Chapter

A Brief Comparative Study on Removal of Toxic Dyes by Different Types of Clay

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Abstract

Increasing amount of organic dyes in the ecosystem particularly in wastewater has propelled the search for more efficient low-cost bio adsorbents. Different techniques have been used for the treatment of wastewater containing toxic dyes such as: biological degradation, oxidation, adsorption, reverse osmosis, and membrane filtration. Among all these processes mentioned, adsorption with low cost adsorbents has been recognized as one of the cost effective and efficient techniques for treatment of industrial wastewater from organic and inorganic pollutants. Clays as material adsorbents for the removal of various toxic dyes from aqueous solutions as potential alternatives to activated carbons has recently received widespread attention because of the environmental-friendly nature of clay materials. This chapter presents a comprehensive account of the techniques used for the removal of industrial cationic and anionic dyes from water during the last 10 years with special reference to the adsorption by using low cost materials in decontamination processes. Effects of different adsorption parameters on the performance of clays as adsorbents have been also discussed. Various challenges encountered in using clay materials are highlighted and a number of future prospects for the adsorbents are proposed.

Keywords: adsorption, toxic dyes, Clays, wastewater treatment

1. Introduction

The treatment of industrial wastewater particularly loaded with dangerous dyes is considered among the global environmental issues and the concerns of researchers [1]. According to recent reports, over one million dyes are available commercially with an annual output of over 7×10^5 tons [2]. The textile industry around the world consumes approximately 10^4 tons of dyes annually and discharges about 100 tons of dyes into wastewater every year [3]. These dyes are highly toxic, carcinogenic, and cause dire consequences for human health and the marine system. The removal of these toxic dyes from polluted water and wastewater is highly desirable in order to meet regulatory obligations for wastewater recycling or discharging into natural environments [4]. Currently, there is several physico-chemical and biological technologies in the use for the treatment of these polluted effluents namely, ion exchange, membrane separation, biological treatment and adsorption [5–10]. Physico-chemical processes such as ion exchange, electro dialysis and reverse osmosis are expensive, difficult to operate and require significant technologies. While in recent years, adsorption has continued to attract the attention of the researchers worldwide [11, 12] and appears to be an alternative, which has some advantages such as simple design, and ease of operation. Whereas, the biological treatment which is based on the microbial digestive metabolism, has the major drawback of the risk of microbiological contamination and a significant production of sludge, which poses problems of storage and handling [13, 14]. In the present work a comparative study between the capacities of raw, synthetic and modified clays for the removal of toxic dyes from aqueous solution has been given, with particular review of the main factors influencing the adsorption of dyes by clays such as pH of the solution, temperature and initial dye concentration on the adsorption capacities of the these clays.

2. Removal methods for toxic dyes

Currently, a number of different technologies and methods such as membrane separation, ion exchange, adsorption and biological methods are widely used for the removal of toxic anionic and cationic dyes from polluted water and wastewaters.

2.1 Membrane filtration

Membrane separation is a pressure driven process. Pressure-focused processes are generally divided into four overlapping classes of increased selectivity: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and hyperfiltration or reverse osmosis (RO). Microfiltration can be used to remove bacteria and suspended solids with pore sizes from 0.1 to microns. Whereas, Ultrafiltration eliminates colloids, viruses, and some proteins by pores from 0.0003 to 0.1 microns. Nanofiltration is based on physical rejection based on molecular size and charge. The pore sizes are between 0.001 and 0.003 microns [15]. Reverse osmosis has a pore size approximately 0.0005 microns and can be used for desalination. High pressures are needed to makepass water through the membrane from a concentrated solution to dilute. Shih [16] has studied the elimination of dyes on membrane and explored the parameters that could influence the efficiency of toxic dyes removal by membrane technologies such as parameters source, membrane type and membrane process.

2.2 Ion exchange

Ion exchange has been widely used to remove dyes due to its many advantages, such as high processing capacity, speed and increasing the efficiency of dye retention [17]. Ion exchange resin, either natural or resin solid synthetic, has the specific ability to exchange its cations with dyes in wastewater. Among materials most used in the ion exchange process, synthetic resins: are commonly preferred because they are effective in virtually removing dyes in solution [18].

2.3 Adsorption

Adsorption is a process in which solids are used for removing organic and inorganic substances from either gaseous or liquid solutions. The phenomena

Removal process		Advantages	Disadvantages
Chemical methods			
	Photo-catalyst	Low cost operational and economically feasible	Some photo catalyst degrades into toxic by-products.
	Ozonation	No sludge generation	Operational cost is very high, half life is short (20 min)
Biological methods			
	Anaerobic degradation	By-products can be used as energy	Resources under aerobic conditions require more treatment and yield of methane and hydrogen sulphide
	Aerobic degradation	Operational cost is low and effective in removal of azo dyes	Provide suitable environment for growth of microorganisms and very slow process
Physico-chemical methods			
	Adsorption	High adsorption capacity for all dyes.	Low surface area and high cost of some adsorbents.
	Ion exchange	No loss of sorbents	For disperse dyes not effective
	Membrane filtration	Effective for dyes with high quality effluents	Production of sludge and suitable for treating low volume

Table 1.
Separation techniques and their advantages and disadvantages [21, 22].

driven adsorption are operative in most natural physical, biological, and chemical systems. The solid adsorbents widely used in the industries for the removal of these pollutants from industrial wastewater are diverse such as activated carbon, metal hydrides and synthetic resins.

The adsorption process involves the separation of a substance from one phase by retaining it on the surface of another. The physical adsorption is mainly due to weak interactions such as van der Waals bonds and the electrostatic forces created between the adsorbate and the atoms which make up the surface of the adsorbent. The capacity of this process depends some parameters namely, adsorbent properties, adsorbate chemical properties, temperature, and pH of the medium. It should be noted that even if the adsorbents are available, they are still expensive and few of them are selective. Therefore, over the last decades the research has been redirected towards the search for other improved materials which will meet certain requirements such as regenerative capacity, easy availability, and cost effectiveness. Consequently, clays adsorbents have drawn attention to many researchers and characteristics as well as application of many such adsorbents are reported [19, 20]. However, clays adsorbents are discussed herein after. A summary of advantages and disadvantages of some separation methods are presented in **Table 1**.

3. Clay materials used as adsorbents for dye treatment

3.1 Layered double hydroxides (LDHs)

Layered double hydroxides (LDHs) are intensively studied because of their high anionic exchange capacity [23], reuse, larger surface area, porosity, and fundamental properties [24]. They have advantages over commercially available adsorbents in terms of low cost, high adsorption properties, and non-toxicity. The use of LDH

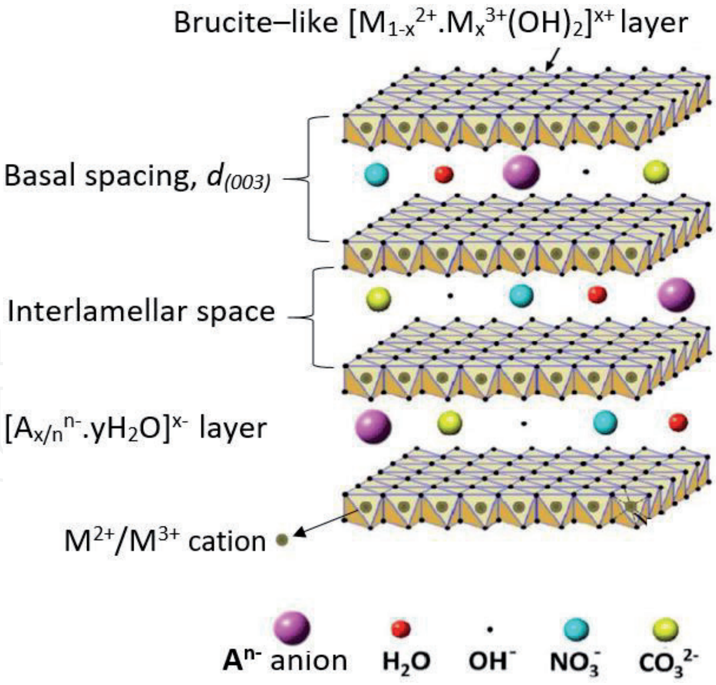

Figure 1.
A schematic representation of the LDH structure [28, 29].

could bring significant economic and environmental benefits to the wastewater treatment industries. Previous works [25] have proven their usefulness as adsorbents for the removal of some organic and inorganic pollutants from polluted water and wastewater. Among the different types of LDH material, a species similar to hydrotalcite, a compound consisting of a double compound of MgAl-LDH hydroxides with carbonate as interlayer anions, is commonly used for various applications [26, 27]. A schematic representation of the general structure of the LDH structure is given in **Figure 1**.

The effectiveness of these compounds in the treatment of polluted water and in particular organic pollutants such as textile dyes has already been demonstrated by various research teams [30–33]. Studies that have been done by Elmoubarki *et al*. [34] demonstrate the effectiveness of Layered double hydroxides based on Mg and Fe for the removal of methyl orange. Shan et al. [35] has studied the trapping of Congo red on carbonated HDL Mg (II) /Al (III), this study showed that the materials are more efficient, and have a very high yield of Congo red elimination. **Table 2** shows some adsorbents of the lamellaires types, used for the removal of some toxic dyes from aqueous solutions.

3.2 Kaolinite

The kaolinite group is comprised of trioctahedral minerals such as, chrysotile, antigorite, cronstedite, and chamosite, dioctahedral minerals such as kaolinite, halloysite, dickite and nacrite. It is white and soft clay, composed primarily of the mineral kaolinite, a hydrated aluminum silicate. Commonly, the kaolinite structure group is known to be composed of silicate sheets (Si_2O_5) linked to aluminum oxide/hydroxide layers ($Al_2(OH)_4$) called gibbsitelayers [51]. Additionally, the primary structural unit of this group is a layer composed of one octahedral sheet condensed with one tetrahedral sheet. About the dioctahedral minerals, the octahedral sites are occupied by aluminum, while those of trioctahedral minerals are occupied by magnesium and iron. Kaolinite and halloysite are single layer structures. Furthermore, kaolinite, nacrite and dickite occur as plates; halloysite, which can have a single

Adsorbent	Dye	Reference
NiFe-LDH	Methyl orange	[36]
ZnMgAl–CO_3	Methyl orange	[37]
MgNiAl	Methyl orange	[38]
MgAl- LDH	Methyl orange	[39]
rGO/Ni/MMO	Methyl orange	[40]
ZnO/CuO/γ-Al_2O_3	Methyl orange	[41]
Fe_3O_4/ZnCr-LDH	Methyl orange	[42]
NiAl-LDH	Congo red	[43]
Mg–Al–LDH	Congo red	[44]
CaAl-NO_3	Congo red	[45]
Ni/Fe-CO_3	Congo red	[46]
Mg/FeCO_3	Congo red	[47]
Mg - Al - Cl	Congo red	[48]
Zn-Fe–LDH	Methylene blue	[49]
Mn-Fe–LDH	Methylene blue	[49]
Mg-Fe–LDH	Methylene blue	[49]
GOaerogels/MgAl	Methylene blue	[49]
Zn- Fe -CO_3	Indigo Carmine	[50]
Zn-Cr -CO_3	Indigo Carmine	[50]
Zn-Mn -CO_3	Indigo Carmine	[50]
Zn-Al -CO_3	Indigo Carmine	[50]

Table 2.
Adsorbents used for the removal of dyes.

layer of water between its sheets, occurs in a tubular form. It consists of feldspar and muscovite formed by the alteration of [51, 52], and is a layered silicate mineral composed of a tetrahedral sheet, bonded through oxygen atoms to an octahedral sheet of alumina, which are layered silicate minerals composed of one tetrahedral sheet, linked through the oxygen atoms to one octahedral sheet of alumina octahedra. Nacrite, kaolinite and dickite exist as plates, halloysite occurs in a tubular form, have a single layer of water between its sheets. Rocks having large amount of kaolinite are referred to as kaolin or china clay [53]. Kaolinite contains heterogeneous surface charge is a well-known fact. It is believed that its basal surface has a constant structural charge which is attributed to isomorphs substitutions of Si^{4+} by Al^{3+}. The charge on the edges is due to protonation or deprotonation of surface hydroxyl groups and so it depends on pH of solution. Adsorption can occur on flat exposed planes of silica and alumina sheets. It is least reactive clay. Kaolin has no side effects, no health problems till the fine dust particle is controlled, thus it is safe environmentally [54, 55].

3.3 Bentonite

The most common group of clay used in water treatment is bentonite. It is a low-cost, effective and eco-friendly adsorbent, and it is commonly impure clay consisting mostly of montmorillonite, although some may consist of the rare clay minerals such as, nontronite saponite, and beidellite. Montmorillonite structure is a layer of gypsum site sandwiched between two sheets of silica to form the structural unit [56, 57]. The substitutes are found mainly in the octahedral layer (Mg^{2+}, Fe^{2+}) and to a lesser extent in the silicate layer. The clay mineral group is mainly composed of a hydroxyl-aluminosilicate framework. As well as, the crystal structures of the clay minerals are composed of a combination of silica tetrahedral sheets and alumino octahedral. Apart of the trivalent Al^{3+} is substituted by Mg^{2+} or Fe^{2+} ions in some cases. In such cases, substitution is accompanied by the addition of alkaline metals like Na^+ and K^+ or alkaline earth metals like Mg^{2+} and Ca^{2+} to provide charge balance [57]. Stockmeyer et al. (1991) [58] have investigated the adsorption of some organic compounds from aqueous solutions by using organophilic bentonites. Phenol, diethyl ketone, nitroethane, aniline ethoxy acetic acid, maleic acid and hexadecyl pyridinium bromide were investigated as test organic compounds. The used organophilic bentonites vary in the degree of their total cation exchange capacity exchanged by organic counter ions [58].

4. Parameters influencing the adsorption of dyes by clays

4.1 Effect of pH

The pH value of the solution is an important factor for the adsorption, which influences the structure of the adsorbates and the surface properties of adsorbents [59]. Commonly, at low pH of solution, the adsorption capacity and percentage removal of anionic dyes from aqueous solution increases due to electrostatic forces between the anionic dye molecule and positive surface charge of adsorbent. There is an electrostatic attraction between the positively charged dye molecule and negatively charged adsorbent. Besides, at high pH, the removal efficiency of anionic dyes decreases with increase in pH [60–62]. Whereas, the percentage removal and the amount adsorbed of cationic dyes at high pH increases because positive charges on the dye molecules ensured that they are attracted by anionic adsorbent, so there are electrostatic attractions between the negative surface of adsorbent and positive charges of dye molecules [63–66].

The previously reported literature indicates that optimized pH depends upon nature of dye and type of clay. Zaghloul et al. [67] studies the effect of pH on the removal of methyl orange (anionic dye) from aqueous solutions using synthetic clay type MgAl-LDH. It was observed in the range of pH from 2 to pH = 10, the percentage removal is very important (98%), due to the electrostatic forces between the anionic dye and the positively charged H^+ surface of the synthetic clay as an adsorbent. At higher pH adsorption capacity and percentage removal of dyes decreased and this decrease has been explained by the fact that at pH = 10, number of hydroxyl ions is more and hence the competition between OH^- ions and anionic molecules for active adsorption sites. A similar investigation of the textile dye removal by another adsorbents has been reported by other researchers in the literature [59, 68].

4.2 Effect of temperature

Temperature is a crucial parameter in adsorption reactions. In general, the influence of temperature on the adsorption kinetics is very variable. Adsorption may increase, decrease, or remain constant with increasing temperature. Some studies have shown that a decrease in toxic dyes retention by clay materials is often accentuated by an increase in temperature [69]. Other works have shown that the adsorption of industrial dyes on different adsorbents increases with increasing temperature [70, 71]. Elmoubarki et al. [72] studied the adsorption of methylene blue and methyl orange on synthetic clays of Ni-LDH, Mg-LDH types, in a temperature range (30 to 50 °C). They have observed that the quantities of MB and MO adsorbed as a function of temperature increase with the increase in temperature. On the other hand, the research carried out by Zaghloul et al. [67] on the adsorption of methyl orange by MgAl-LDH (2:1) have shown that the temperature increase from 30 to 35 °C disadvantages the adsorption of methyl orange onto LDH.

4.3 Effect of initial dye concentration

The initial concentration of adsorbate and adsorbent has a great importance in batch and fixed bed column adsorption experiments, because it depends on the nature of the system used. Sureshkumar et al. [73] showed that an increase in the retention of dyes by clays is promoted by an increase in the initial concentration of these dyes. Likewise, the others work [74] shows that the retained concentration of dyes (methyl orange, crystal violet, blue acid) increases with the initial concentration of these dyes. In our previous reports [67], we have studied the effect of initial concentration of methyl orange by MgAl-LDH (2:1), it was observed that the amount of methyl orange adsorbed as a function of temperature increases with increase in concentration. The same remark was recorded by Krika and Benlahbib [75] during the retention of methyl orange by cork powder. They have demonstrated that adsorption process is an effective method because of its efficiency, capacity, and applicability on large scale dye-removal, as well as the potential for regeneration, recovery, and recycling of adsorbents.

5. Equilibrium studies

Equilibrium studies explore the relationship between adsorbent and adsorbate which is described by adsorption isotherms [76]. The adsorption isotherm studies are important both a theoretical and a practical point of view. Further, isotherm data must precisely fit different isotherm models to find an appropriate model that can be used for the design process [77, 78]. The obtained parameters from the different models provide important information on the adsorption mechanisms, the surface properties and affinities of the adsorbent. Several models have been published in the literature to describe experimental equilibrium data of adsorption isotherms. The most famous adsorption models for single-solute systems are Freundlich, Langmuir, Redlich–Peterson, Radke–Prausnitz, Koble–Corrigan, Temkin, Dubinin–Radushkevich (D–R), BET (Brunauner, Emmett, Teller), Sips and Generalized isotherms.

Langmuir adsorption isotherm assumes that the solid surface has a finite number of identical sites which shows homogeneous surfaces. Langmuir equation may be represented as [79]:

$$q_e = q_L \frac{K_L C_e}{1 + K_L C_e} \tag{1}$$

where q_e (mg/g) is the amount of the dye adsorbed per unit weight of clay at equilibrium, C_e (g/L) is the equilibrium concentration of dye in the solution, q_L (mg/g) is Langmuir maximum adsorption capacity and K_L (L/g) is Langmuir constant related to a free energy of adsorption.

The Freundlich isotherm is an empirical equation that assumes that the adsorption surface becomes heterogeneous during the adsorption process. The Freundlich isotherm is expressed by the following Equation [80].

$$q_e = K_F C_e^{1/n} \tag{2}$$

where, q_e (mg/g) is the amount of the dye adsorbed per unit weight of clay; C_e (g/L) is the equilibrium concentration of the dye in the bulk solution; K_f is Freundlich constant, which is a comparative measure of the adsorption capacity for the clay, and n_f is an empirical constant related to the heterogeneity of the material surface.

Zaghloul et al. [67] use a synthetic clay type MgAl-HDL for the removal of methyl orange. The Langmuir and Freundlich models were applied to the experimental data. The results indicated that the Langmuir isotherm fully describes the nature and sorption mechanism of methyl orange (MO) on the synthetic clay used. The adsorption capacity of MgAl-LDH calculated from the Langmuir model was found to be 1250 mg. g^{-1}. The value of 1/n at 298 K was 0.34 (i.e. $(1 < n < 10)$ indicating that the adsorption system solid–liquid studied was favorable. Bentahar et al. [81] have used clay minerals like bentonite, kaolin and zeolite for removal of Congo red dye from aqueous solutions. The results of both Freundlich and Langmuir models indicates that zeolite and bentonite were best described by the Freundlich model, however Langmuir model provided a better fit on the experimental data of kaolin with high R^2 value ($R^2 = 0.98$).

6. Kinetic studies

Kinetic studies are very important in regards of adsorption studies because they can describe the adsorption rate and provide valuable data for understanding the mechanism of adsorption reactions [82]. In order to understand the behavior of the adsorbent and to investigate the controlling mechanism of the adsorption procedure, the pseudo first-order, pseudo second order and intraparticle diffusion models are useful to check the kinetic information [83]. To explore the mechanism of adsorption regarding the adsorptive removal of methylene bleu (MB) by using amino-functionalized attapulgite clay nanoparticle Zhou et al. [84] fitted the experimental data to pseudo-first-order and pseudo-second-order kinetic models. The correlation coefficients of the pseudo second-order kinetic model were relatively greater than those of the pseudo first order kinetic model, implying that the MB adsorption can be described more appropriately by the pseudo-second-order model. Therefore, it can be concluded that a large number of vacant surface sites were available for adsorption during initial stage.

The reviewed research articles regarding kinetic studies show that pseudo-second order kinetic model is more suited to the experimental data compared to other models, however; depending upon the reaction other kinetic models also show correlation to the data.

7. Thermodynamic studies

Thermodynamic investigations are another important parameter of adsorption studies. The determination of thermodynamic parameters is an essential means of describing the energetic mechanism which operates in an adsorbent / adsorbate system during the adsorption process. For thermodynamic studies, the adsorption experiment should carry out at different temperature conditions and calculated parameters included standard enthalpy (ΔH°), standard entropy (ΔS°), and standard Gibbs free energy (ΔG°) [59].

$$K_d = \frac{q_e}{C_e} \quad (3)$$

$$\Delta G^\circ = -RTLnK_d \quad (4)$$

$$LnK_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (5)$$

Fan et al. [85] have studied the effect of temperature on the removal of methylene bleu by adsorption onto Mt-SB12. The thermodynamic study provides good information about the energetic changes related to adsorption process. The standard Gibbs free energy (ΔG°) values at different temperatures were found negative and standard enthalpy (ΔH°) were positive. These results indicates a spontaneous and endothermic nature of the adsorption process. Furthermore, the positive values of ΔS° reflected an increase in randomness at the solid/solution interface during the adsorption of methylene bleu onto Mt-SB12 [86]. In the same context, Zaghloul et al. [67] studied the effect of temperature on the removal of methyl orange using synthetic clay (MgAl-LDH) at different temperatures 25, 30 and 35 °C. ΔG° values at all temperatures were found to be negative implied that the adsorption of MO on MgAl-LDH was thermodynamically feasible and spontaneous [87]. The negative values of ΔH indicated that the adsorption process was exothermic in nature, and the negative values of ΔS designated a greater order of reaction during adsorption of MO dye by MgAl-LDH, which may be attributed to the adherence of dye molecule with MgAl-LDH adsorbent resulting a decrease in the degree of freedom of the system solid/ liquid [72]. Summary of the thermodynamic studies shows that the sorption process may be exothermic or endothermic for dyes adsorption onto clays.

8. Comparison of adsorption capacities

In order to justify the validity of low cost adsorbent for removal of toxic dyes, its adsorption potential must be compared with other materials used for this purpose. The values of maximum adsorption capacities in term of percentage removal of textile dyes onto different adsorbents reported in the literature are given in **Table 3**. The direct comparison of adsorption capacities of the adsorbents reported in the literature is difficult due to the varying experimental conditions employed in those studies. The adsorption capacity differences of toxic dyes uptake are ascribed to the properties of each adsorbent such as adsorbent structure, functional groups and surface areas.

9. Conclusion

For many decades, the raw, synthetic and modified clays have been considered low-cost and effective adsorbents, which have been successfully used for the adsorption of cationic and anionic dyes from polluted water and wastewater in the laboratory scale, although these several experiments but up to day few of researchers have focused on the use of these clays as adsorbent for the removal of industrial dyes from real effluents. The performance of different types of clays, whether raw,

Adsorbent	Adsorbate	% removal	Reference
NiFe-CO_3	Methyl orange	88	[59]
Mg/Fe-CO_3	Methyl orange	33	[88]
Montmorillonite	Methyl orange	90	[89]
Bentonite modified	Methyl orange	98	[90]
Ni/Al-CO_3	Congo Red	92	[91]
Mg/Al-CO_3	Congo Red	90	[92]
Natural kaolinitic clay	Congo Red	84	[93]
Ca-bentonite	Congo Red	95	[94]
Ghassoul	Methylene Blue	90	[95]
Algerian bentonite	Methylene Blue	91	[96]
Alginate/PVA–kaolin	Methylene Blue	99	[97]
Zeolite	Methylene Blue	88	[98]
Mg/Fe-CO_3	Malachite Green	86	[90]
Raw Moroccan clay	Malachite Green	—	[89]
Bentonite	Malachite Green	90	[98]
Moroccan clay	Basic Red 46	95	[98]
Raw clay (smectite)	Reactive Red 120	88	[99]
Raw clay (kaolinite)	Reactive Red 120	94	[99]

Table 3.
Adsorption capacities of some clay adsorbents for the removal of toxic dyes from water and wastewater.

synthetic or modified, was compared with regard to removing dyes based on some experimental parameters including pH, temperature and initial dye concentration. It was found that synthetic and modified clays provide a greater efficiency relating the removal of these organic pollutants.

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References

[1] Yao W., Yu S., Wang J., Zou Y., Lu S., Ai Y., Alharbi N.S., Alsaedi A., Hayat T., Wang X., Chem. Eng. J. 307 (2017) p. 476-486

[2] Robinson T., McMullan G., Marchant R., Nigam P., Bioresour. Technol. 77 (2001) p.247-255

[3] Yagub M.T., Sen T.K., Afroze S., Ang H.M., Adv. Colloid Interf. Sci. 209 (2014) p.172-184

[4] Han R, Ding D, Xu Y, Zo W, Wang Y, Li Y, Bioresour Technol. 99(2008) p.2938-46

[5] Chiban M., Soudani A., Zerbet M., Sinan F., Wastewater treatment processes. Chap. 10, Handbook of Wastewater treatment: Biological Methods, Technology and Environmental Impact, Editors: Cesaro J. Valdez and Enrique M. Maradona, Nova science publishers, Inc. New York, 2013, pp. 249-262, ISBN: 978-1-62257-591-6.

[6] Rijn J. V., Tal Y., Schreier H., J. Engg. 34 (2006) p. 364-376.

[7] Bhatnagar A., Sillanpaa M.,. Chem. Eng. J., 168 (2) (2011) p. 493-504

[8] Rozada F., Calv L.F., García A.I., Martín-Villacorta J., Otero M., Bioresour. Technol. 87 (2003) p. 221-230.

[9] Chiou M.S., Ho P.Y., Li H.Y., Dyes Pigments.60 (2004) p. 69-84.

[10] Janos P., Buchtova H., Rznarova M., Water Res. 37 (2003) p. 4938-4944.

[11] Wu X., Wang W., Li F., Khaimanov S., Tsidaeva N., Appl. Surf. Sci.389 (2016) p. 1003-1011.

[12] Wang S.L., Hseu R.J., Chang R.R., Chiang P.N., Chen J.H., Tzou Y.M., Colloids Surf. A: Physicochem. Eng. Aspects 277 (2006) p. 8-14

[13] Gou Y., Yang S., Fu W., Qi J., Li R., Wang Z., Xu H., Dyes Pigments. 56 (2003) p. 219-229.

[14] Ozdemir O., Armagan B., Turan M., Çelik M.S., Dyes Pigments 62 (2004) p. 49-60.

[15] Chiban M., Zerbet M., Carja G. Sinan F., Environ. Chem. Ecotox. 4(2012) p. 91-102

[16] Shih MC. Desalination. 172 (2005) p. 85-97.

[17] Kang S.Y, LEE J.U, Moon S.H, Kim K.W. Chemosphere. 56 (2004) p. 141-147

[18] Alyuz, B, Veli, S.. J. Hazard Mater. 167 (2009) p. 482-488

[19] Huang CP, Fu PLK.. J. Water Pollut. Control Fed 56 (1984) p. 233-242.

[20] Gimbel R, Hobby R, Discharge of arsenic and heavy metals from activated carbon filters during drinking water treatment. Wasser Rohrbau, 51 (2000) p. 15-16.

[21] Salleh M.A.M., Mahmoud D.K., Karim W.A.W.A., Idris A., Desalination 280 (2011) p. 1-13.

[22] Dawood S., Sen T.K., J. Chem. Process. Eng. 1 (2013) p. 1-7

[23] Ming Ni Z., Jie Xia S., Geng Wang L., Fang Xing F., Xiang Pan G., J. Colloid Interface Sci. 316 (2007) p.284-291.

[24] Li F., Wang Y., Yang Q., Evans D.G., Forano C., Duan X., J. Hazard. Mater. 125 (2005) p.89-95.

[25] Ait Ichou A., Abali M., Chiban M., Carja G., Zerbet M., Eddaoudi E., Sinan F., J. Mater. Environ. Sci. 5 (2014) p. 2444-2448.

[26] Aschenbrenner O., Guire P., Alsamaq S., Wang J., Supasitmongkol S., Al-Duri B., Styring P., J. Wood, Chem. Eng. Res. Des. 89 (2011) p.1711-1721.

[27] Reichle W.T., Solid State Ion. 22 (1986) p.135-141.

[28] Ait Ichou A., Élaboration et caractérisation d'argiles de type hydroxyde double lamellaire : Application à l'adsorption des ions métalliques en milieu aqueux, thesis of Ibn Zohr University, Morocco, 2019.

[29] Richetta M, Medaglia PG, Mattoccia A, Varone A, Pizzoferrato R (2017) Layered Double Hydroxides: Tailoring Interlamellar Nanospace for a Vast Field of Applications. J Material Sci Eng 6: 360.

[30] Krikaa F., Benlahbiba O.F., Desalin. Water Treat. 53 (2015) p.3711-3723

[31] Mekatel E., Amokrane S., Aid A., Nibou D., Trari M., Comptes Rendus Chimie .18 (2015) p.336-344

[32] Zheng Y.M., Li N., De Zhang W., Colloids Surf. A. Physicochem. Eng. Asp, 415 (2012) p. 195-201

[33] Ni Z., Xia S., Wang L., Xing F., Pan G., J. Colloid Interface Sci., 316 (2007) p. 284-291

[34] Kang H. T., Lv K., Yuan S. L., Appl. Clay Sci, 72 (2013) p.184-190.

[35] Ran-ran Shan , Liang-guo Yan, , Yan-ming Yang, Kun Yang , Shu-jun Yu , Hai-qin Yu , Bao-cun Zhu , Bin Du, J. Ind. Eng. Chem. 21 (2015)p. 561-568

[36] Zubair M., Jarrah N., Ihsanullah, A. Khalid, M. Manzar, T. Kazeem, M. Al-Harthi A., J. Mol. Liq. 249 (2018) p. 254-264

[37] Zheng Y.M., Li N., De Zhang W., Colloids Surf. A. Physicochem. Eng. Asp, 415 (2012) p. 195-201

[38] Zaghouane-Boudiaf H., Boutahala M., Arab L., Chem. Eng. J. 187(2012) p.142-149

[39] Aisawa S., Hirahara H., Uchiyama H., Takahashi S., Narita E., J. Solid State Chem., 167 (2002) p.152-159.

[40] Yang Z., Ji S., Gao W., Zhang C., Ren L., Weei W., Zhang Z., Pan J., Liu T., J. Colloid Interface Sci. 408 (2013) p. 25-32,

[41] Hassanzadeh-Tabrizi S.A., Motlagh M.M., Salahshour S., Appl. Surf. Sci. 384 (2016) p. 237-243.

[42] Chen C D., Li Y., Zhang J., Li W., Zhou J., Shao L., Qian G., , J. Hazard. Mater. 243 (2012) p. 152-160

[43] Bharali D., Deka R.C., Adsorptive removal of congo red from aqueous solution by sonochemically synthesized NiAl layered double hydroxide, J. Environ. Chem. Eng., , 5 (2017) p. 2056-2067.

[44] Lafi R., Charradi K., Djebbi M.A., Amara A.B.H., Hafiane A., Adv. Powder Technol. 27 (2016) 232-237.

[45] Nguyen Thi H. T., Nguyen D.C., Nguyen T.T., Tran V.T., Nguyen H.V., Bach L.G., Vo D.V.N., Nguyen D.H., Thuan D.V., Do S.T., Nguyen T. D., Key Engineering Materials, 814 (2019) p 463-468

[46] Ayawei N., godwin J. and wankasi D., Int. J. Chem. Sci. 13(3), (2015) p. 1197-1217

[47] Ayawei, N, Angaye S.S. Wankasi, D, Int. J. Appl. Sci. 7 (2017) 83-92.

[48] Selim Y., J. Disper. Sci. Technol. 7 (2017) 83-92.

[49] Shi Z., Wang Y., Sun S., Zhang C., Wan H., Water Sci. Technol. 81 (2020) p. 2522-2532

[50] Bouteraa S., Boukraa F. Saiah D., Hamouda S., Bettahar N., Bulletin of Chemical Reaction Engineering & Catalysis, 15 (2020) p.43-54

[51] Chaari I., Medhioub M., Jamoussi F., J. Appl. Sci. Environ. Sanitat. 6(2011) p.143-148.

[52] Moore D.M., Reynolds R.C., Oxford university press, Oxford, 1989.

[53] Murray H.H., Applied Clay Mineralogy: Occurrences, Processing and Applications of Kaolins, Bentonites, Palygorskitesepiolite, and Common Clays, Elsevier (2006)

[54] Liu P., Zhang L., Sep. Purif. Technol. 58 (2007) 32-39

[55] Nandi B.K., Goswami A., Purkait M.K., J. Hazard. Mater. 161 (2009) p.387-395.

[56] Tunega D, Haberhauer G, Gerzabek MH, Lischka. Langmuir 18 (2002) p.139-147

[57] Zakaria RM, Hassan I, El-Abd MZ, El-Tawil international water technology conference (IWTC), Hurghada, 13 (2009) p 403-416

[58] Stockmeyer M, Kruse K, Clay Miner 26 (1991) p.431-434

[59] Zubair M., Jarrah N., Ihsanullah A., Khalid M., Manzar T., Kazeem M., Al-Harthi A., J. Mol. Liq. 249 (2018) p.254-264.

[60] Nadeem R., Manzoor Q., Iqbal M., Nisar J., J. Ind. Eng. Chem. 35(2016) p.185-194.

[61] Naeem H., Bhatti H.N., Sadaf S., Iqbal M., Appl. Radiat. Isot. 123(2017) p.94-101.

[62] Shoukat S., Bhatti H.N., Iqbal M., Noreen S., Microporous Mesoporous Mater. 239 (2017) p.180-189.

[63] Tahir M.A., Bhatti H.N., Iqbal M., J. Environ. Chem. Eng. 4 (2016) p.2431-2439.

[64] Tahir N., Bhatti H.N., Iqbal M., Noreen S., Int. J. Biol. Macromol. 94(2016) p.210-220.

[65] Rashid A., Bhatti H.N., Iqbal M., Noreen S., Ecol. Eng. 91 (2016) p.459-471.

[66] Tahir M., Iqbal M., Abbas M., Tahir M., Nazir A., Iqbal D.N., Kanwal Q., Hassan F., Younas U., , Acta Ecol. Sin. 37 (2017) p.207-212.

[67] Zaghloul A., Ait Ichou A., Benhiti R., Abali M., Soudani A., Chiban M., Zerbet M., Sinan F., Mediterr.J. Chem. 9(2) (2019) p.155-163

[68] Huang R., Adsorption of methyl orange onto protonated cross-linked chitosan, Arab. J. Chem. 10 (2017) p.24-32

[69] Boumchita S., Lahrichi A., Benjelloun Y., Lairini S., Nenov V., Zerrouq F., J. Mater. Environ. Sci. 7 (1) (2016) p.73-84

[70] Janos P., Buchtova H., Rznarova M., Water Res 37 (2003), p.4938-4944.

[71] Gou Y., Yang S., Fu W., Qi J., Li R., Wang Z., Xu H., Dyes Pigments, 56 (2003), p.219-229.

[72] Elmoubarki R., Mahjoubi F., Tonsadi A., Abdennouri M., Sadiq M., Qourzal S., Zouhri A., Barka N.., J. Mater. Res. Technol. 3(2017) p.271-283.

[73] Sureshkumar M.V, Namasivayam C., Colloids Surf. A: Physico chem. Eng. Aspects, 317(2008): p.277-283

[74] Aziam R., Chiban M., Eddaoudi H., Soudani A., Zerbet M. and Sinan F., Eur. Phys. J. Special Topics 226 (2017) p.977-992.

[75] Krikaa F., Benlahbiba O.F., Desalination and Water Treatment 53 (2015) 3711-3723

[76] Toor M., Jin B., J. Am. Chem. Soc, 38 (1916), p.2221-2295

[77] Chiban M. (2011) Élaboration et Évaluation d'un Nouveau Procédé d'Épuration des Eaux : Application à des solutions modèles et d'eaux usées domestiques et industrielles de la région d'Agadir. Editions Universitaires Européennes, ISBN: 978-613-1-58836-5, 272p.

[78] Chiban M., Zerbet M., Sinan F. (2012) Low-cost materials for phosphate removal from aqueous solutions. Chap.1, Handbook of Phosphates: Sources, Properties and Applications, Nova Science Publishers, Inc. New York, pp.1-42, ISBN: 978-1-61942-123-3.

[79] Huang R., Arab. J. Chem, (2017) 10: p.24-32

[80] Freundlich H.M.F., Phys. Chem, (1906) 57: p.385-47029.

[81] Bentahar S., Dbik A., El Khomri M., El Messaoudi N., Bakiz B., Lacherai A.,. Res. Chem. Chem. Eng. Biotechnol. Food Ind. 17 (2016) p.295

[82] Shamsayei M., Yamini Y., Asiabi H., J. Colloid Interface Sci (2018) 529: p.255-264

[83] Elass K., Laachach A., Alaoui A., Azzi M., Appl. Clay Sci. 54 (2011) p.90-96

[84] Zhou Q., Gao Q., Luo W., Yan C., Ji Z., Duan P., Colloid. Surf. A Physicochem. Eng. Asp.470 (2015) p.248-257.

[85] Fan H., Zhou L., Jiang X., Huang Q., Lang W., Appl. Clay Sci. 95(2014) p.150-158.

[86] Dalhat N., Haladu S.A., Jarrah N., Zubair M., Essa M.H., Ali S.A., J. Hazard. Mater, 342 (2018) p.58-68.

[87] Shan R., Yan L., , Yang K., , Yu S., , Hao Y., , Yu H., , Du B,., Chem. Eng. J. 2014, 252, p.38-46.

[88] Chen D., Chen J., Luan X., Ji H., Xia Z.. Chemical Engineering Journal 171 (2011) p.1150-1158

[89] Tahir S.S., Naseem R., Chemosphere 63(2006): p.1842-1848

[90] Bharalia D., Deka R.C., Environmental Chemical Engineering 2017

[91] Lafi R., Charradi K., Djebbi M.A., Amara A.B.H, Hafiane A Adv. Powder Technol. (2016) 27: p.232-237

[92] Nwokem N.C., Nwokem C.O., Ayuba A.A., Usman Y.O., Odjobo B.O., Ocholi O.J., Batari M.L., Osunlaja A.A., Arch Appl Sci Res(2012) 4: p.939-946

[93] Lian L, Guo L, Guo C . J Hazard Mater (2009) 161: p.126-131

[94] Elass K, Laachach A, Alaoui A, Azzi M Appl Ecol Environ Res 8(2010) p.153-163

[95] Bellir K, Bencheikh-Lehocine M, Meniai A-H. Int Renew Energy Congr (2010): p.360-367

[96] Abd El-Latif MM., El-Kady MF., Ibrahim AM., Ossman ME., J Am Sci (2010) 6: p.280-292

[97] Zhu J., Wang Y., Liu J., Zhang Y., Ind. Eng. Chem. Res. 53 (2014) p.13711-13717.

[98] Bennani-Karim A, Mounir B, Hachkar M, Bakasse M, Yaacoubi A . Can J Environ Constr Civ Eng(2011) 2: p.5-13

[99] Errais E, Duplaya J, Elhabiri M, Khodjac M, Ocampod R, Baltenweck-Guyote R, Darragi F. Colloids Surf A. 403(2012) : p.69-78.