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Removal of environmental pollutants azo dye Acid Red 18 in aqueous solution using adsorbent activated carbon of walnut shell

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Abstract

In this paper, removal of Acid Red 18 dye (AR18) from aqueous solutions using activated carbon of walnut shell (ACWS) adsorbent was studied. The prepared ACWS adsorbent was characterized by scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) surface area analysis. The kinetic and isotherm of dye adsorption was studied. The effects of operational parameter such as: adsorbent dosage, pH and contact time on the process were studied and optimized. The optimal amount of adsorbent dosage 0.3 g, pH= 5 and contact time 15 min respectively. The results showed that the dye adsorption onto adsorbent followed Freundlich isotherm. Adsorption kinetics of AR18 dye onto the adsorbent followed the pseudo- first-order kinetic model. The results showed that ACWS adsorbent might be a suitable alternative to remove dye from colored aqueous solutions.

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Introduction

More than 10,000 species of dyes and pigments are utilized every year, and over 50% of these dyes are azo dyes which contain one or more azo bonds ($-N=N-$) and aromatics (Sahel *et al.*, 2007). The chronic toxicity of azo dye to humans and the environment has been well documented. It is essential to remove azo dye from industrial wastewater before being discharged (Chen *et al.*, 2008, Chegrouche *et al.*, 2009).

Pollutant removal from wastewater using adsorption process is interested because different adsorbents are able to concentrate specific substances from solution onto their surfaces (Mahmoodi, 2013). Different types of dyes have been extensively used in industry for applications such as textiles, leathers, papers, food-tuffs, additives, gasoline, cosmetics, xerography, laser materials and so on (Navarro and Sanz, 1999, Tao *et al.*, 1999, Dakiky and Nemcova, 2000, Isak *et al.*, 2000, Karpicz *et al.*, 2000, Bhaskar *et al.*, 2003). Removal azo dyes pollutants using adsorption process is interested because different adsorbents are able to concentrate specific substances from solution onto their surfaces (Mahmoodi, 2013). Specified amounts of dye are lost in the process of manufacturing and utilization and often cause environmental pollution problems. The wastewaters generated by the textile industry contain considerable amounts of azo dyes. The discharge of these coloured wastewaters in the ecosystem has been problematic due to their toxicity and resistance to biodegradability. Among Different techniques for the removal of coloured compounds, the traditional ones, such as adsorption, ultra-filtration, coagulation–flocculation, ozonation, H_2O_2 oxidation, photo-oxidation, and combination of several techniques have been applied (Gong *et al.*, 2005, Madaeni and Mansourpanah, 2004, Guibal and Roussy, 2007).

The cell walls of walnut shell consist of cellulose, silica, lignin, carbohydrates which have hydroxyl groups in their structures. Activated carbon is relatively adsorbent that can adsorb trace pollutants

from wastewater (Chan *et al.*, 2008, Schreiber *et al.*, 2007). Recently, walnut shell has been characterized as efficient adsorbents with a capacity that surpasses that of activated carbon. The scientific contribution and aim of this paper are: 1) the process offers great potential as an industrial technology to detoxify wastewaters; 2) wastewater treatment sectors and textile industry will benefit from the results. In this paper, the prepared ACWS adsorbent were characterized by SEM and BET analysis. The kinetic and isotherm of dye adsorption were studied. The effects of operational parameter such as adsorbent dosage, pH and contact time on the process were studied and optimized.

Materials and methods

Materials

The azo dye AR18, $C_{20}H_{11}N_2Na_3O_{10}S_3$ was provided from Alvan Sabet Company (Iran) and was used without further purification. The chemical structure of AR18 is shown in Fig. 1. Walnut shell obtained from orchards Toyserkan City (Iran). Other chemicals used in the project were purchased from the Merck Company (Germany).

Synthesis of ACWS

First, 50 g of walnut shell was added to 1 L of distilled water and was boiled for 5 h. After filtration, the action was repeated once more. The moist walnut shell was put in a vacuum oven for 8 h in $105^\circ C$. The resulted dried walnut shell was put in furnace with inert nitrogen for 5 h under the temperature of $350^\circ C$. The obtained carbon was passed through the standard sieve of ASTM with 100 meshes. The resulted active carbon was washed and cleared for several times using distilled water and when the pH solution (pH =7) the active carbon drying in a vacuum oven for 3 h in $105^\circ C$.

Apparatus

For analyzing the morphology and ACWS adsorbent surface, scanning electron microscope (SEM) model Philips XL30 was used and BET method the base to nitrogen adsorption/desorption isotherms measured

at 77 K. UV/VIS Spectrophotometer, Jenway (6505) was employed for measuring absorbance using glass cells of path length 1 Cm.

Adsorption procedure

Batch adsorption experiments were carried out in Erlenmeyer flask (250 mL), where solution of dye (200 mL) with initial dye concentration of 20 mg L⁻¹ was placed. The effects of solution pH values, adsorbent dosage and contact time on dye removal were investigated. The solution pH values (5-11) were adjusted at the desired level using dilute NaOH 0.1N or H₂SO₄ 0.1N (the pH values were measured with Horiba M12 pH meter). The dye adsorption was done by mixing of adsorbent in flask for 24 minutes. The solution samples were taken at certain time intervals (0-24) minutes and adsorbent was separated by centrifuged at 3600 rpm for 10 minutes. The change on the absorbance of all solution samples was monitored and determined at certain time intervals during the adsorption process. At the end of the equilibrium period, the dye concentration was determined by using a spectrophotometer (UV-vis spectrophotometer, Jenway (6505) at λ_{max} = 512 nm. The kinetics and isotherm of dye adsorption were studied by contacting 200 mL of dye solution with initial dye concentration of 20 mg L⁻¹ at room temperature (20 °C) for 24 minutes at a constant stirring speed of 150 rpm at different adsorbent dosages. Different amounts of ACWS (0.3–0.6 g) was applied to removal dye. The amount of dye adsorbed at equilibrium q_e (mg g⁻¹) was calculated by following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad \text{(Equation.1)}$$

Where, C_0 (mg L⁻¹) is the initial dye concentration, C_e (mg L⁻¹) the dye concentration at equilibrium, V (L) the volume of the solution and m (g) is the mass of the adsorbent. The amount of dye adsorbed at time t q_t (mg g⁻¹) was calculated by following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad \text{(Equation.2)}$$

where C_0 (mg L⁻¹) is the initial dye concentration, C_t (mg L⁻¹) the dye concentration at any time t , V (L) the volume of the solution and m (g) is the mass of the adsorbent.

Results and discussion

The characterization of ACWS

Fig. 2 shows the SEM image of ACWS. Regarding the specified scale in the Fig. 2, the size of particles is micrometer. The particle size reduction in SEM image cause improved adsorption capacity. SEM image showed homogeneous structure with macropores cavities. Cavities are created in adsorbent cause adsorption material. Specific surface areas are commonly reported as BET surface areas obtained by applying the theory of BET to nitrogen adsorption/desorption isotherms measured at 77 K. The BET surface area of ACWS was 521 m²g⁻¹, respectively.

Adsorption kinetics

The controlling mechanism of the adsorption process, kinetic models are used to analysis the experimental data. The rate of adsorption process can be identified with the kinetic adsorption data. Many kinetic sorption models studied for test the experimental data in adsorption process. Using the correlation coefficients (R^2), confirms the experimental data with the model. If the higher value is closed to unity, it means that model used for the kinetics is justified. In this research, we choose two kinetic models, pseudo- first-order kinetic model and pseudo-second-order kinetic model, are tested to find the best fitted model for the experimental data. The pseudo-first-order kinetic model (Lagergren, 1898) is generally shown as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad \text{(Equation.3)}$$

Where, q_t and k_1 are the amount of dye adsorbed at time t (mg g⁻¹) and the rate constant of pseudo-first-order kinetics (min⁻¹), respectively. Integrating Eq. (3) with the boundary conditions ($t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$) show the linear equation as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (\text{Equation.4})$$

or

$$q_t = q_e [1 - \exp(-k_1 t)] \quad (\text{Equation.5})$$

A plot of $\ln (q_e - q_t)$ versus t presents a linear relationship from which k_1 and q_e are the slope and the intercept, respectively. The pseudo-second-order kinetic model (Ho, 1995) applied to adsorption kinetic, can be written as follow:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (\text{Equation.6})$$

Where, k_2 is the rate constant of pseudo-second-order kinetics ($\text{g mg}^{-1} \text{min}^{-1}$). Integrating Eq. (6) with the boundary conditions ($q=0$ to $q=q_t$ and $t=0$ to $t=t$) show the linear equation as follows:

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \left(\frac{1}{q_e}\right)t \quad (\text{Equation.7})$$

or

$$q_t = \frac{k_2 t q_e^2}{1 + (k_2 t q_e^2)} \quad (\text{Equation.8})$$

If the second-order kinetics is applicable, the plot of t/q_t versus t will be a linear relation. The values of k_2 and q_e will be determined from the intercept and the slope of the plot. Kinetic constants obtained by linear regression (Fig. 3 A, B) for the two models are listed in Table 1. The correlation coefficients (R^2) for the pseudo-second-order kinetic model are relatively low. For the pseudo-first-order kinetic model, the R^2 value is 0.978 the first-order model to describe the adsorption process of dye onto the adsorbent.

Adsorption isotherm

Adsorption isotherm demonstrates the relationship between equilibrium concentrations of adsorbate in the solid phase, and in the liquid phase at the constant temperatures. The adsorption isotherms are often obtained in the laboratory using batch tests in which the equilibrium data are attempted by various isotherm models. There are the initial experimental tests that determine feasibility of adsorption

treatment. There are many different isotherm models have been suggested for the adsorption of solutes in a liquid solution onto a solid surface. In this study, the Langmuir and Freundlich isotherms were used to describe the equilibrium adsorption. The Langmuir isotherm model assumes monolayer coverage of adsorbate over a homogenous adsorbent surface with a finite number of identical sites, and there is no interaction between the adsorbate molecules. The Langmuir model can be described as follows (Langmuir, 1916):

$$q_e = \frac{b q_m C_e}{1 + b C_e} \quad (\text{Equation.9})$$

A linear expression for the Langmuir isotherm can be expressed as following:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m} \quad (\text{Equation.10})$$

Where, C_e is the equilibrium concentration of dye solution (mg L^{-1}), q_e the equilibrium capacity of dye on the adsorbent (mg g^{-1}), q_m is the monolayer adsorption capacity of the adsorbent (mg g^{-1}), and b is the Langmuir adsorption constant (L mg^{-1}) and related to the free energy of adsorption.

The empirical Freundlich adsorption isotherm is obtained on the assumption that the sorption takes place on a heterogeneous adsorbent surface, where the sorption energy distribution decreases exponentially. This equation is also applicable to multi layer adsorption and is expressed by the following equation (Freundlich, 1906):

$$q_e = K_f C_e^{\frac{1}{n}} \quad (\text{Equation.11})$$

Where, K_f and n are the Freundlich constants which represent the adsorption capacity and adsorption intensity of the sorbent, respectively. Eq. (11) can be linearized by taking logarithms as:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (\text{Equation.12})$$

From which the Freundlich constants can be determined.

To study the applicability of the Langmuir and Freundlich isotherms for the dye adsorption onto ACWS, linear plots of C_e/q_e against C_e , $\log q_e$ versus $\log C_e$ are plotted (Fig. 4 A, B). The values are shown in Table 2. The R^2 values show that the dye removal isotherm does not follow the Langmuir isotherm (Table 2). The linear fit between the $\log q_e$ versus $\log C_e$ and the calculated R^2 values for Freundlich isotherm model show that the dye removal isotherm can be approximated as Freundlich model. This means that the adsorption of dyes takes place at specific heterogeneous sites and a multi layer adsorption onto adsorbent surface.

Effect of adsorbent dosage

Fig. 5 plots the effects of different ACWS dosages (g) on dye percent removal. The decrease in dye removal with adsorbent dosage can be attributed to an increase in the adsorbent surface, which increased the availability of adsorption sites. This Fig. indicates that in the presence of ACWS, 71.12% of dye was adsorbed with 0.3 g of ACWS adsorbent. However, the adsorption capacity (mg g^{-1}) decreased with the increasing amount of adsorbent. The decreased is due to adsorption sites remaining unsaturated during the adsorption process (Chao-Yin *et al.*, 2008). Another reason for this result may be the overlapping of adsorption sites due to overcrowding of adsorbent particles.

Effect of contact time

The effect of contact time on dye percent removal the ACWS adsorbent is shown in Fig. 6. The percent

removal increase during the initial adsorption stage and then continue to increase at a relatively then decrease with contact time until a state of equilibrium is attained in 15 min. This phenomenon is attributed to the fact that a large number of vacant surface sites are available for adsorption at the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases (Azizian, 2004).

Effect of pH

The pH of a dye solution is an important influencing factor for the adsorption of dye onto ACWS. Fig. 7 shows the percent removal of dye onto ACWS at different pH from 5 to 11, which clearly shows that the best results were obtained in acidic solution, (pH= 5). The charge of adsorbent, its surface is presumably positively charged in acidic solution and negatively charged in alkaline solution. For adsorbents with bases as agents, the adsorbent surface charge varies with pH changes. In low pH, the H_3O^+ ions accumulate near the surface ligands and cause the adsorbent surface charge to increase (Xuan *et al.*, 2006). As shown in Fig. 7, the more pH increases the more adsorbing covalence of the absorber decreases. Based on the theory of surface complexation, this decrease can be due to the increased competition between OH^- and adsorbing varieties for active sites as well as the increase in negative charge of the surface (Krishnani *et al.*, 2008).

Table 1. Adsorption kinetic parameters of dye adsorption onto the ACWS.

| Pseudo-first-order | | | Pseudo-second-order | | |
|-----------------------------|--------------------------------|-------|--|--------------------------------|--------|
| k_1 (min^{-1}) | q_e , (mg g^{-1}) | R^2 | k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) | q_e , (mg g^{-1}) | R^2 |
| 0.0994 | 9.98 | 0.978 | 4.59×10^{-7} | 3.30 | 0.6254 |

Table 2. Adsorption isotherm parameters of dye adsorption onto the ACWS.

| Langmuir | | | Freundlich | | |
|------------------------------|----------------------------|--------|------------------------------|------|-------|
| q_m (mg g^{-1}) | b (L mg^{-1}) | R^2 | K_f (mg g^{-1}) | n | R^2 |
| 2 | 6.63×10^{-6} | 0.9001 | 3.3×10^3 | 2.72 | 0.971 |

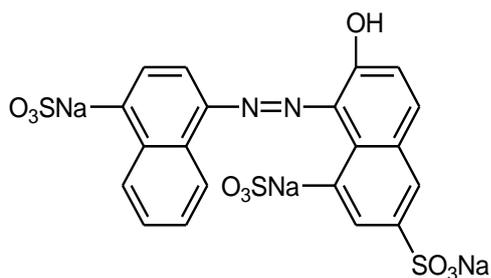


Fig. 1. The chemical structure of AR18.

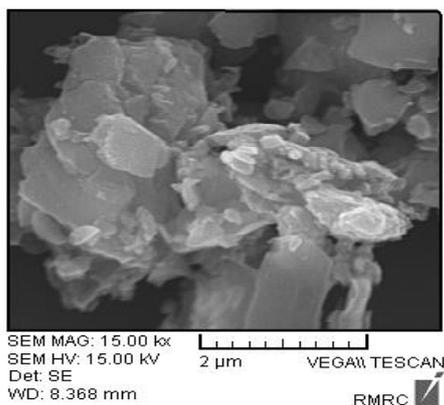


Fig. 2. SEM image of ACWS.

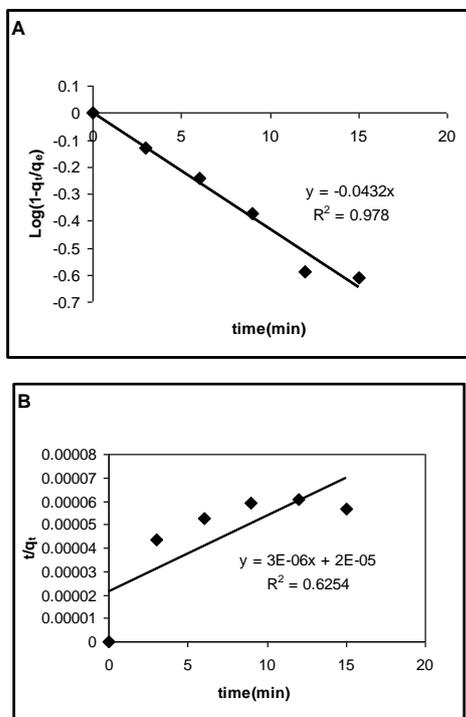


Fig. 3. (A) Pseudo-first-order kinetic and (B) pseudo-second-order kinetic of adsorption of dye onto ACWS (concentration of dye = 20 ppm , adsorbent dosage = 0.3 g , contact time=15 min, pH= 5, T=20 °C).

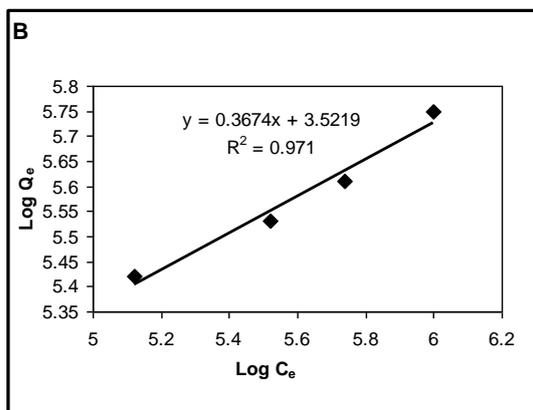
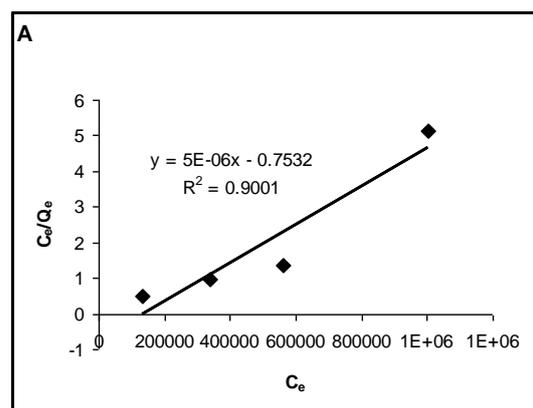


Fig. 4. (A) Langmuir model for adsorption of dye onto ACWS (B) Freundlich model for adsorption of dye onto ACWS (concentration of dye= 20 ppm, adsorbent dosage= 0.3 g, contact time=15 min, pH= 5, T=20 °C).

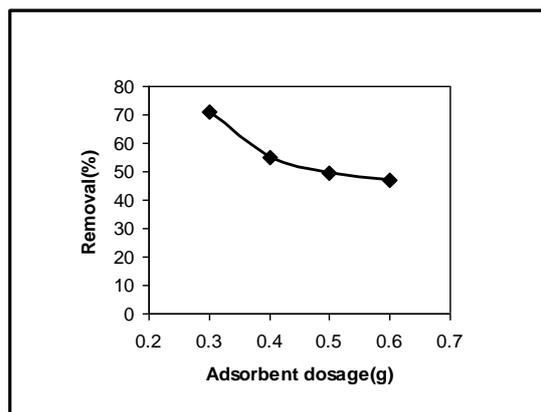


Fig. 5. Effect of adsorbent dosage on dye removal by ACWS (concentration of dye= 20 ppm, contact time=15 min, pH= 5, T=20 °C).

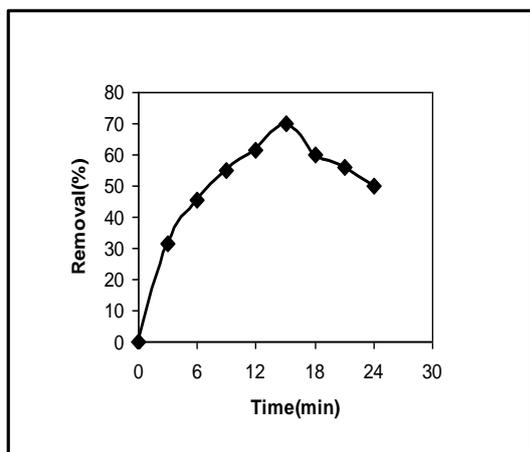


Fig. 6. Effect of contact time on dye removal by ACWS (concentration of dye= 20 ppm , adsorbent dosage= 0.3 g , pH= 5, T=20 °C).

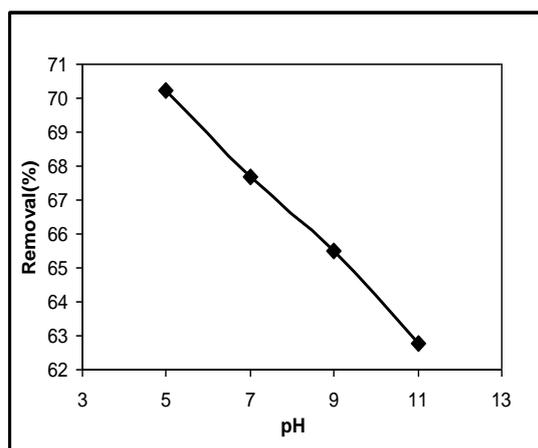


Fig. 7. Effect of pH on dye removal by ACWS (concentration of dye= 20 ppm , adsorbent dosage= 0.3 g , contact time=15 min, T=20 °C).

Conclusion

In this study, ACWS synthesized for removal AR18 dye in water solution. The prepared ACWS were characterized by SEM and BET analysis. The effects of operational parameter such as: adsorbent dosage, pH and contact time on the process were studied and optimized. The results showed that the dye adsorption onto ACWS followed Freundlich isotherm. Adsorption kinetics of dye followed the pseudo- first-order kinetic model. The results showed that ACWS adsorbent can be suitable to removal dyes from colored wastewaters.

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References

adsorption equilibrium of dissolved organic matter and atrazine on granular activated carbon. *Environmental Science and Technology* **41**, 6448-6453.

Azizian S, Jafari SH, Jaleh B. 2012. Enhancement of methyl violet removal by modification of TiO₂ nanoparticles with AgI. *Journal Industrial and Engineering Chemistry* **18**, 2124-2128.

Bhaskar M, Gnanamani A, Ganeshjeevan RJ, Chandrasekar R, Sadulla S, Radhakrishnan G. 2003. Analyses of carcinogenic aromatic amines released from harmful azo colorants by Streptomyces SP. SS07. *Journal Chromatography A* **1018**, 117-123.

Chan LS, Cheung WH, McKay G. 2008. Adsorption of acid dyes by bamboo derived activated carbon. *Desalination* **218**, 304-312.

Chao-Yin K, Chung-Hsin W, Jane-Yii W. 2008. Adsorption of direct dyes from aqueous.

Chegrouche S, Mellah A, Barkat M. 2009. Removal of strontium from aqueous solutions by adsorption onto activated carbon: kinetic and thermodynamic studies. *Desalination* **235**, 306-318.

Chen CL, Hu J, Xu D, Tan XI, Meng YD, Wang XK. 2008. Surface complexation modeling of Sr(II) and Eu(III) adsorption onto oxidized multiwall carbon nanotubes. *Journal Colloid Interface Science* **323**, 33-41.

Dakiky M, Nemcova, I. 2000. Aggregation of o,o'-Dihydroxy azo Dyes III. Effect of cationic, anionic and non-ionic surfactants on the electronic spectra of 2-hydroxy-5-nitrophenylazo-4-[3-methyl-1-(4"-sulfo-phenyl)-5-pyrazolone]. *Dyes Pigments* **44**, 181-193.

Dye Removal Ability. *Water Air Soil Pollution* **224**, 1419.

- Freundlich HMF.** 1906. Über die adsorption in lasugen. Zeitschrift für Physikalische Chemie (Leipzig) **57**, 385–470.
- Gong R, Li M, Yang C, Sun Y, Chen J.** 2005. Removal of cationic dyes from aqueous solution by adsorption on peanut hull. Journal Hazardous Material **121**, 247-250.
- Guibal E, Roussy, J.** 2007. Coagulation and flocculation of dye-containing solutions using a biopolymer (Chitosan). React. Funct. Polym. **67**, 33-42.
- Ho YS.** 1995. Adsorption of heavy metals from waste streams by peat, Ph.D. Thesis, The.
- Isak SJ, Eyring EM, Spikes JD, Meekins PA.** 2000. Direct blue dye solutions: photo properties. Journal Photochemistry Photobiology A: Chemistry **134**, 77-85.
- Karpicz R, Gulbinas V, Undzenas A.** 2000. Picosecond Spectroscopic Studies of Tautomers of a Bisazo Compound in Solutions. Journal Chinese Chemistry Society **47**, 589-595.
- Krishnani K, Meng X, Christodoulatos C, Boddun M.** 2008. Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk. Journal Hazardous Material **153**, 1222-1234.
- Lagergren S.** 1898. Zur theorie der sogenannten adsorption gelöster stoffe. K. Sven. Vetenskapsakad. Handling **24**, 1-39.
- Langmuir I.** 1916. The constitution and fundamental properties of solids and liquids. I. Solids. Journal of the American Chemical Society **38**, 2221–2295.
- Madaeni SS, Mansourpanah Y.** 2004. Chemical cleaning of reverse osmosis membranes fouled by whey. Desalination **161**, 13-24.
- Mahmoodi NM.** 2013. Nickel Ferrite Nanoparticle: Synthesis, Modification by Surfactant and.
- Navarro A, Sanz F.** 1999. Dye aggregation in solution: study of C.I. direct red I. Dyes Pigments **40**,131-139.
- parameters. Journal of Colloid and Interface Science **327**, 308-315.
- Sahel K, Perol N, Chermette H.** 2007. Photocatalytic decolorization of Remazol Black 5 (RB5) and Procion Red M X-5B-isotherm of adsorption, kinetic of decolorization and mineralization. Applied Catalysis B: Environmental **77**, 100-109.
- Schreiber B, Schmalz V, Brinkmann T, Worch E.** 2007. The effect of water temperature on the solutions by carbon nanotubes: Determination of equilibrium, kinetics and thermodynamics.
- Tao J, Mao G, Daehne L.** 1999. Asymmetrical Molecular Aggregation in Spherulitic Dye Films. Journal of the American Chemistry Society **121**, 3475-3485.
- University of Birmingham, Birmingham, UK
- Xuan Z, Tang Y, Li X, Liu Y, Luo F.** 2006. Study on the equilibrium, kinetics and isotherm of biosorption of lead ions onto pretreated chemically modified orange peel. Biochemical Engineering Journal **30**, 117-123.