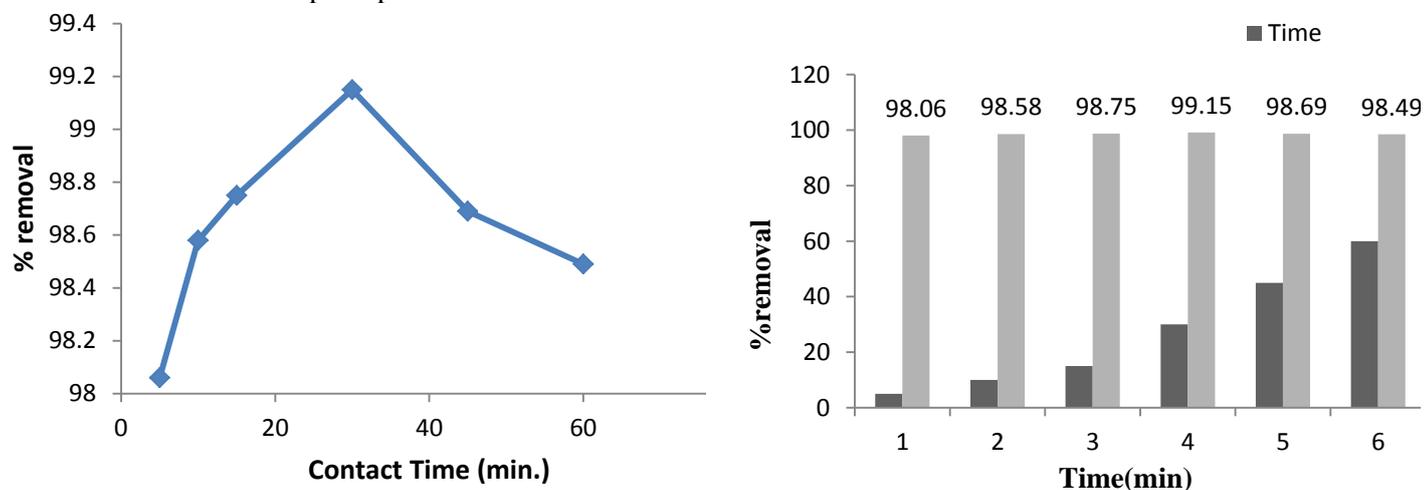


Fig-1: Time dependence of the adsorption of the dye on charcoal

3.2 Effect of acridine orange concentration

The effect of adsorption of acridine orange concentration onto charcoal shows that adsorption of acridine orange increases with increase in adsorbent concentration. An increase in acridine orange dye concentration caused an increase in its adsorption is shown in Figure 2. The amount of equilibrium adsorption of the dye increased as long as the dye saturated all available active sites of adsorbent. The percentage adsorption of acridine orange onto charcoal was increased from 98% to 99.95%. Similar results are reported in literature^{15, 16}.

The amount of methylene blue absorbed increase with the increase in the concentration of methylene blue. This means, when the initial concentration increases from 25 to 125 mg/L. It was because the initial concentration plays an important role which provided the necessary driving force to overcome the resistance to the mass transfer of methylene blue between the aqueous and the solid phases¹⁵. The interaction between adsorbate and adsorbent was also found to enhance with the increase in the initial concentration. Thus it can be concluded that higher initial concentration enhances the adsorption uptake of methylene blue¹⁶.

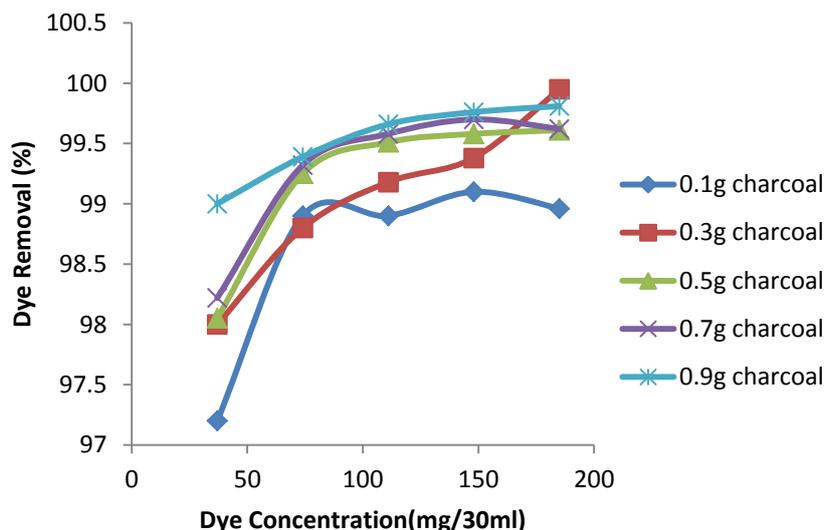


Fig-2: Influence of initial AO concentration on adsorption of AO on charcoal

3.3 Effect of adsorbent concentration

The adsorption of acridine orange varied with varying adsorbent concentration. The amount of adsorbed dye increases with increase in adsorbent concentration (Figure-3). This increase is due to the greater availability of the adsorption binding sites.

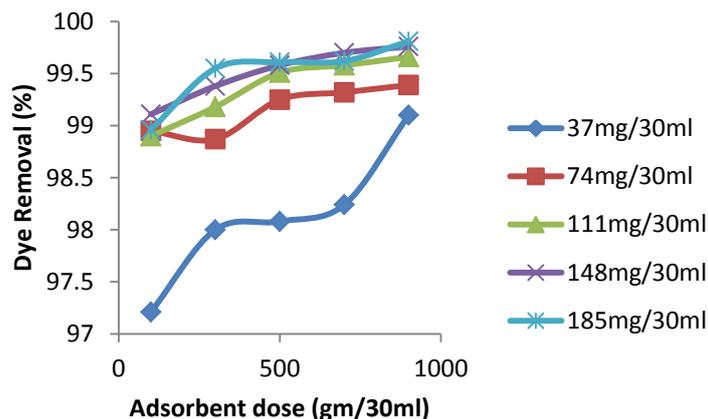


Fig-3: Influence of adsorbent concentration on adsorption of AO on charcoal

3.4 Effect of pH

The effect of pH on adsorption of acridine orange was also investigated, it was found that the optimum pH for adsorption of dye is 8 (Figure 4). It was also observed that dye has low adsorption capacity in the acidic medium, because the adsorbent surface and dye both are positively charged at low pH. Thus, higher pH favors strong adsorption due to strong interaction of negatively charged adsorbent surface and cationic dye¹⁷.

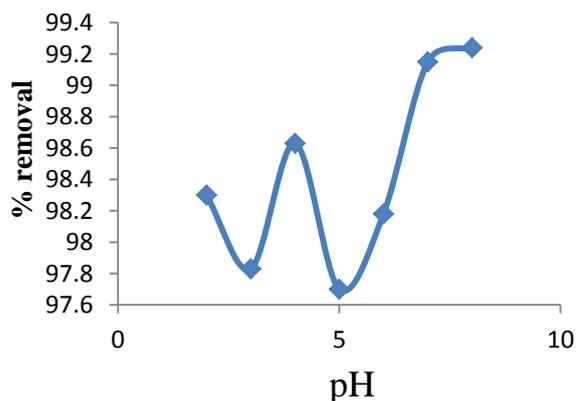


Fig-4: Influence of pH on adsorption of AO on charcoal

3.5 Effect of Adsorption Isotherms (Langmuir and Freundlich)

Among various adsorption isotherms we study the two adsorption isotherms which are Langmuir isotherm and Freundlich isotherm. These adsorption isotherms indicate how the adsorption molecules distribute between the solid phase and liquid phase when the adsorption processes reaches the equilibrium state. Adsorption isotherms are the basic requirements for the design of the adsorption systems¹⁸.

3.5.1 Freundlich isotherm

According to Freundlich adsorption isotherm^{19,20} is

$$\log x/m = \log K + 1/n \log C$$

This isotherm is an empirical equation and can be employed to describe heterogeneous systems. Where K and n are Freundlich constants, K related to bonding energy or measure the intensity of adsorption and n related to extent of adsorption or measure of deviation from linearity of adsorption. The values of K and n are calculated from the intercepts and slope of the plots $\log x/m$ vs. $\log C$ (Figure 5) and the results are presented in Table 1. The decreasing in the values of K with the rise in concentration of dye indicates that adsorption affinity of dye on charcoal is less favorable at higher concentration. While the values of n were also calculated they represent the binding capacity of adsorbate on the surface of adsorbent. The n values in Freundlich isotherm was found to be $n < 1$ for adsorbent, this shows the chemical adsorption.

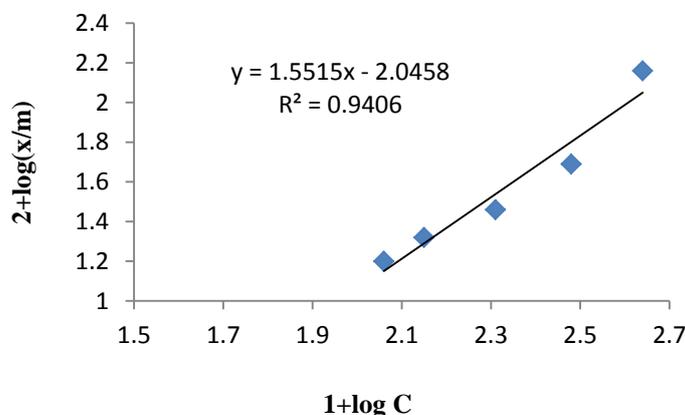


Fig-5: The Freundlich plot for the adsorption of AO on charcoal.

3.5.2 Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled; no further adsorption can take place at that site²¹.

According to Langmuir isotherm^{21,22}

$$1/(x/m) = 1/(x_m K) \times 1/C + 1/x_m$$

Where x/m is the adsorption density (mg/g) at equilibrium of dye, C is the equilibrium concentration in mg/L of the dye solution, x_m is the monolayer adsorption capacity in mg/g and K is the Langmuir constant related to the free energy of adsorption in L/mg. the values of x_m , K and regression coefficient R^2 were calculated from the slope ($1/x_m$) and the intercept ($1/x_m K$) of the linear plots of $1/(x/m)$ vs. $1/C$ (Figure 6) and presented in Table-1.

Table-1: Langmuir and Freundlich Parameters and Regression Coefficient

Initial Conc. (mol/30ml)	Langmuir parameters		Regression Coefficient	Freundlich parameters		Regression Coefficient
	x_m	K		K	n	
1×10^{-4}	0.625	0.005	0.7142	0.486	0.581	0.6771
2×10^{-4}	0.109	0.028	0.9094	0.702	0.365	0.697
3×10^{-4}	0.491	0.016	0.9795	0.437	0.553	0.918
4×10^{-4}	1.155	0.010	0.9873	0.310	0.644	0.9406
5×10^{-4}	7.137	0.002	0.8101	0.183	0.754	0.8833

Result tabulated in the Table 1 reveal that as the concentration of acridine orange increases the value of x_m is increased which shows that monolayer adsorption capacity increases or indicating high affinity of cationic dye at high concentration of dye. So when dye molecule strike a part of this uncovered surface of the adsorbent at that moment the

separation of dye from aqueous solutions and adsorption on adsorbent starts and ends when a thick layer is formed. The decrease in the values of K with the rise in concentration of dye indicating the weakening of adsorbate-adsorbent interaction at high concentration. From Table 1, the regression coefficient values ($R^2 = 0.9873$ for Langmuir model) indicate that the adsorption of acridine orange dye onto charcoal follows the Langmuir model better than the Freundlich model.

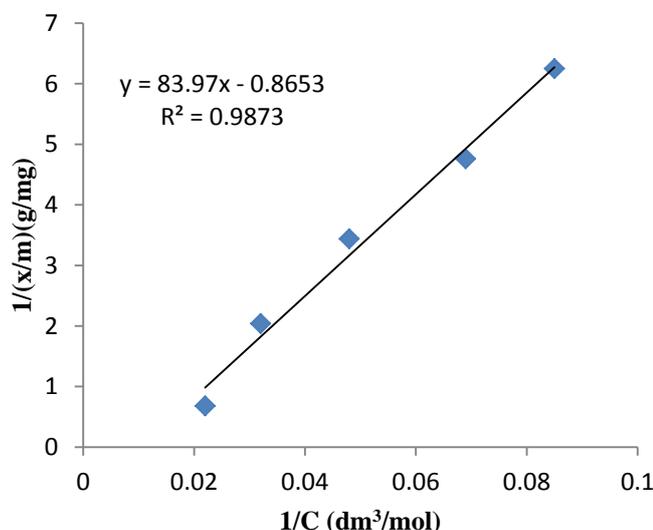


Fig-6: The Langmuir plot for the adsorption of AO on charcoal.

3.6 Effect of Adsorption Kinetics

The kinetics of the removal of AO^+ with the charcoal was investigated to understand the behavior of the adsorbent. The kinetics of adsorption describes the rate of AO adsorption and this rate controls the equilibrium time. It is important to be able to predict the rate at which contamination is removed from aqueous solution in order to design an adsorption treatment plant. The kinetics of the adsorption data analyzed using pseudo-first-order and pseudo-second-order models. We find that it best fits the pseudo second order reaction because straight line is come in pseudo second order. Pseudo-second order kinetics shows that chemical adsorption is a rate limiting stage that controls adsorption process.

The Lagergren first-order model was used to treat the kinetic data.

$$\ln (q_e - q_t) = \ln q_e - k_1 t$$

In the present study, the plot of $\ln (q_e - q_t)$ versus time t was not linear as shown in Figure 7, indicating that more than one mechanism involved in adsorption²³. The slopes and intercepts of the plot of $\ln (q_e - q_t)$ against time t can be used to obtained $k_1 \text{min}^{-1}$ and q_e , the values obtained being presented in Table 2. These results showed the pseudo-first-order kinetic model was not suitable to describe the kinetic profile for adsorption systems²⁴.

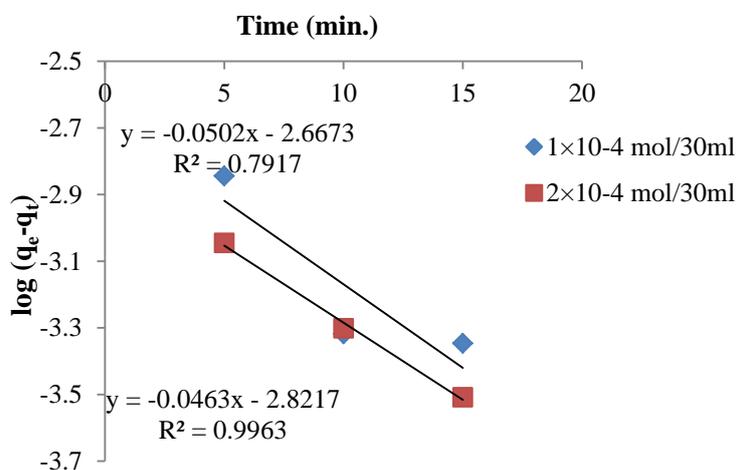


Fig-7: Pseudo-first-order kinetics plots for the adsorption of AO on charcoal.

The equation of pseudo second order is

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

The values of k_2 and q_e were calculated from the intercepts and the slopes of the plots of t/q_t vs. t (Figure 8, Table 2). The results show that regression coefficient (R^2) is unity which confirms that adsorption of AO on to charcoal follows pseudo second order kinetic model.

Table-2: Values of adsorption rate constants for pseudo-second order, pseudo-first order models

Initial Conc. (mol/30ml)	Pseudo-first order		Regression Coefficient	Pseudo-second order		Regression Coefficient
	k_1 (min^{-1})	q_e (mg/g)		k_2 (g/mg.min)	q_e (mg/g)	
1×10^{-4}	0.050	0.069	0.791	5.810	0.040	1
2×10^{-4}	0.046	0.059	0.996	17.78	0.081	1

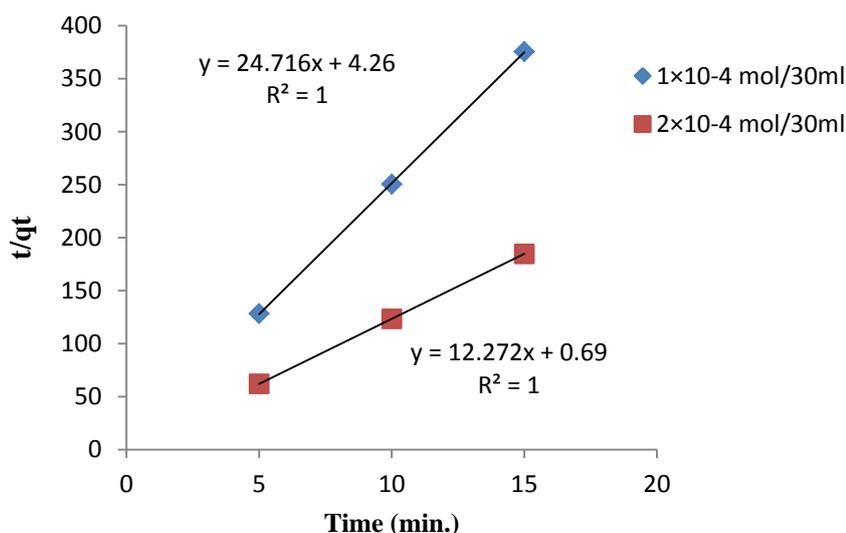


Fig-8: pseudo-second-order kinetics plots for the adsorption of AO on charcoal.

4. CONCLUSION

The present work investigated elimination one of the toxic dyes which has a mutagenic potential, like Acridine Orange, It was found that the proposed method is simple, cheap and useful. The current study also emphasizes on the ability of charcoal to adsorb AO from aqueous solution and optimal conditions of each variable were determined. Activated carbon is often used for adsorption and separation of a variety of compounds. In this study the adsorption was dependent on charcoal concentration and agitation time. As can be seen from the results, charcoal is a promising adsorbent for the removal of dye. The adsorption process followed pseudo-second-order kinetics and obeyed Freundlich and Langumir Isotherms. The results showed that, from a biochemical point of view, adsorption is a suitable method for the elimination of environmental contaminants, particularly dyes, and it can be economically justified compared with conventional methods. These phenomena will be studied in the near future.

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