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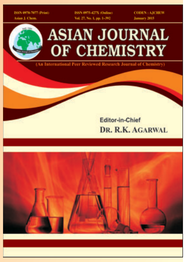

Adsorption Characteristics of Methyl Orange onto Different Adsorbents

Ahmed H. Abdel Salam[1,2,3,*], Islam H. Abd El Maksod[1,4], Medhat A. Shaker[1,3,5] and Hassan M. Faidallah[1]

[1]Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia
[2]Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt
[3]Chemistry Department, Faculty of Science, University of Jeddah, Jeddah, Saudi Arabia
[4]Physical Chemistry Department, National Research Centre, Dokki, Cairo, Egypt
[5]Chemistry Department, Faculty of Science, Damanhour University, Damanhour, Egypt

*Corresponding author: E-mail: ahmedhassan179@yahoo.com

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In this work, batch experiments were conducted to test the adsorptive properties of a synergistic composite made of activated carbon coupled with titanium dioxide, alumina, silica or Saudi white sand silica. The created integrated adsorbent was proved to adsorb methyl orange dye better than the two separate ingredients of integrated adsorbent. Methyl orange was chosen as a model organic pollutant in the environment that has the potential to cause health risks for humans and biota. Adsorption studies indicated that synergism or inhibition occur in the composite adsorption capacity depending on the integrated adsorbent composition compared to the single adsorbents.

Keywords: Adsorption, Methyl orange, Active carbon, Silica, Alumina, Titanium oxide.

INTRODUCTION

Synthetic dyes are commonly used in a number of industries, including textile, food, pharmaceutical, leather, cosmetic and paper industry and they should be carefully removed from the environment. The complex molecular structure of dyes makes them very stable and difficult for biodegradation. Pollution of the biosphere with toxic non-biodegradable dyes has increased dramatically due to the disposal of large quantities of aqueous effluents containing synthetic dyes[1-4]. Their presence disturbs the metabolic processes of the aquatic living organisms, causes water colouring giving it anaesthetic or repelling look and weakens light permeability inhibiting the photosynthesis processes. Also, they can be incorporated relatively easy in the food chain and accumulate causing adverse effect on human physiology. These detrimental effects make it necessary to apply ever increasing standards of pollutant detection and treatment. The conventional physical, chemical and biological methods used for removal of dyes from wastewater and sewage are not always successful and are often costly[5-7]. The search for new and more efficient methods ensuring more effective dye removal has become the focus of much international attention. Among different treatment technologies, adsorption often used to remove toxic dyes from industrial effluents with less energy, high efficiency and minimal impact on the environment[7-13]. The activated carbons characterized by highly-developed surface area and chemical inertness have been widely applied as adsorbents, but the dominance of micropores (< 2 nm) in their structure limits the transfer of bulky dye molecules from the surface of activated carbon into the pores. The efficiency of adsorption of organic dyes from liquid phase onto activated carbon surfaces depends on the type of interactions between the adsorbent and the adsorbate, including, electrostatic, hydrogen bonding, acid–base interaction and hydrophobic interactions, besides the pore texture of the adsorbent, that is pore size, surface area and pore volume[14,15]. In the present work, we have demonstrated the application of a stable integrated adsorbent composed of activated carbon coupled with other inorganic solids such as TiO_2, Al_2O_3, SiO_2 or white sand silica to create a synergistic composite with improved combined adsorptive properties that can be successfully applied for capturing of methyl orange from aqueous media with high sensitivity, simplicity and removing efficiency. The inorganic supports offer several advantages to activated carbon including better mechanical stability and more chelating groups on the surface.

EXPERIMENTAL

Activated carbon and TiO_2 (anatase form) were purchased from Sigma-Aldrich. Methyl orange and silica precipitated were purchased from Merck. All other necessary chemicals used in this study were of high purity and of analytical reagent

(AR) grade and were used without further purification. Water used was double distilled and was used throughout the work. All pH measurements of working solutions were measured using an Orion pH meter model 420A (Thermo Scientific, USA). The methyl orange concentration in the water was monitored using an ultraviolet spectrophotometer 750/650 UV/visible (Perkin Elmer) at an absorption wavelength of 467 nm.

Preparation of activated carbon and integrated adsorbents: Activated carbon was modified by heat treatment where it was washed with double distilled water and then heated to 450 °C for 4 h. This prepared activated carbon was mechanically mixed with the corresponding required ratio of additive silica, titania or Saudi white silica adsorbent.

Preparation of Saudi white silica: The Saudi white silica was prepared by dissolving white sand silica (50 g) in appropriate amount of 150 mL of 5 M NaOH solution and stirred for 0.5 h to get well dispersed suspension. Then, the white silica was precipitated by the addition of concentrated H_2SO_4 to the suspension. The obtained particles were filtered from the mixture, washed with double distilled water many times till pH = 7 and dried at 100 °C and activated at 500 °C for 4 h.

Batch adsorption experiments: The adsorption of methyl orange dye by the fabricated composite adsorbents at room temperature was studied using batch experiments. Definite milligram amounts of composite adsorbent were added to 100 mL of aqueous solutions of methyl orange (500 ppm). The mixture was agitated at 100 rpm at room temperature for 4 h. Methyl orange bound solids were separated by centrifugation at 15000 rpm. The residual methyl orange concentrations were determined by ultraviolet-visible electronic absorption spectrophotometer analysis. The amount of methyl orange adsorbed onto investigated composite adsorbents was calculated by eqn. 1.

$$q_e = \frac{[(C]_i - C_e)V}{m} \quad (1)$$

where q_e (mg g^{-1}) is the equilibrium adsorbate amount per 1 g adsorbent, C_i and C_e (mg L^{-1}) are the initial and final equilibrium adsorbate concentrations, respectively, V (L) is the volume of adsorbate solution and m (g) is the adsorbent mass.

RESULTS AND DISCUSSION

In the water treatment field, activated carbons (ACs) have wide applications in adsorptions. Here, activated carbon/Al_2O_3, TiO_2 or SiO_2 composites, which combine the adsorption features of powdered activated carbon (PAC) with the excellent adsorptive properties of the investigated additives, were fabricated by mechanical mixing method. The obtained composites were applied to evaluate their performance for the removal of methyl orange (Fig. 1) by adsorption from aqueous solution. Generally, the adsorption of an adsorbate onto a solid adsorbent surface is due to attractive forces between the adsorbent-adsorbate functional groups. The composites with high specific surface area, porosity and super-adsorptive property showed different synergistic mechanisms depending on the type and ratio of ingredients in the composites during methyl orange sorption processes. Methyl orange structure, Fig. 1 is small (less benzene rings) compared to other dyes and thus occupy less space and its functional groups can link together to form multi-layers on the adsorbent active sites. Methyl orange has two different functional moieties; one could be assigned as polar moiety (head) and the rest of the structure could be assigned as non-polar moiety (tail).

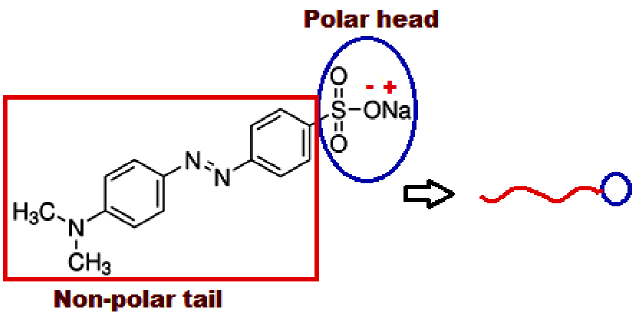

Fig. 1. Chemical structure of methyl orange dye (4-dimethylaminoazobenzene-4'-sulphonic acid sodium salt)

The active carbon adsorbent usually is very active towards the non-polar groups otherwise it functionalized to adsorb the polar one. Moreover the silica, alumina and titania could concern mainly with the polar group. In order to study the effect of mixed adsorbents with active carbon we mechanically mixed the active carbon with different ratios of adsorbents (SiO_2, white Saudi SiO_2, Al_2O_3 and TiO_2) depending on what is called linear theoretical percent of removal. These calculated values could be given from the capacity of each adsorbent alone towards methyl orange. Different ratios of total linear removal were examined (Table-1). Table-2 shows the capacity of each adsorbent compared to activated carbon.

TABLE-1
DIFFERENT RATIOS OF TOTAL LINEAR METHYL ORANGE REMOVAL

Amount of activated carbon (g)	Theoretical methyl orange removal (%)	Amount of TiO_2 (g)	Theoretical methyl orange removal (%)	Sum theoretical removal (%)
0.096	30	3.208	30	60
0.128	40	2.139	20	60
0.160	50	1.069	10	60
0.064	20	4.278	40	60
0.032	10	5.347	50	60
0.112	35	2.674	25	60

TABLE-2
RELATIVE METHYL ORANGE REMOVAL CAPACITY OF EACH ADSORBENT COMPARED TO ACTIVATED CARBON

Adsorbent	Capacity (mg/g)
Active carbon	155.700
Al_2O_3	2.860
TiO_2	0.935
SiO_2	1.380
Saudi white silica	19.800

The synergism effect of additive adsorbents with active carbon could be defined as the difference between the theoretical calculated linear values with the actual ones over the theoretical values (eqn. 2).

$$\text{Synergism (\%)} = \frac{\text{Actual removal value-Linear addition theoritical removal value}}{\text{Linear addition theoritical removal value}} \times 100 \quad (2)$$

When negative values of % synergism are obtained this means that the composite mixture could adsorb less than that of the linear adsorbent capacity of each adsorbent and thus an inhibition effect towards methyl orange adsorption occurs. The % synergism of all mixed adsorbent *versus* the active carbon % in each mixture is represented in Fig. 2. It is concluded from Fig. 2 that at large contribution of additive adsorbents (% activated carbon < 50), an inhibition effect occurs. This could be explained if we assume a competitive adsorption between active carbon and additive adsorbent from two different sites (polar and non-polar sites). This competition inhibits the allover adsorption process hence adsorption occurs from solution as represented in Fig. 3.

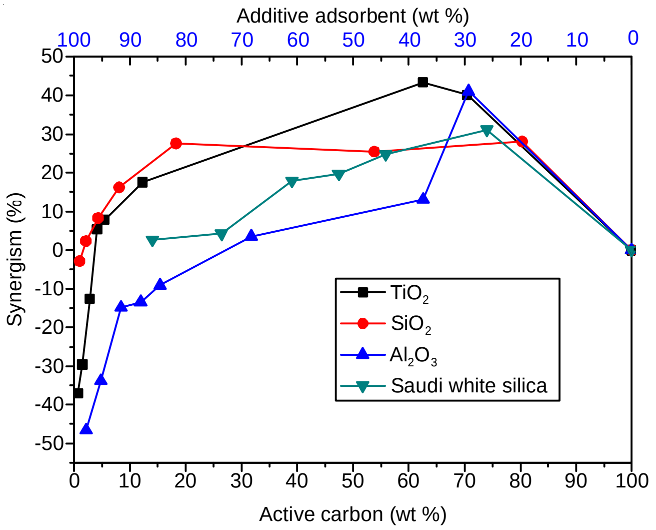

Fig. 2. % Synergism of all mixed adsorbent *versus* the active carbon % in each mixture

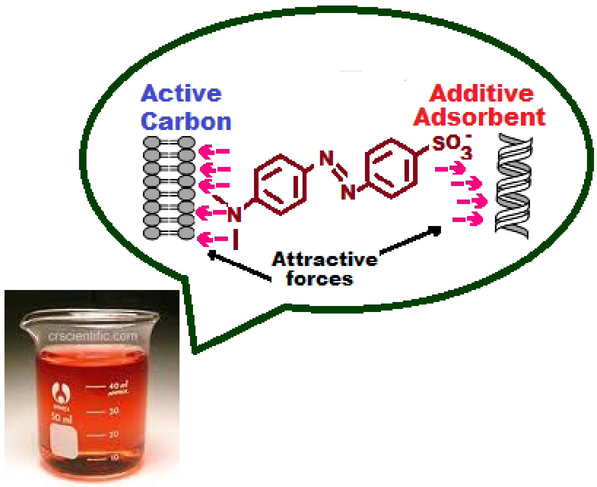

Fig. 3. A competitive adsorption between activated carbon and additive adsorbent for methyl orange from two different sites

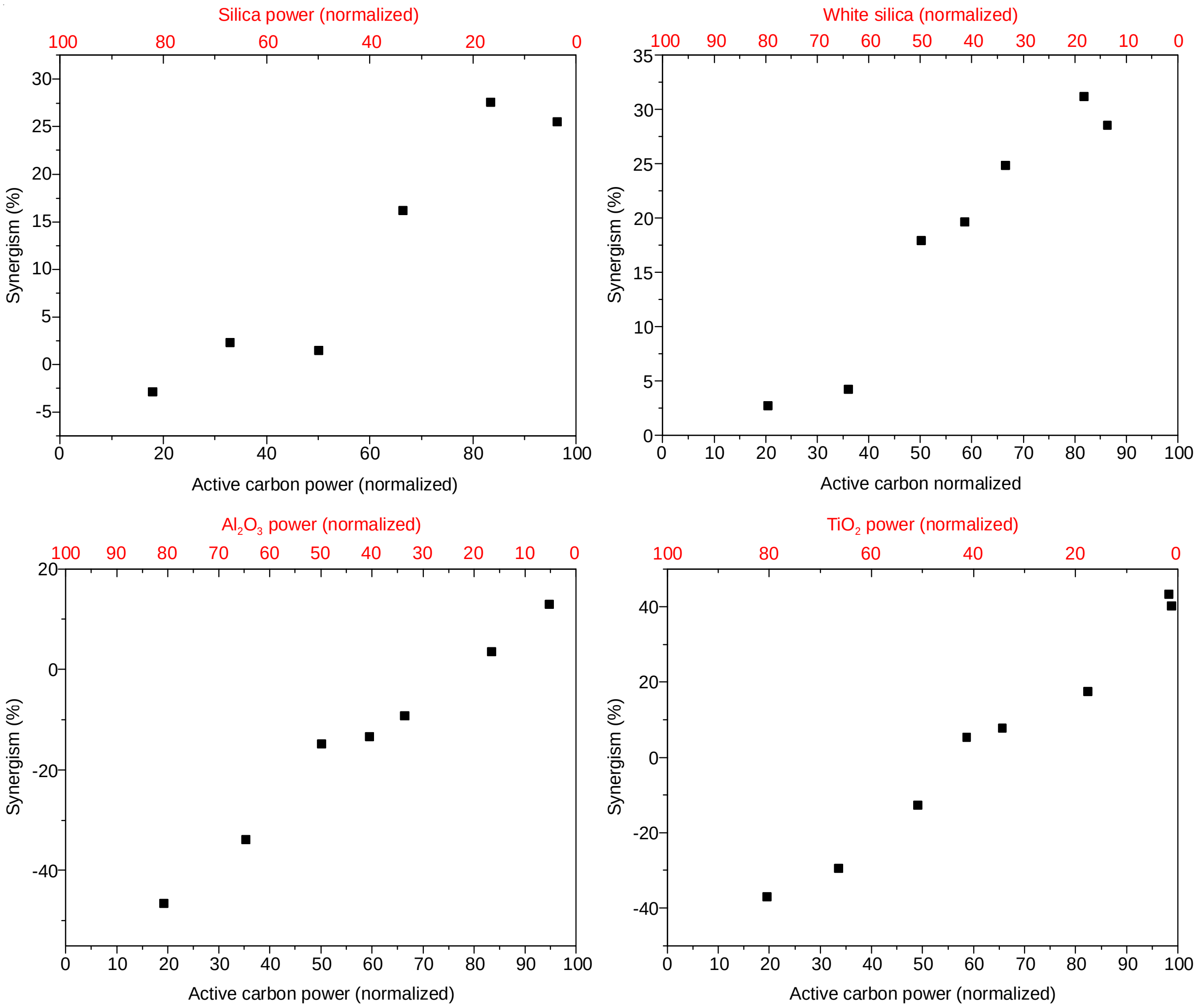

Fig. 4. Normalization to 100 % of the individual theoretical removal capacity as indication for the adsorption power

In other aspect, the individual theoretical removal capacity as indication for the power of adsorption can be normalized to 100 % (Fig. 4). From Fig. 4 ,we could observe that silica and Saudi white silica exhibit more or less different behaviour hence it showed nearly no inhibition (negative values) while titania and alumina showed a high inhibition at lower values of their adsorption powers.

This could be explained by assuming that silica and Saudi white silica adsorb with same mode as active carbon (from non-polar sites) while both titania and alumina adsorb with different modes from activated carbon (from polar sites). By this methodology, it is assumed that when the power of adsorption of both adsorbents is the same the synergism should be zero. However, this is not the case because of the different dielectric constant of the solvent which affects mainly these theoretical power values. As a general speaking we can assume that the competition of adsorption occurs in all cases between two adsorbents either from the same sites or different sites. After high values of adsorption power of activated carbon it is capable of adsorbing both adsorbent and adsorbates resulting in generation of new vacancies for more adsorption and this explains the obtained synergism (Fig. 5). Although titania showed high inhibition values it also showed the highest synergetic values at high power values of activated carbon.

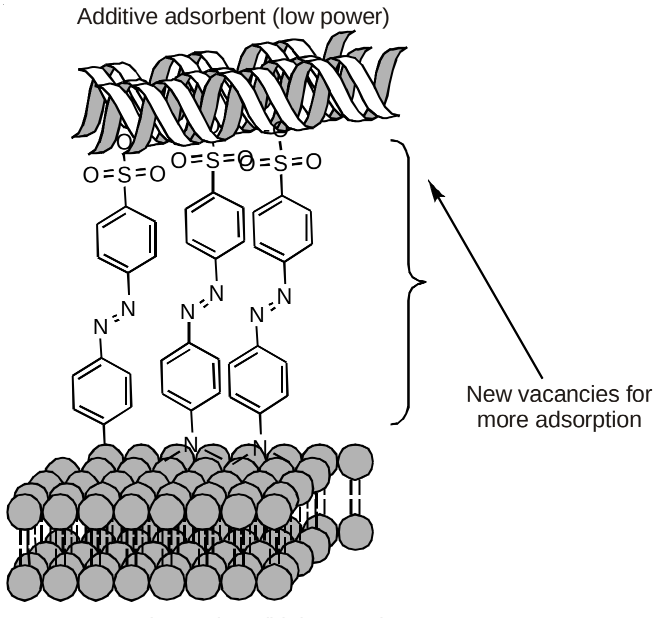

Fig. 5. Generation of new vacancies as a result of strong withdrawal of adsorbent and adsorbate by activated carbon

Conclusion

This work reports the investigation of the synergistic adsorptive properties of various composites made of activated carbon coupled with TiO_2, Al_2O_3, SiO_2 or Saudi white silica towards methyl orange as a model organic environmental pollutant. It was proved that the fabricated integrated adsorbents adsorb methyl orange better than the two separate ingredients. Adsorption studies indicated that synergism or inhibition occur in the composite adsorption capacity depending on the integrated adsorbent composition.

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