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Adsorption of Congo red on multiwall carbon nanotubes: Effect of operational parameters

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ABSTRACT

The removal efficiency of an aqueous solution of Congo Red (CR) dye of wastewater treatment to study the treatment activity of multiwall carbon nanotubes (MWCNTs). The removal of an aqueous solution of CR onto MWCNTs surface was investigated, such as adsorbent mass, initial concentration, ionic strength, pH and temperature.

KEY WORDS: Adsorption, MWCNTs, Congo Red (CR), ionic strength, pH.

1. INTRODUCTION

Dyes used in different types of industries such as, plastics, papers, dyeing and cosmetic. The main sources of color stuff from these industries pose hazards and has an environmental impact (Maneerung 2016). Different problems were caused in presences of dyes in water.

The classified of azo dyes are depending to the presence of azo bonds (–N=N–) in the molecule; these involve mono azo, diazo, triazo etc. (Sobana and Krishnakumar, 2013).

The effect of light and the oxidation agents have resisted by dyes, therefore they cannot be completely treated by normal processes of anaerobic digestion. Huge types of dye uses led to pollute the surface water and groundwater., there are different methods used for water treatment in our previous work (Saleh 1974; Alkhateeb 2005; 2008; 2010; Mashkour, 2011; Matloob 2011; Mohamed, 2011; 2015; Aljebori and Alshirifi 2012; Alkaim, 2012; 2013; 2014; 2015; Jasim 2013; Aljeboree, 2014; 2015; Hadi, 2014; Jabbar, 2014; Kamil 2014; 2016; Al-Gubury, 2015; 2016; Al-Khafaji 2015; Algubili, 2015; Ali, 2015; Karam, 2016; Abdulrazzak 2016; Aljeboree 2016; Fairooz 2016)

The adsorption technique promising to be a very important in term of initial cost, insensitivity to toxic substance, excellent efficiency, ease of operation, easy recovery and simplicity of design (Aljeboree, 2015; Alkaim, 2015).

Carbon nanotubes (CNTs) are consider a new adsorbents that can absorb organic pollutants from wastewater (Alkaim, 2015). The interaction of CNTs with gases or any species adsorbed on their internal or external surface open up the possibility of using them for gas storage. It has been shown that the curvature of graphene sheets can result in a lower heat of adsorption compared with a planar graphitic surface. In fact, the rolling of the graphene sheet around itself to produce a tube causes a re-hybridization of the carbon orbital, thus leading to a modification of the π density of the graphene sheet (Barpuzary, 2013). CNTs tend to aggregate together as bundles because of Van der Waals interactions.

The available adsorption sites of CNTs bundles involved the external surface, the interstitial and groove areas formed between the CNTs, and the inner pores of the tubes, as depicted in Figure 1. In this work, MWCNTs were used as an adsorbent to remove CR from aqueous solution. The effects of MWCNTs amount, dye concentration, pH of solution, temperature and ionic strength on adsorption capacity were studied.

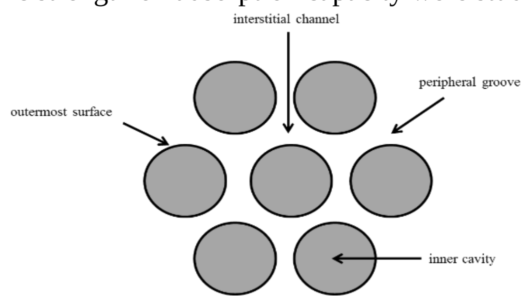

Figure.1. Schematic structure of CNTs bundles.

2. MATERIALS AND METHODS

Adsorbent: Multiwall carbon nanotubes (MWCNTs) with diameter of 20-30nm and length of 10-30µm was purchased from NANOSHEL. MWCNTs were used without further treatment.

Adsorbate: CR, having molecular formula $C_{32}H_{22}N_6Na_2O_6S_2$ was chosen as the adsorbate. CR is the sodium salt of 3, 3'-([1,1'-biphenyl]-4, 4'-diyl) bis (4-aminonaphthalene-1-sulfonic acid). The structure of CR is shown in Fig. 2.

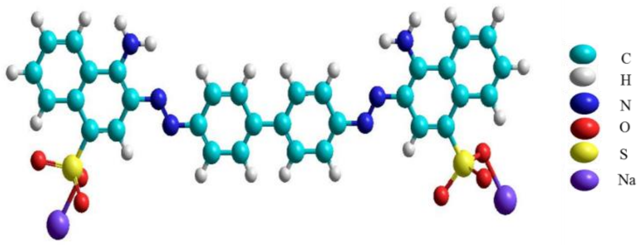

Figure.2.Chemical structure of CR dye

Adsorption Equilibrium Experiments: For equilibrium studies, solutions of 40ppm CR, at the initial concentration, were treated with 0.025g of MWCNTs. The mixtures were agitated on shakers (Gemmy orbit, van 480 Gemmy Industrial Corp-Taiwan) continuously for 60 min, as the equilibrium time, at different temperature and pH. After 60 min, the suspensions were centrifuged, then analyzed for residual CR concentration by UV visible spectrophotometer (PG instruments Ltd- Japan) at 499 nm in pH above 5 and at 566 nm at pH below 3. The amount of CR uptake by MWCNTs in each flask was calculated using the mass balance equation:

$$q_e = \frac{(C_0 - C_e) \times V}{W} \qquad 1$$

Where q_e is the amount of Bismarck Brown R adsorbed by CNTs at equilibrium, C_o and C_e are the initial and final dye concentrations (M), respectively, V is the volume of solution (L), and W is the adsorbent weight (g). The dye percent removal (%) was calculated using the following equation:

$$Removal\ \% = \frac{C_0 - C_t}{C_0} \times 100 \qquad 2$$

3. RESULTS AND DISCUSSION

Comparison between Multiwall Carbon Nanotubes and Activated Carbon: 0.025g from MWCNTs and AC with 40ppm CR was selected to study the comparison in adsorption capacity. Figure 3 shows the adsorption comparison of MWCNTs and AC. The result show that the removal percentage in the presence of MWCNTs is more than AC (Ozer, 2012).

Effect of MWCNT Dosage: The effect of adsorbent dose on the removal of CR dye (40 ppm) have been shown in Fig. 4. The increasing of adsorbent dosage from 0.010 to 0035g, the percentage of dye removal enhanced from 63.9 to 97.8% after 60min of adsorption time. This result attributed to as that increasing in the number of active sites caused by increasing the adsorbent amount (Moradi 2013; Kumar 2014).

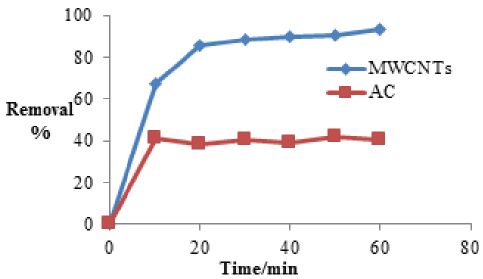

Figure.3.The comparison between MWCNTs and AC

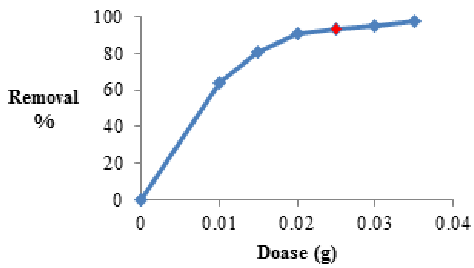

Figure.4.Effect of MWCNTs dose on the adsorption percentage of CR

Effect of Initial Concentration of CR Dye: Different concentrations of CR 40, 50, 60 and 80 ppm, were selected to study the effect of initial concentration of dye onto MWCNTs. The amounts of dye adsorbed at pH 6, adsorbent dosage 0.025g and 298.15K are given in Figure 5. With increasing initial concentration of CR from 40 to 80ppm, the removal of dye molecules decreases from 93.1 to 53.9% after 1 hr of equilibrium adsorption time.

Effect of pH: An important role in the adsorption process played by pH of solution, particularly on the adsorption efficiency. The surface charge of the adsorbent and the degree of the ionization of different pollutants can be affected by pH of solution. Zero Point Charge (pH_{zpc}), is a concept relating to the adsorption phenomenon and is defined as the condition when the electrical charge density on a surface is zero. The effect of pH on the CR dye adsorption capacities of the MWCNTs was studied at varying pH (2-10) with 40ppm fixed initial dye concentration and adsorbent dosage 0.025g for 60min. Figure 6 shows that the adsorption capacity of CR dye increases with increasing the pH of solution from 2 to 5 and decrease when solution pH reach to above 5. The maximum adsorption capacity of MWCNTs was 165.2 mg/g at pH 5. It is well known the CNTs surface contains hydroxyl and carboxylic groups after purification method by acid treatment. The change in solution pH will effect on the ionization status of these functional groups (Alkaim, 2014).

In an acidic medium, the MWCNTs surfaces remain positively charged (pH <5), while in the case of an alkaline medium, they are negatively charged (pH >5) as shown in Figure 7.

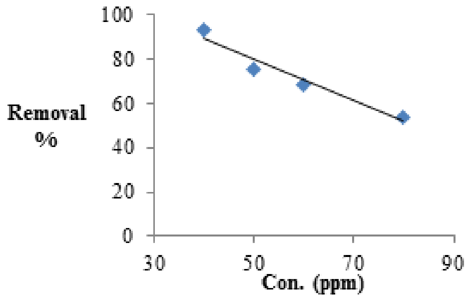

Figure.5.Effect of initial concentrations on the adsorption percentage of CR on MWCNTs

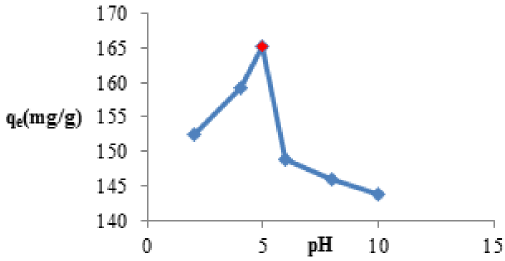

Figure.6.Effect of initial solution pH on the adsorbed amount of CR on MWCNTs

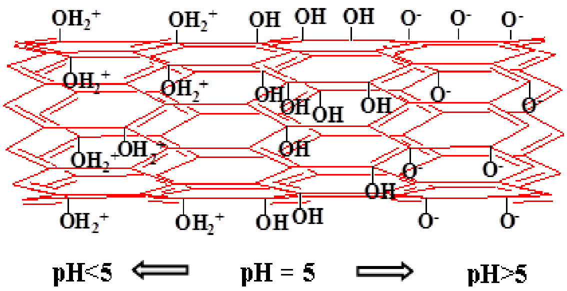

Figure.7.Effects of pH on surface charge

Effect of Ionic Strength: As shown in Figure 8 and 9, adsorption of CR on MWCNTs was increased upon addition of small quantities of Na_2SO_4 and NaCl, respectively. The effect of ionic strength on dye adsorption was studied at pH 6, where dyes and MWCNTs were negatively charged (pH_{zpc} is 5 of MWCNTs and pKa is 4 of CR). The addition of salt causes a partial neutralization of the negative charge on the MWCNTs surface and a consequent compression of the electrical double layer by the Na^+ cation. This enables the surface to absorb more of the negative dye ions, since the repulsive forces between the surface and the dye are decreased. Similar results were given by other worker for different organic materials. Figure 10 shows the proposed mechanism for the effect of salt on adsorption.

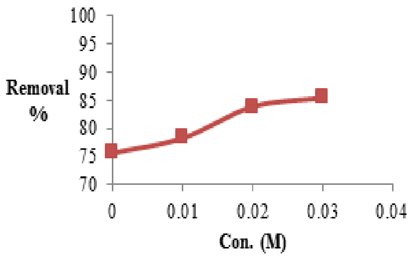

Figure.8.Effect of Na_2SO_4 on CR adsorption on MWCNTs

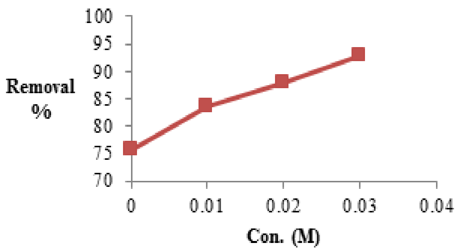

Figure.9.Effect of NaCl on CR adsorption on MWCNTs

Figure.10.The mechanism for effect of salt on adsorption

Effect of Temperature on Dye Adsorption and Thermodynamics: The adsorption of CR on MWCNTs was studied at temperatures of 278to 298K. Figure 11 shows the effect of temperature on the adsorption of dye on MWCNTs. The results indicate that the adsorption efficiency of CR onto the adsorbent surface of MWCNTs was

found to be temperature dependent, additionally the viscosity of dye solution decreased with rise in temperature and as a result, it increases the rate of diffusion of molecules dye.
The free energy of adsorption (ΔG°) was calculated from the following equation:

$$\Delta G^\circ = -RT \ln K_{ad} \qquad 3$$

The apparent enthalpy of adsorption (ΔH°) and entropy of adsorption (ΔS°) were calculated from adsorption data at different temperatures using the Van't Hoff equation:

$$\ln K_{ad} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad 4$$

Where R is universal gas constant (8.314J $mol^{-1}K^{-1}$), and T is the absolute temperature in Kelvin. Thermodynamic parameters were summarized in Table 1.

The negative values of ΔG° indicate that the adsorption process was a spontaneous. The positive values of ΔH° indicate that the adsorption of CR dye onto MWCNTs is endothermic. Figure 12 shows the Van't Hoff plot for the adsorption of CR dye on MWCNTs.

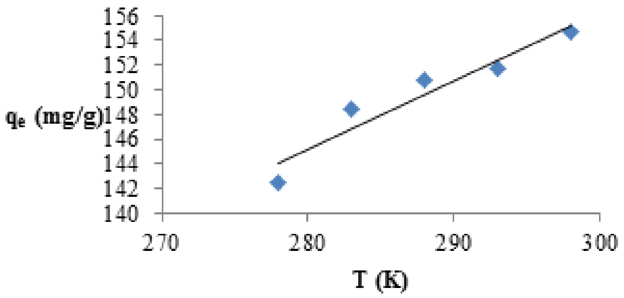

Figure.11.Effect of temperature on the adsorption amount of BBR on MWCNTs

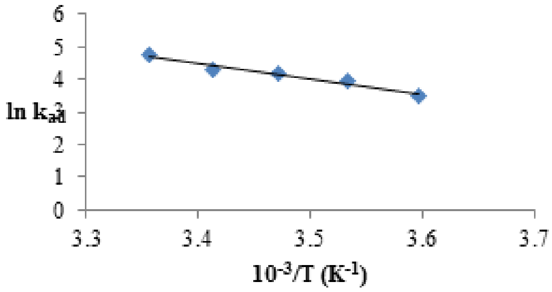

Figure.12.The Van't Hoff plot for the adsorption of CR on MWCNTs

Table.1.The thermodynamic parameters of the adsorption CR onto MWCNTs.

Con./ppm	ΔG°/ k J mol^{-1}					ΔH°/kJ mol^{-1}	ΔS°/J mol^{-1} K^{-1}
	5^0C	10^0C	15^0C	20^0C	25^0C		
40	-8.05	-9.27	-10.00	-10.48	-11.82	40.43	174.87

4. CONCLUSION

MWCNTs can be used effectively for the removal of CR from aqueous solution. 0.025g and 5 are the optimum dosage of MWCNTs and pH respectively. The adsorption capacity of the CR dye on MWCNTs increased with the increasing of initial concentration of CR. The removal percent was increased with the increase the salinity due to the change of electrostatic forces. Also results show the adsorption process was spontaneous and endothermic.

REFERENCES

Abdulrazzak FH, Enhance photocatalytic Activity of TiO_2 by Carbon Nanotubes, International Journal of Chem Tech Research, 9(3), 2016, 431-443.

Algubili AM, Alrobayi EM, and Alkaim AF, Photocatalytic degradation of remozal briliant blue dye by ZnO/UV process, Int. J. Chem. Sci., 13(2), 2015, 911-921.

Al-Gubury HY, Almaamory ES, Alsaady HH, and Almurshidy GS, Photocatalytic Degradation of Aquatic Rhodamine B Solution Using Ultraviolet Light and Zinc Oxide, Research Journal of Pharmaceutical, Biological and Chemical Sciences, 6(3), 2015, 929-939.

Al-Gubury HY, and Al-Murshidy GS, Photocatalytic Decolorization of Brilliant Cresyl Blue using Zinc Oxide, International Journal of Pharm Tech Research, 8(2), 2015, 289-297.

Al-Gubury HY, Fairooz NY, Aljeboree AM, Alqaraguly MB, and Alkaim AF, Photocatalytic degradation n-undecane using couple ZnO-Co_2O_3, Int. J. Chem. Sci., 13(2), 2015, 863-874.

Al-gubury HY, The effect of coupled titanium dioxide and cobalt oxide on photo catalytic degradation of malachite green, International Journal of Chem Tech Research, 9(2), 2016, 227-235.

Ali MM, and Fairooz NY, Preparing and characterizing study of the photocatalytic activity of new couple semiconductor Nb_2O_5/Sb_2O_3, Research Journal of Pharmaceutical, Biological and Chemical Sciences 6(4), 2015, 1176-1182.

Aljeboree AM, Adsorption of crystal violet dye by Fugas Sawdust from aqueous solution, International Journal of Chem Tech Research, 9(3), 2016, 412-423.

Aljeboree AM, Adsorption of methylene blue dye by using modified Fe/Attapulgite clay, Research Journal of Pharmaceutical, Biological and Chemical Sciences, 6(4), 2015, 778-788.

Aljeboree AM, Alkaim A.F, Adsorption isotherm, kinetic modeling and thermodynamics of crystal violet dye on coconut husk-based activated carbon, Desalination and Water Treatment 53(13), 2015, 3656-3667.

Aljeboree AM, Alshirifi A.N, and Alkaim A.F, Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon, Arabian J. Chem., 2014.

Aljeboree AM, Radi N, Ahmed Z, and Alkaim A.F, The use of sawdust as by product adsorbent of organic pollutant from wastewater: adsorption of maxilon blue dye, Int. J. Chem. Sci., 12(4), 2014, 1239-1252.

Aljebori AM, and Alshirifi AN, Effect of Different Parameters on the Adsorption of Textile Dye Maxilon Blue GRL from Aqueous Solution by Using White Marble, Asian journal of chemistry, 24(12), 2012, 5813-5816.

Alkaim AF, Aljeboree AM, Alrazaq NA, Baqir SJ, Hussein FH, and Lilo AJ, Effect of pH on Adsorption and Photocatalytic Degradation Efficiency of Different Catalysts on Removal of Methylene Blue, Asian Journal of Chemistry, 26(24), 2014, 8445-8448.

Alkaim AF, and Alqaragully MB, Adsorption of basic yellow dye from aqueous solutions by Activated carbon derived from waste apricot stones (ASAC): Equilibrium, and thermodynamic aspects, Int. J. Chem. Sci., 11(2), 2013, 797-814.

Alkaim AF, and Hussein FH, Photocatalytic degradation of EDTA by using TiO_2 suspension, Int J Chem Sci., 10(1), 2012, 586-598.

Alkaim AF, Dillert R, & Bahnemann D.W, Effect of polar and movable (OH or NH_2 groups) on the photocatalytic H_2 production of alkyl-alkanolamine: a comparative study, Environ. Technol., 36(17), 2015, 2190–2197.

Alkaim AF, Sadik Z, Mahdi DK, Alshrefi S.M, Al-Sammarraie A.M, Alamgir F.M, Singh P.M, and Aljeboree A.M, Preparation, structure and adsorption properties of synthesized multiwall carbon nano tubes for highly effective removal of maxilon blue dye, Korean J. Chem. Eng., 32(12), 2015, 2456-2462.

Al-Khafaji NSK, Shareef HK, and Al-Dahmoshi H.O.M, Analysis of β-lactamases among multi drug resistant Klebsiella pneumoniae in Hilla city-Iraq, Research Journal of Pharmaceutical, Biological and Chemical Sciences, 6(4), 2015, 903-907.

Alkhateeb AN, Hussein FH, and Asker KA, Photocatalytic decolonization of industrial wastewater under natural weathering conditions, Asian journal of chemistry, 17(2), 2005, 1155-1159.

Barpuzary D, and Qureshi M, Enhanced Photovoltaic Performance of Semiconductor-Sensitized ZnO-CdS Coupled with Graphene Oxide as a Novel Photoactive Material, ACS Applied Materials & Interfaces, 5(22), 2013, 11673-11682.

Fairooz NY, Evaluation of new couple Nb2O5/Sb2O3 oxide for photocatalytic degradation of Orange G dye, International Journal of Chem Tech Research, 9(3), 2016, 456-461.

Hadi ZA, Aljeboree AM, and Alkaim AF, Adsorption of a cationic dye from aqueous solutions by using waste glass materials: isotherm and thermodynamic studies, Int. J. Chem. Sci., 12(4), 2014, 1273-1288.

Hussein FH, Alkhateeb AN, and Ismail JK, Solar photolysis and photocatalytic decolorization of thymol blue, E-Journal of Chemistry, 5(2), 2008, 243-250.

Hussein FH, and Alkhateeb AN, Photo-oxidation of benzyl alcohol under natural weathering conditions, Desalination, 209 (1-3 Special Issue), 2007, 350-355.

Hussein FH, Halbus AF, Hassan HAK, and Hussein WAK, Photocatalytic degradation of bismarck brown G using irradiated ZnO in aqueous solutions, E-Journal of Chemistry, 7(2), 2010, 540-544.

Jabbar AZ, Hadi AG, and Sami F, Removal of azo dye from aqueous solutions using chitosan, Oriental Journal of Chemistry, 30(2), 2014, 571-575.

Jasim FA, Lafta F, Hashim A, Ali M, and Hadi AG, Characterization of palm fronds-polystyrene composites, Journal of Engineering and Applied Sciences, 8(5), 2013, 140-142.

Kamil AM, Hussein FH, Halbus AF, and Bahnemann DW, Preparation, characterization, and photocatalytic applications of MWCNTs/TiO_2 composite, International Journal of Photoenergy, 2014.

Kamil AM, Karam MA, Balakit AA, and Hussein F.H, Synthesis and characterization of iron oxide nanoparticles and applications in the removal of reactive black 5H from wastewater, Research Journal of Pharmaceutical, Biological and Chemical Sciences, 7(1), 2016, 1740-1751.

Kumar R, Ansari M.O, and Barakat M.A, Adsorption of Brilliant Green by Surfactant Doped Polyaniline/MWCNTs Composite: Evaluation of the Kinetic, Thermodynamic, and Isotherm, Ind. Eng. Chem. Res., 53(17), 2014, 7167-7175.

Maneerung T, Liew J, Dai Y, Kawi S, Chong C, & Wang C, Activated carbon derived from carbon residue from biomass gasification and its application for dye adsorption: Kinetics, isotherms and thermodynamic studies, Bioresource Technology, 200, 2016, 350-359.

Mashkour MS, Al-Kaim AF, Ahmed LM, and Hussein FH, Zinc oxide assisted photocatalytic decolorization of reactive red 2 dye, Int. J. Chem. Sci., 9(3), 2011, 969-979.

Matloob MH, Fluoride concentration of drinking water in Babil-Iraq, Journal of Applied Sciences, 11, 2011, 3315-3321.

Mohamed FF, Allah PM, Mehdi AP, and Baseem M, Photoremoval of Malachite Green (MG) using advanced oxidation process, Res.J.Chem.Environ., 15(3), 2011, 65-70.

Mohammed B Alqaragully, Hazim Y AL-Gubury, Aseel M Aljeboree, Fiaq F Karam, and Ayad F Alkaim, Monoethanolamine: Production Plant, Research Journal of Pharmaceutical, Biological and Chemical Sciences, 6(5), 2015, 1287-1296.

Moradi O, Maleki MS, Removal of COD from Dairy Wastewater by MWCNTs: Adsorption Isotherm Modeling, Fuller. Nanotub Car. N, 21(10), 2013, 836-848.

Ozer C, Imamoglu M, Removal of methylene blue from aqueous solutions using phosphoric acid activated carbon produced from hazelnut husks, Toxicological and Environmental Chemistry, 94(7), 2012, 1283-1293.

Saleh JM, and Matloob MH, Oxidation of titanium, tantalum, and niobium films by oxygen and nitrous oxide, Journal of Physical Chemistry, 78, 1974, 2486-2489.

Sobana N, Krishnakumar B, Synergism and effect of operational parameters on solar photocatalytic degradation of an azo dye (Direct Yellow 4) using activated carbon-loaded zinc oxide, Mat. Sci. Semicon. Proc., 16(3), 2013, 1046-1051.