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ADSORPTIVE REMOVAL OF SYNTHETIC DYE EFFLUENT USING MAGNETIC $Cd_{0.4}$ $Ni_{0.6}$ $Zn_{0.4}$ Fe_2O_4 SPINEL NANOFERRITES

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ABSTRACT

Experimental investigations were carried out using laboratory made $Cd_{0.4}$ $Ni_{0.6}$ $Zn_{0.4}$ Fe_2O_4 (CNZ) spinel nanoferrite as alternative adsorbent for removal of toxic anionic dye namely Congo red (CR) from aqueous solutions. The use of CNZ as an adsorbent for the removal of CR dye from aqueous solutions at different contact times, pH, adsorbent doses and initial dye concentration were experimentally studied in batch mode to evaluate the adsorption capacity, kinetic and equilibrium. Experimental results revealed that optimal adsorption took place at basic pH and high dye concentration. The dye uptake process obeyed the pseudo second order kinetic expression and was best described by the freundlich isotherm.

1. Introduction

Underground water is the major source of drinking water. This underground water is being polluted by the wastewater containing a large number of contaminants like acids, bases, toxic organics, inorganics, heavy metals[1], dissolved solids and colors disposed by leather and textile industries. Out of all such contaminants, color is the most visible pollutant and the presence of very minute quantity makes it undesirable for use. Some of the dyes are toxic, stable and non-biodegradable[2]. Thus, the removal of color from dye-bearing effluents becomes a major challenge due to the difficulty in treating such wastewaters by conventional treatment methods such as chemical and biological oxidation methods[3]. However, adsorption technique proved to be an efficient and economical process for the treatment of these dye-bearing effluents. But the efficiency of the process lies in choosing the suitable adsorbent

In recent years, discharge of waste products (mainly dye effluents) from difficult industries leading to aquatic and environmental pollution is a serious global problem of great concern[4]. Due to toxicity of dyes, it is necessary to remove them from wastewater before them discharge to the natural environment. The removal of organic pollutants and dyes from industries remain as a challenge as these dye molecules are difficult to decompose. Varieties of organic and heavy metal pollutants were removed by nano adsorbents by various research groups. Various methods have been devised for the degradation of dyes in aqueous solution. Conventional methods for the removal of dyes from wastewater include adsorption onto solid substrates, chemical coagulation, oxidation, filtration and biological treatment. Adsorption is one of the effective separation techniques to remove dilute pollutants [5]. All the above said methods are successful to certain extent. Spinels are the class of compounds of the type $M^{2+}M_2^{3+}O_4$, which has attracted researches because of its versatile properties and applications in various fields. When M^{3+} = Fe, we get spinel ferrites with the general formula MFe_2O_4 and the transition metal spinel ferrites are obtained when M = Cu, Fe, Mn, Ni, Zn etc. These spinel ferrites are studied more due to their magnetic property and semiconducting property[6]. The fabrication of nano ferrites has attracted much greater interest because of their large surface-tovolume ratio yielding remarkable material properties. The sol gel method for preparing ferrites has many advantages with respect to good stoichiometric control and particle size distribution at a lower temperature[7]. Previous publications reported that ferrites were used for magnetic separation technology, as a rapid and effective technology for adsorption[8]. Due to large specific surface area, excellent physicochemical characteristics and easy separation under external magnetic fields, spinel ferrite magnetic nanoparticles have been regarded as a promising adsorbent and widely used for dye removal from wastewaters. Zui Ding, et al[9] synthesized $CoFe_2O_4$ ferrite nanoparticles for removal Congo red from aqueous solution by an ethanol-assisted hydrothermal method, where the ethanol is mixed with water as the solution. The maximum adsorption capacity for CR of $CoFe_2O_4$ nanoparticle is 190.5 mg/g when the volume ratio of ethanol to water is 4/3. Congo red (CR) or 1-naphthalenesulfonic acid, 3,3′-(4,4′-biphenylenebis (azo)) bis (4-amino-) disodium salt is a benzidine-based anionic diazo dye prepared by coupling tetrazotised benzidine with two molecules of napthionic acid [19] (Fig. 1). In this work, $Cd_{0.4}$ $Ni_{0.6}$ $Zn_{0.4}$ Fe_2O_4 (CNZ) spinel nanoferrite was directly prepared by a sol-gel method , and they were employed to absorb Congo red in water. The adsorption efficiency has been investigated in details.

Experimental

Materials and method

The adsorbent sample $Cd_{0.4}$ $Ni_{0.6}$ $Zn_{0.4}$ Fe_2O_4 (CNZ) spinel nanoferrite was prepared by sol-gel technique. All chemicals and solvents were AR grade or better purchased from Merck Co.Pvt Ltd and Sd. fine chemical used without any further purification. The stoichiometric amounts of metal nitrates viz. Cadmium nitrate ($Fe(NO_3)_2{\cdot}4H_2O$) (>99%), nickel nitrate $Ni(NO_3)_2{\cdot}6H_2O$, Ferric Nitrate [$Fe(NO_3)_2$ $9H_2O$] and Zinc Nitrate – $Zn(NO_3)_2{\cdot}6H_2O$, Citric acid - ($C_6H_8O_7.H_2O$) used as starting materials for the synthesis. Metal nitrates in required proportions were dissolved in a minimum quantity of distilled water and mixed together. Aqueous solution of Citric acid was then added to the mixed metal nitrate solution (with and without Lanthanum nitrate). Ammonia solution was then added with constant stirring by maintaining the neutral pH (7.0). The solutions were heated at 90ºC under continuously stirring to remove the excess of the solvent. By raising the temperature up to 200°C lead the ignition of gel. The dried gel burnt completely in a self-propagating combustion manner to form powder like substance. The burnt powder was ground in Agate Mortar and Pestle to get a fine Ferrite powder. Finally the burnt powder was calcined in air at 700°C temperature for 2 hours and cooled to room temperature.

Dye Solution Preparation

The dye congo red (C.I name = Direct Red 28, C.I No. = 22120, Chemical formula = $C_{32}H_{22}N_6O_6S_2Na_2$, Formula weight = 696.65) is supplied by S.D fine Chemicals, Mumbai, India, was used as such without further purification. An accurately weighed quantity of dye was dissolved in double distilled water to prepare the stock solution (1000mg/L). Serial dilutions were made by diluting it with double distilled water.

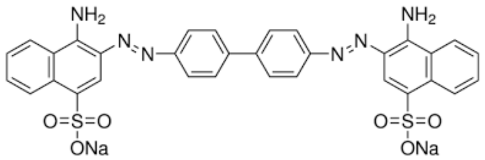


Figure 1: The chemical structure of Congo Red dye and Solution

Adsorption experiments

All adsorption studies were carried out using Congo Red dye (CR) as the standard dye.Into the CR solution is inserted a CNZ ferrite. Effect of pH was studied by adjusting the pH of dye solutions using 0.1 N HCl and 0.1 N NaOH solutions. Batch equilibrium adsorption experiments were carried out by shaking 100 mL solution of various dye concentrations at pH 7.0 with 100mg of adsorbents at room temperature. Agitation rate was held constant at 200 rpm. On Remi shaker,filter , and concentration in supernatan was analyzed spectrophotometrically (Shimadzu UV 160) at 540 nm. The amount of CR adsorbed onto the compounds (%) was calculated as:

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

where C_o is the initial CR concentration (mg/L), C_t is the concentration of CR (mg/L) at equilibrium time, t.. All the experiments were carried out in duplicates.

Results and discussion

Effect of pH

100ml of CR dye solution with dye conc. 100 mg/L is prepared in a conical flask and adsorbent conc.(1g/100ml) and the conical flask initial pH value is to be measured. The pH of the dye solutions was adjusted with dilute HCl (0.05N) or NaOH (0.05N) solution by using a pH meter.100 ml of dye solution was already prepared and the pH of solution is changed from 2 to 9. All the conical flasks were placed in the shaker (100 rpm fixed through out the study) maintained at room temperature and the final concentration of dye was measured using UV spectrophotometer with the calibration plot of the dye after 40 minutes. A graph is drawn with % Removal Vs initial pH (Figure 2).

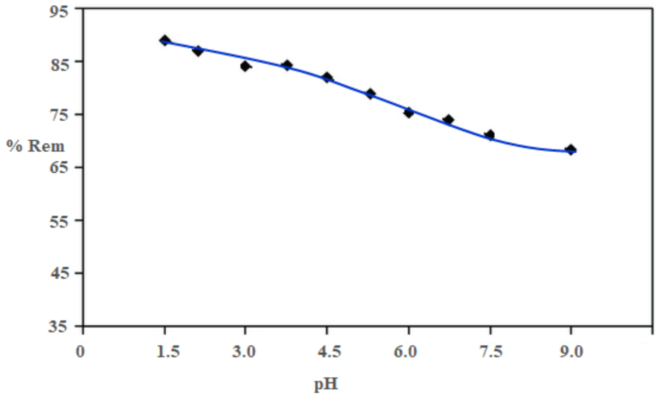


Figure 2: Effetc of pH on adsorption of CR dye onto CNZ Adsorbent

The percentage of dye adsorption at different pH is shown in Figure 2. The initial pH of dye solution plays an important role particularly on the adsorption capacity by influencing the chemistry of both dye molecule and adsorbent (CNZ) in aqueous solutions. The color of CR in aqueous solution is solid red at pH around 7. The color of CR changes to dark blue at acid pH and to red at alkaline pH (9-10), but this red color is slightly different from original red at the neutral pH. CR exists as an anionic form at basic pH (sulfonate groups) and as a cationic form at acid pH. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent does not favor the adsorption of dye anions due to the electrostatic repulsion. Also, lower adsorption of CR at alkaline pH is due to the presence of excess OH^- ions competing with the dye anions for the adsorption sites. Nevertheless, significant adsorption of anionic dye on the adsorbent still occurred above pH_{ZPC} due to the fact that a chemical interaction between the dye and CNZ, respectively. Similar results have been reported for the adsorption of CR on waste orange peel[10] and activated carbon[11].

Effect of Dose

Adsorption of the CR dye on CNZ adsorbent sample studied at different initial concentrations (0.5 to 7.5 g/L) of CNZ and 100mg/L of CR at 30°C. Study of results represented in Figure 3 shows presence of relation between the concentration of dye and the available binding sites on adsorbent surface, it shows high removal of dye concentration in the start of adsorption process, then the removal of dye decreases due to the completion of the available sites. The removal of initial concentration of dye decreases with the increases of its concentration. The amount of CR adsorbed at equilibrium (qe) increase CNZ sample as an adsorbent. This may be attributed to the fact that the increase of the initial concentration of the adsorbate represents a driving force to overcome the mass transfer resistance of dye between the aqueous and solid phases.

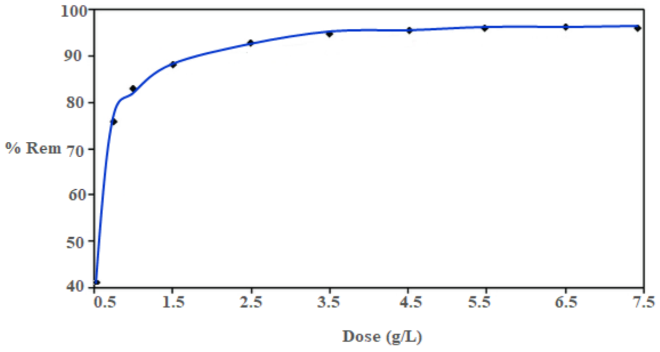


Figure 3: Effetc of Dose on adsorption of CR dye onto CNZ Adsorbent

Effect of concentration

The initial concentration provides an important driving force to overcome all mass transfer resistances of all molecules between the aqueous and solid phases. Figure 4 shows the plot of amount of dye adsorbed versus different initial dye concentrations. From the figure it was observed that the amount of dye adsorbed gets increased at alower concnetrations By considering the amount of dye adsorbed per unit of CNZ (mg/g), adsorption capacity of CNZ increased as the initial dye concentration increased.The maximum adsorption capacity attained for CNZ 75.64 mg/g. The adsorption was preceding the saturation of CNZ at 100 mg/L of dye. It can be proposed that an increase in the initial dye concentration leads to an increase in mass gradient between the solution and adsorbent, and thus acts as a driving force for the transfer of dye molecules from bulk solution to the particle surface. The increase in the proportional dye adsorption is attributed to the equilibrium shift during the clay adsorption process.

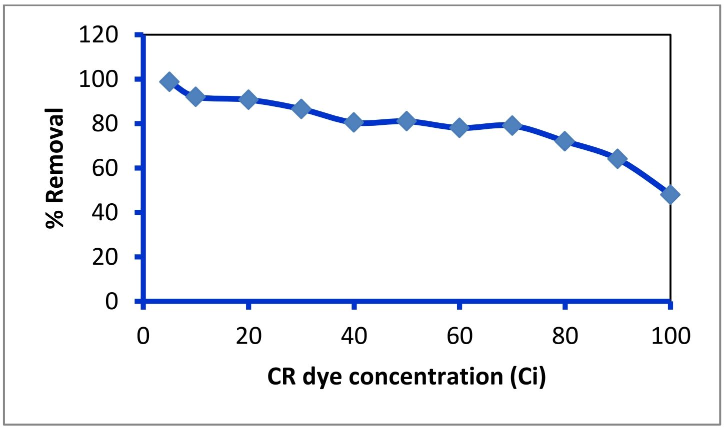


Figure 4: Effetc of CR dye concentration on adsorption with CNZ Adsorbent

Adsortion Isotherm Study

The equilibrium adsorption data are analyzed using Langmuir and Freundlich isotherm models. The Langmuir isotherm model assumes that the adsorption occurs on the homogeneous surface of the adsorbent. The Freundlich isotherm model is commonly used to describe the surface heterogeneity.

The Langmuir adsorption isotherm can be described by the following[12]

$$\frac{Ce}{qe} = \frac{1}{q_m\, b} + \frac{Ce}{qm}$$

where b (L/mg) is a constant related to the energy of adsorption and qm (mg/g) is the monolayer adsorption capacity. The values of b and qm are calculated from the intercept and slope of the linear plot Ce/qe versus Ce (Figure 5).

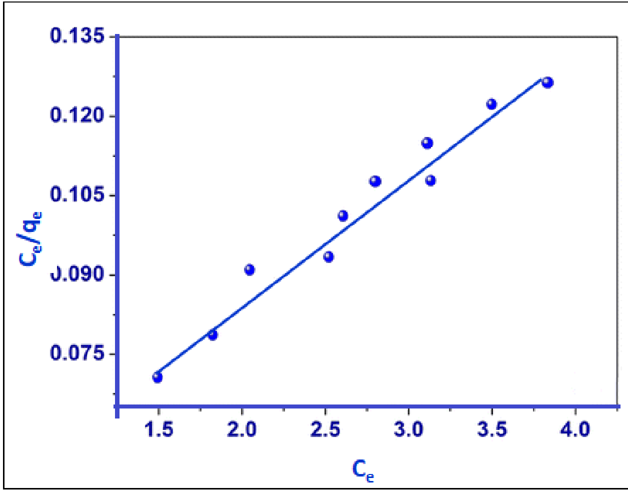


Figure 5: Langmuir Isotherm

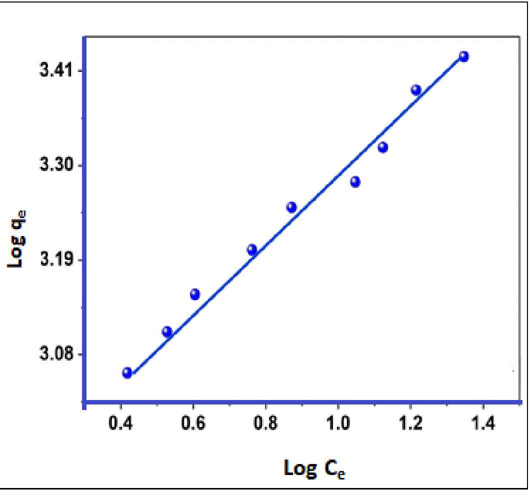


Figure 6: Freundlich Isotherm

The linear form of Freundlich isotherm is shown by the following[13]

$$\ln qe - \ln(k_f) + \frac{1}{n}\ln(C_e)$$

where n and Kf (mg/g) are Freundlich constants, which represent adsorption strength and adsorption capacity, respectively. The values of n and Kf can be determined by the slope and intercept of the linear plot $ln(qe)$ versus $ln(Ce)$. When n>1, it indicates that the adsorption process is favorable.

Figure 5 and 6 shows the linearized forms of the Langmuir and Freundlich isotherm models based on the experimental data, respectively. The values of these adsorption isotherm parameters are shown in Table 1. According to the table, Freundlich model is best fit (R^2 0.9847) as compared with the other model, which suggests the surface heterogeneity of the surface adsorption of CR dye onto CNZ.

Table 1: The parameters of Langmuir and Freundlich equation

Adsorbent	**Langmuir equation**			**Freundlich equation**		
	Qe (mg/g)	**b (L/mg)**	**R^2**	**1/n**	**K_f**	**R^2**
CNZ	84.27	0.684	0.894	0.357	75.68	0.984

Effect of stirring Time

The adsorption of CR dye onto CNZ sample was studied as a function of contact time in order to decide whether the equilibrium was reached. For this, 100 mg/L of CR dye solutions at pH 3 were contacted with 4 g/L of CNZ. The samples were taken at different periods of time and analyzed for their CR dye concentration (Figure 7). Dye adsorption onto CNZ increased from 48.4% to 98.74% when the contact time was increased from 5-40 min. The CR dye adsorption rate is high at the beginning of the experiment because initially the adsorption sites are more available and CR dye molecules are easily adsorbed on these sites[14]. The equilibrium can be reached within 40 min, and thus, further adsorption experiments were carried out for a contact time of 40 min.

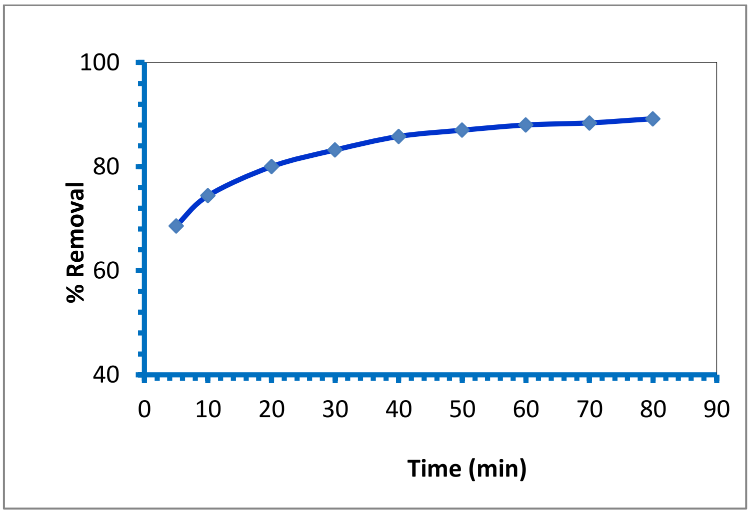


Figure 7: Effetc stirring time on adsorption of CR dye onto CNZ Adsorbent

Adsorption Kinetics

The adsorption kinetics study was determined by evaluation of dye quantity adsorbed onto magnetic CNZ at different time intervals (5–90 min). The initial concentration of dye solution was 50 mg/L. Amount of adsorbent, volume of dye solution and sample analysis were kept in the same way as isotherm studies.

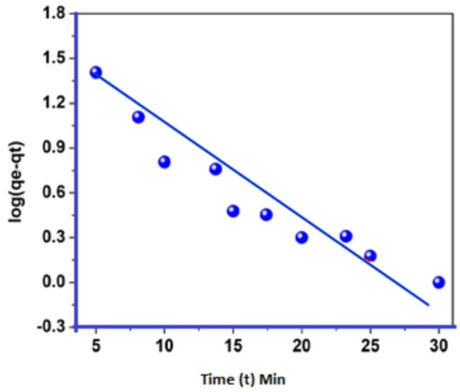
The data were analyzed using the Lagergren equation (pseudo-first-order model)[15] and pseudosecond-order model[16]. The linear form of Lagergren pseudo-first-order model is represented by following equation

$$\ln(qe - qt) = \ln qe - k_1 t$$

Where k_1 and qe were calculated from the slope and intercept of the plots of ln(qe - qt) versus t (Figure 8). The linear form of pseudo-second-order kinetic model is presented by following equation:

$$\frac{t}{qt} = \frac{i}{k_2 q_e^2} + \frac{t}{q_e} t$$

where the values of k_2 and qe were calculated from the slope and intercept of the plots of t/q_t versus t (Figure 9). Taking the correlation coefficient into consideration, the experimental data for adsorption of CR dye is best fit with the pseudo-second-order model (R^2: 0.9975). Furthermore, the experimental values q_e,exp are basically close to the values q_e, cal obtained in the pseudo-second-order kinetic model.



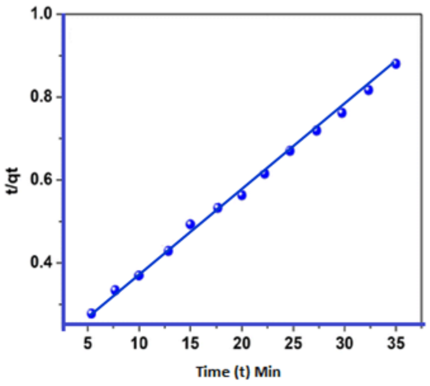


Figure 8: Pseudo-First order Kinetics

Figure 9: Pseudo-Second-order Kinetics

Degree of fit of the model is evaluated on the basis of the correlation coefficient R^2 value. The fitting of the kinetic data demonstrate that the dynamics of sorption could be better described by pseudo second-order model indicating a chemisorptive rate-limiting for all the three adsorbent CNZ.

Magnetic Properties

Room-temperature magnetic properties of $Cd_x\ Ni_{1-x}\ Zn_x\ Fe_2O_4$ (x =0.0, 0.2, 0.4,) nanoferrites were measured using pulse field hysteresis loop tracer technique by applying a magnetic field of 1000 Oe. Using *M-H* plots (Figure) of nanoferrites, the saturation magnetization (M_s), remanence magnetization (M_r), coercivity (H_c), and squareness ratio ($M_{r/}\ M_s$) were determined. From Table 1 it is evident that magnetic parameters of CNZ nanoferrites decrease as a function of cadmium content which is associated with linkage between (A) and [B] sites. It may be due to the fact that nonmagnetic Cd^{2+} ions (0 M_B) replace magnetic Ni^{2+} ions (2M_B)[6]. The magneton number increases up to x=0.2 and then decreases with increasing Cd^{2+} content.

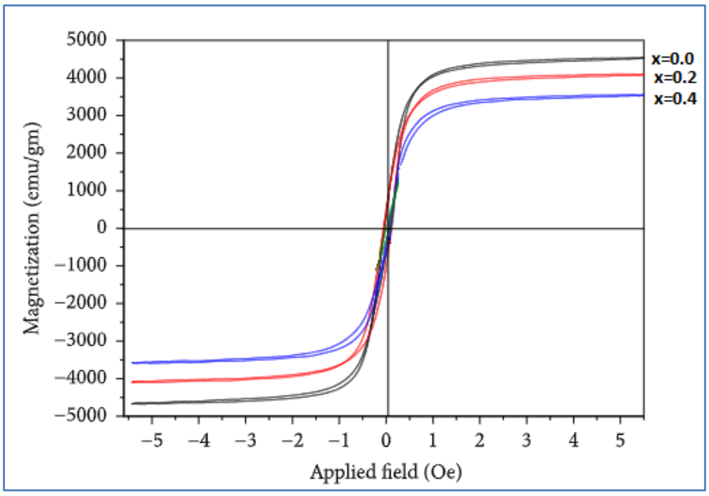


Figure 10: Magnetic hysteresis loops of $Cd_xNi_{1-x}Zn_x\ Fe_2O_4$ (x =0.0, 0.2, 0.4,)

Conclusion

The $Cd_{0.4}\ Ni_{0.6}\ Zn_{0.4}\ Fe_2O_4$ (CNZ) spinel nanoferrite as an adsorbent is an effective material for removal of the toxic anionic dye, congo red, from aqueous solution. The adsorption was highly dependent on various operating parameters, like: contact time, pH, initial concentration and dye. The results gained from this study were well described by the Freundlich equation represented the best fit of experimental data. The kinetic data indicated that the adsorption process was controlled by pseudo-second-order equation The ferrite with composition X = 0.4 shows highest value of saturation magnetization and magnetic moment.

References

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1 Repo E, Kurniawan TA, Warchol JK, Sillanpaa MET (2010) Adsorption of Co(II) and Ni(II) on EDTA- and/or DTPA-modified chitosan: kinetic and equilibrium modeling. Chem Eng J 161:73–82

2 Gupta VK, Mittal A, Krishnan L, Gajbe V (2004) Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash. Sep Purif Technol 40:87–96

3 Vadivelan V, Vasanth Kumar K (2005) Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. J Colloid Interface Sci 286:90–100

4 Gupta VK, Gupta B, Rastogi A, Agarwal S, Nayak A (2011) A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye-Acid Blue 113. J Hazard Mater 186: 891-901.

5 Haralkar, S.J.: Substitutional effect of Cr3+ ions on the properties of Mg–Zn ferrite nanoparticles. Phys. B Condens. Matter **407**, 4338–4346 (2012)
6 Ali, I.: New generation adsorbents for water treatment. Chem. Rev. 112, 5073–5091 (2012)
7 Siemons, M., Weirich, Th., Mayer, J., Simon, U. 2004. Preparation of nanosized perovskitetype oxide via polyol method. Journal of Inorganic and General Chemistry, 630: 2083-2089
8 Rashad.M.M.2006. Synthesis and magnetic properties of manganese ferrite from low grade manganese ore. Materials Science and Engineering B, 127:123-129
9 Zui Ding, Wei Wang, Yajun Zhang, Feng Li, J. Ping Liu. 2015. Synthesis, characterization and adsorption capability for Congo red of CoFe2O4 ferrite nanoparticles. Journal of Alloys and Compounds, 640 : 362-370
10 C. Namasivayam, N. Muniasamy, K. Gayatri, M. Rani, and K. Ranganathan, “Removal of dyes from aqueous solutions by cellulosic waste orange peel,” Bioresource Technology, vol. 57, no. 1, pp. 37–43, 1996.
11 C. Namasivayam and D. Kavitha, “Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste,” Dyes and Pigments, vol. 54, no. 1, pp. 47–58, 2002
12 Langmuir I (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc 40:1361–1403
13 Freundlich HMF (1906) Over the adsorption in solution. J Phys Chem 57:385–470
14 Hameed BH, Ahmad AL, Latiff KNA (2007) Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. Dyes Pigments 75: 143–149.
15 Chairat M, Rattanaphani S, Bremner JB, Rattanaphani V (2008) Adsorption kinetic study of lac dyeing on cotton. Dyes Pigm 76:435–439.
16 Ho YS (2006) Review of second-order models for adsorption systems. J Hazard Mater 136:681–689.