International Journal of Chemical and Biochemical Sciences
(ISSN 2226-9614)
Journal Home page: www.iscientific.org/Journal.html

Adsorption of dyes through bentonite and zeolite based composite materials – A comprehensive review

Ifrah Javed[1], Jamal Nasser Al-Sabahi[2], Farwa Nadeem[1]* and Muhammad Idrees Jilani[3]

[1]Department of Chemistry, University of Agriculture, Faisalabad-38040-Pakistan, [2]Central Instrumental Laboratory, College of Agricultural and Marine Sciences, Sultan Qaboos University, Muscat, Oman and [3]Department of Chemistry, University of Sahiwal, Sahiwal, Pakistan

Abstract

Removal of dyes from wastewater discharge by textile industries has been a matter of great concern both in aesthetic sense and health point of view. Various technologies for dye removal from wastewater are classified into chemical, physical and biological methods. Among all techniques reported so far, effectiveness of adsorption has made it an ideal alternative to others. This technique is economical, shows promising results and overcome different demerits of other techniques such as high cost and sludge problem. Adsorption method offers unique advantages owing to the use of natural absorbents such as bentonite clay and zeolite materials for dyes removal due to its easy availability, low cost, eco-friendly nature and great affinity for dyes. This review summarizes previous studies on adsorption capacities concerning bentonite clay, zeolite materials and composites as absorbents for removing wastewater pollutants. Results obtained from the studies suggested that composite materials exhibit better adsorption efficiency for adsorptive removal of dyes. This article also evaluates the effect of various parameters on adsorption phenomenon such as contact time, pH, temperature, adsorbent dosage and initial dye concentration. Generally at low pH, the anionic dye removal percentage from solution increases with increase of pH. Characterization technique such as scanning electron microscopy (SEM) is described for structural analysis and ordering determination. X-ray diffraction (XRD) and fourier transform infrared spectroscopy (FTIR) techniques are also discussed here for determination of chemical arrangement, structure of adsorbent and functional groups.

Keywords: Wastewater, Dyes, Bentonite, Zeolite, Composite Adsorbent, XRD, FTIR

Full length article **Corresponding Author*, e-mail: farwa668@gmail.com

1. Botany

1.1 Introduction

Water is the basic requirement for the sustenance of all life forms on earth. Good quality water should be accessible for continuation of numerous activities of life. In the present universal scenario, availability of freshwater is very serious concern towards population growth, anthropogenic activities, unplanned urbanization, fast industrialization, agricultural, domestic activities and unskilled application of natural water that generate wastewater containing inorganic and organic pollutants [1]. For health of human, most severe effect is the absence of safe drinking water and improved sanitation, which presently affects more than a third part of the world's population. The United Nations Environment Programme (UNEP) and United Nations World Water Assessment Programme reported that approximately 70% industrial wastes in few developing countries might be cleared without treatments into shallow water and polluting the usable supply of water. The World Health Organization (WHO) reported that health of about 250 million people in the world has been affected by water pollution and approximately 3.5 billion people in 2025 will face the shortage of water due to pollution of water possessions [2].

Wastewater pollution has become a worldwide critical issue due to industrial revolution regarding industrialized and developing countries [3]. Intense industrial events contaminate the wastewater with numerous contaminants such as dyes, phenols, toxic heavy metals and other persistent organic pollutants. These pollutants pass in the food chain and cause toxic effects such as cancer, irrigating of plants with contaminated water, thereby affecting the marine biota and human health [4]. Among all industries, textile dyeing industry is the major contributor in environmental pollution because of immense release of wastewater which contains high concentrations of dyes. These industries use dyes for colouring process and after usage 15-20% of dyes are released into the wastewater. Approximately over 7×10^5 tons of dyes are produced per annum for textile fibres and they have world annual generation of over 80 million tons. These dyes present in water even at low proportion, e.g. 10% exert vast negative impacts on environment [5].

Dyes are colourful materials which are designed to give colour to the supplies such as papers, fabrics or any other type of colourable constituents. Humans have been applying these materials for over thousands of years for number of applications [6]. Dyes have complex structure and are not easily biodegradable. When dyes have served their purpose, they are mostly released without additional care into the environment and natural water bodies. Discharge of these dyes in water is aesthetically displeasing, very harmful to human bodies, biological organisms and cause different environmental issues. Dye wastes can endanger the lives of humans and animals because they are carcinogenic and naturally poisonous. Dyes give colour to water bodies so it is easy to advert these water resources [7]. Occurrence of dye wastes in water sources is not acceptable because water is essential for humans and animals for regular events such as drinking, cooking, washing and bathing [6]. Removal of these dye pollutants from polluted wastewater has gained attention between the scientific community and it is important to treat wastewater before being discharged [1].

Many procedures for wastewater treatment have been applied for dyes removal such as chemical coagulation/flocculation, fenton process, ozonation, electrochemical degradation, adsorption process, oxidation, chemical precipitation, nano-filtration, ion exchange, sorption and biosorption. These methods have numerous drawbacks during practical application such as deficiency of complete dye removal and production of dangerous secondary wastes. So, adsorption is rapidly gaining prominence due to availability of known procedure equipment, low cost, sludge-free operation and regaining of adsorbent [8]. Various materials are used as adsorbents such as activated carbon, chitin, cellulose, agriculture wastes, zeolites and clays for dyes removal. But clay minerals show strong attraction for adsorption of dyes due to their high surface area, morphology and ion-exchange potentials.

Clay is a natural material that is used as adsorbent for decontamination of water [9]. It is usually ultrafine-grained material (usually less than 2 micrometres in size) which requires distinct analytical procedures for identification. Mostly, natural clay minerals such as hectorite, montmorillonite (MMT), laponite, sepiolite, bentonite, kaolinite (KLN), zeolite and chlorite are used. It mainly exists in form of hydrous aluminium phyllosilicates along with magnesium, iron, alkali metals and various other potential compounds [10]. Bentonite (BT) is a type of layered silicate clay mineral which is composed of atleast 50% smectite and more precisely montmorillonite. It is used as adsorbent material on industrial scale. Bentonite is modified by numerous procedures to improve adsorption capacity such as thermal activation, acid activation and composites formation [11]. Zeolite minerals exhibit high ion exchange capacity, sorption potentials, surface area and chemical stability. These are nano-porous aluminosilicates. They are known to have negatively charged surface, high ion exchange capability and smaller number of cations to balance the surface charge [12]. Composite materials are mostly based on principle of combining two or more materials in a specific manner. They exhibit modified properties compared with their individual components. In this study, adsorption behaviour of bentonite, zeolite and different clay composite materials for dyes and other pollutants are evaluated [13].

2. Contamination of Wastewater

Wastewater contamination is very serious environmental hazard all around the world due to excessive urbanization and rapid industrialization. This contamination is produced by adding biological and chemical materials either naturally or manufactured to the natural water forms [14]. Sources of wastewater pollutants include domestic and hospital effluents, runoff from agriculture, livestock and aquaculture, landfill leachates and wastewater from cities and industries. Different organic, inorganic and biological impurities are added in water through anthropogenic and natural activities [15]. These contaminants arrive in food chain and cause deadly effects such as cancer, irrigating of plants with contaminated water, so they affect human health and aquatic biota [16].

2.1 Inorganic Pollutants

These are non-biodegradable compounds and persist in environment. Their presence in water makes them harmful for biological life. They contain inorganic salts, mineral acids, trace elements, heavy metal compounds, complexes of organic compounds with metals, sulphates and cyanides etc. Toxic heavy metals are most common inorganic pollutants. Heavy metals such as arsenic (As^{3+}), mercury (Hg^{2+}), cadmium (Cd^{2+}), chromium (Cr^{6+}) and lead (Pb^{2+}) are numerous destructive inorganic pollutants that are found in the surroundings [17]. Accumulation of heavy metals has hostile effect on marine flora and fauna and cause public health issues. Water contamination due to potentially toxic rudiments has increased over the last few decades and it characterizes health hazards to animals, humans and plants [2].

2.2 Radioactive Pollutants

Radioactive materials initiate from processing of ores and mining and used in agriculture, research, industrial activities and medicines for example P^{32}, Co^{60}, Ca^{45}, S^{35} and C^{14} etc. These isotopes are lethal to all life forms when collected in teeth, bones and cause serious syndromes. Safe concentration for life period consumption is $1x10^{-7}$ micro curies per ml.

2.3 Organic Pollutants

Organic pollutants contain dyes, pathogens, polyaromatic hydrocarbons, alkyl phenols polychlorinated biphenyls, dioxins and furans, chlorinated solvents, paints, antibiotics, insecticides and pharmaceuticals in wastewater [18]. The agriculture wastewater contains substantial concentration of organic pollutants such as nitrogen and phosphorous [15]. During the last years, antibiotics recognized as new class of water pollutants [19]. These contaminants are continuously discharge in environment from some anthropogenic sources for example urban wastewater treatment plants. Some antibiotics are not entirely metabolised during the therapeutic use, so enter through excretion to the sewage in unchanged form [20]. Organic compounds such as pharmaceuticals are also detected in the groundwater and surface. They are linked with disposal of wastewater. They comprise human and veterinary antibiotics e.g. erythromycin, ciprofloxacin, sulfamethoxazole and various other prescription drugs such as codeine, carbamazepine and salbutamol. Some of these pollutants can accumulate in the environment and be a part of living organisms through food chain [18].

3. Dyes as Pollutants

Dyes are coloured complexes that are widely used in industries such as textiles, plastics, rubber, leather, printing and cosmetics to colour their stuff that resultantly generate a huge amount of coloured wastewater. Dyes are mostly derived from the natural sources without use of any chemical action such as insects, plants, minerals and animals. These dyes are always found in industrial waste after usage and released in the water body [1]. Dye contaminated wastewater in the environment is considered as a harmful source of pollution for organisms. Approximately more than 10,000 dyes are available commercially with over 7×10^5 tonnes of dye material produced per annum. It is estimated that 2% of dyes are annually produced and discharged in the effluents from linked industries. Among numerous industries, textile industry lines first in use of dyes for the process of coloration of fibres. Textile industry (54%) discharges highest amount of dye effluents, which contribute in more than half of present dye effluents seen in environment around the world. Consumption of textile dyes is more than 1000 tones/year and about 10-15% dyes are released into wastewater during the process of dyeing which leads to the special environmental concern [21]. Textile wastewater is categorized by some fluctuations in the parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), colour, salinity and pH. Composition of wastewater depends on various organic compounds, dyes and chemicals. Recalcitrant organic toxicant, coloured chlorinated compounds, heavy metals ions and dyes are main contaminants in textile effluents [22].

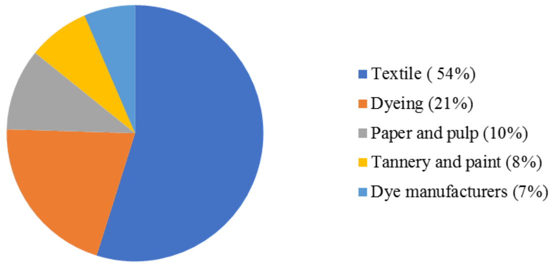

Fig 1 Presence of dye effluents in different industries

4. Harmful Consequences of Contaminated Water

Dye contaminated wastewater is discharged into the rivers and natural streams which cause severe problems to food web, aquatic life and causes damage to aesthetic nature of environment. Dyes can absorb sunlight and reflect it while entering in water, so can hinder the bacterial growth and resist photosynthesis in aquatic plants. Moreover, they resist to aerobic biodegradation, causing challenge to the environmental researchers [23]. Hence, dye-bearing wastewater pose serious hazard to the health of humans and cause skin irritation, allergic dermatitis, mutation, cancer, shortness of breath, produce burning sensation and very toxic to aquatic life. Wastewater contains BOD (biochemical oxygen demand), COD (chemical oxygen demand) in high concentration, huge amount of suspended solids and other contaminants [24]. Dyes molecules are stable to the light and cannot biologically degrade easily. These molecules are resistant to aerobic digestion and difficult group to be removed from industrial wastewater [25]. Dyes have different classes such as cationic (basic dyes), anionic (direct, acid and reactive dyes) and dispersive dyes (non-ionic) [21]. Keeping the essentiality of colour removal, industries require some efficient and precise methods to treat dye contamination before discarding into water bodies.

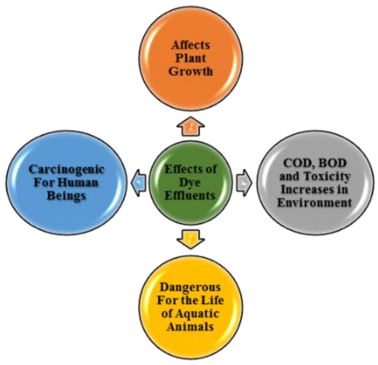

Fig 2 Different effects of taxtile dye effluents

5. Methods for Dye Removal

To avoid resources of water from dyes contaminants and for healthy environment, development of some eco-friendly and efficient methods for toxic dyes removal from industrial wastewater is highly desirable before they are released into freshwater reserves [26]. Several physical, chemical and biological methods for example membrane process, adsorption, photocatalytic degradation, osmosis, coagulation/flocculation, ion exchange and flotation have been used usually for removal of toxic pollutants from wastewater and natural water bodies [1]. The selection of treatment process for contaminated water depends on the nature of pollutants. Some procedures have some disadvantages such as high operating cost, incomplete removal and high energy requirements [2].

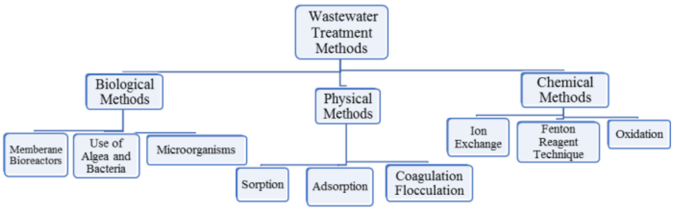

Fig 3 Various dye removal methods from wastewater

5.1 Biological Methods

Biological methods include use of algae, bacteria and fungi species. Biological method is appropriate to eliminate dissolved organic materials from textile effluents. Removal efficiency of these materials depends on organic load ratio vs. dye load and load of micro-organism, range of temperature and concentration of oxygen [27]. Many micro-organisms can be used in bio-colorization process such as fungi, algae and bacteria. These bio-sorbents are highly economical and easily available as dead or living micro-organism, from breeding of mushrooms, chitosan, peat and wastes of plants [28]. Various bacterial sp. such as *Pseudomonas putida, Pseudomonas aeruginosa, Aeromonas hydrophila, Lysin bacillus fusiformis, Coma monas testosterone* and *Corynebacterium glutamicum* can be used for dye removal. The most important disadvantage for biological treatment methods is that many of these processes are very time consuming. For example, mix bacteria decolorization needs upto 30 hours for completion [29].

5.2 Chemical Methods

Chemical methods include advanced oxidation method using Fenton's reagent, hydrogen peroxide, ozonisation, solvent-extraction method, ion exchange and oxidation. Chemical methods include advanced oxidation process, which is based on mechanism of hydroxyl radical's generation. These radicals are used as oxidising agents. Organic peroxide radicals are generated by the attack on chromo-genic groups. Similarly, H_2O, CO_2 and inorganic salts formation also takes place as a result of these chemical reactions. Using hydrogen peroxide has attained prominent position among oxidising agents because of its commercial availability and its oxidative nature. It can be used for oxidation process directly or in combination with catalysts or with UV radiation. However, some drawbacks have been found with its use as it fails to oxidize some organic pollutants [30].

5.3 Physical Methods

Physical methods include process of adsorption involving natural adsorbents, agricultural and industrial adsorbents, surfactant, sorption, electro-kinetic coagulation and coagulation-flocculation etc.

5.3.1 Electrocoagulation Process

It is simple, reliable physico-chemical technique and effective tool for the removal of dyes, which shows promising better results. This method contains 3 stages. In 1st stage, oxidation of sacrificial anodic electrodes and then generation of coagulants occur. Stage 2 involves destabilization of pollutants and their emulsions break out. In stage 3 formation of flocs occur. This method contains coagulants formation in the reactor site without using help of any external agency by the oxidation of sacrificial anodic electrodes such as aluminium, stainless steel, iron and many others. Process is found to be quite effective in removal of contaminants, colloidal particles, metal ions and dyes [31]. But this treatment produce foul odour and by products and is quite expensive in nature.

5.3.2 Coagulation Flocculation

This technique is widely used in solid–liquid separation procedure for the elimination of dissolved and suspended solids, organic matter and colloids present in the industrial wastewater. Coagulation-flocculation is efficient and simple technique that is extensively used in treatment of several wastewater effluents such as palm oil mill effluent, pulp mill wastewater and textile wastewater. Dispersed or finely divided particles are gathered to form the large particles (flocs) when coagulants and/or flocculants add. They settle down and clarify the system [32].

6. Adsorption

Among many treatment techniques, adsorption is gaining importance rapidly as a process of treating aqueous effluent [4]. It is best technology for decontamination of water and removal of almost all type of contaminants. This physico-chemical technique has advantages of having availability of known process equipment, low cost, recovery of adsorbent and sludge-free operation [29]. Adsorption is top quality treatment process for dissolved organic contaminants removal like dyes from wastewater of industries. In this process, concentration of constituents takes place on the surface of solid bodies as surface phenomenon always deals with operation of surface forces. When absorbable solute, also known as adsorbate, in solution, meets a solid (adsorbent) with highly porous surface, then liquid-solid intermolecular forces of attraction cause the solute molecules to be concentrated at the surface of solids. An adsorption phenomenon has gained interest for dyes removal due to its flexibility in design and low cost and this procedure does not generate any harmful substances after removal of the target compounds. Characteristics that can affect the removal of contaminations are specific surface area, adsorption capacity, grain size, pore volume and pore size distribution. At present year, various commercially available and cost-effective adsorbents have been used for dyes removal from textile wastewater [21].

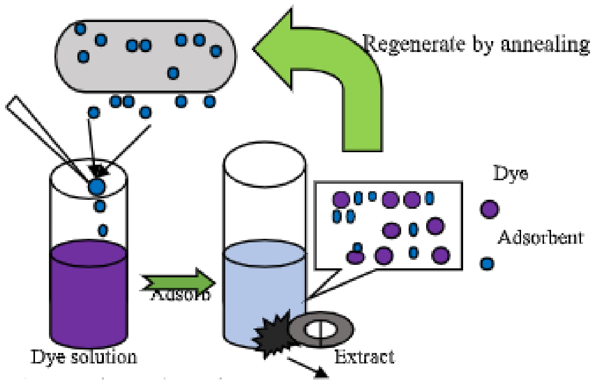

Fig 4 The process of adsorption

7. Types of Adsorbents

Adsorbent is insoluble sponge-like porous material with ability to trap adsorbate elements onto itself. Natural materials and sometime waste materials are used as adsorbent for dye removal from textile wastewater [33]. Some high efficiency and low cost materials can be used as adsorbents for dye removal [6].

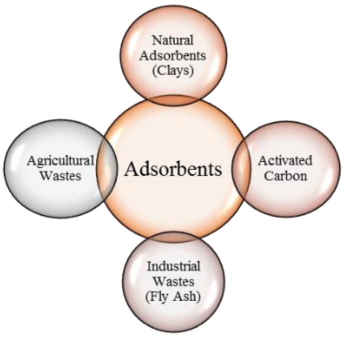

Fig 5 Types of adsorbents for water treatment

7.1 Activated Carbon

This material is widely used as adsorbent for the removal of dyes due to its micro-pore structures, extended surface area, high degree of surface reactivity and adsorption capacity. Still, commercially accessible activated carbon has high regeneration price when it is exhausted and expensive. Besides, production using solution generates small supplementary effluents, whereas regeneration by refractory method results in 10–15% loss of adsorbent and its uptake capability [4].

7.2 Chitin and Chitosan

The use of adsorbents comprising natural polymers for example chitin and its derivative chitosan has received reorganization in recent few years. Chitin contains 2-acetamido-2-deoxy-β-D-glucose through a β (1→4) linkage. Chitin is considered to be a second most copious biopolymer worldwide approaching from renewable organic resource [34]. Initial form of chitin (pure) molecule is not expensive and easily available. Chitosan comprises 2-acetamido-2-deoxyβ-D-glucopyranose and 2-amino-2-deoxy-β-D-glucopyranose remainders. Chitosan is effective biosorbent for wastewater contaminants including dyes, metals, fluoride and phenols due to its low cost as compared to activated carbon. High contents of hydroxyl and amino functional groups, shows high adsorption capacity for numerous aquatic contaminants. These biopolymers are substitute to the other biomaterials because of chemical stability, physico-chemical characteristics, high selectivity and reactivity toward contaminants [1].

7.3 Agricultural Waste Materials

Utilization of agricultural waste material has great significance. Many agricultural wastes are being considered for different dyes removal from aqueous solutions at diverse operating conditions. These materials proved to be inexpensive adsorbents and are easily available. They have high potential for the dyes removal [35]. Agricultural waste materials include "orange peel", "coir pith", "rice husk", "banana peel", "straw", "almond shell", "pomelo peel", "broad bean peel", "casuarina equisetifolia needle" (CEN), "durian seeds" and "annona squamosa seeds" etc. They have minute or no economic value and frequently pose a disposal issue.

7.4 Clays (Natural Adsorbent)

Clays are naturally occurring adsorbent materials which are composed of fine-grained minerals. Clay minerals are hydrous aluminium phyllosilicates and exhibit excellent ion exchange potential, high sorption capacity and large abundance in nature. These naturally occurring adsorbents are cheap and work effectively for dye removal [29]. They are effective adsorbents because of layered structure and their particles possess strong attraction towards anions and cations because surface area has exchangeable ions that play significant role in the adsorption phenomena. Clay minerals are naturally available on the surface of earth, pose no threat to environment. They have silica and alumina as main components [36]. Different clays such as sepiolite, bentonite, smectite, zeolite, montmorillonite, alunite and perlite are valuable because of their high chemical and mechanical stability, high specific surface area and different surface and structural properties [37]. Naturally occurring raw and modified clays have revealed good results as adsorbents for several dyes removal [38].

8. Bentonite Clay as Adsorbent

Bentonite is the most extensively used adsorbent [39]. It exhibits different exclusive properties such as high cation exchange capacity, adsorption capability, porosity, high surface area and structural properties. It is usually used in applications of water decontamination. Bentonite is composed of smectite minerals with smaller amounts of other non-clay or clay minerals. It is impermeable, plastic and highly viscous when suspended in the water. It is available in almost all regions of the world [17]. Natural bentonite clay is generally used for the removal of different pollutants from wastewater because of its low cost, easy availability and eco-friendly nature [40]. It is modified by numerous methods to increase adsorption capacity, including thermal activation, acid activation and composites formation [41].

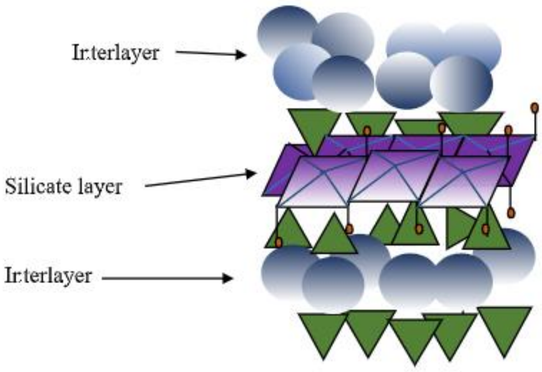

Fig 6 Structure of bentonite clay

9. Zeolite as Adsorbent

Zeolite minerals are nano-porous aluminosilicates that display sorption, high ion exchange potential, chemical stability and high surface area. They are crystalline solids with well-defined structures that contain aluminium, silicon and oxygen in their regular framework; water and cations in the structure are positioned in the pores. Zeolites are selective adsorbents which can be found in the environment and can also be synthesized in laboratory. These natural adsorbents are good contenders for contaminants elimination in water treatment application due to their micro-porous structure and three-dimensional network with the interconnected pore. Zeolite has different cavity structures, highly porous and have negative charge [29]. More than forty (40) different kinds of zeolite materials are obtainable in nature. Zeolite materials are specially featured by the high reactivity for complete recalcitrant pollutants removal and environmental remediation. It has received interest due to controllable pore structure, adsorption strength, exceptional chemical properties and higher ability for many organic and inorganic contaminants removal dissolved in aqueous media and even from gaseous environment [42].

10. Composite Materials

More recently, composite materials have gained widespread interest for treatment of wastewater. Clay composites exhibit a promising class of adsorbent materials for contaminants removal from wastewater to be used for drinking purposes. Composites are those materials which are made up of minimum two components and show improved physical or chemical properties as compared to individual components [41]. Individual characteristics of zeolite, activated carbon, bentonite and other adsorbents toward processes like adsorption are not very promising and identical. Due to this reason, idea of forming effective composite materials by combining them for the removal of dyes was conceptualized. Furthermore, inherited issues linked with individual adsorbent materials might be diminished by joining them. The present work is designed to investigate the adsorption efficiency of bentonite and zeolite materials individually and then their composite materials for dyes removal from wastewater [43].

Table 1 Maximum adsorption capacity and characteristics of bentonite based adsorbents

Clay (Adsorbents)	Pollutants Removed	Maximum Adsorption Efficiency mg g^{-1}	pH	Characterization of Adsorbent	References
Natural Bentonite Clay	Cadmium	13.5	6	SEM and XRD	[44]
Organobentonite	Remazol Blue RN	211	2	XRD, CHN Elemental Analysis, IR, Thermo-gravimetry and Zeta Potential	[45]
Hydroxyapatite-Bentonite Clay- Nano-crystalline Cellulose Composite	Arsenic As(III)	53.89	4.0-7.0	FTIR, TEM, EDX and SEM	[46]
Bentonite	Acid Blue 113 Dye	8.5	3	SEM, FTIR and TG/DTA	[47]
Bentonite Clay	Reactive Black 5 (RB5)	29-24	10	FTIR and XRD	[48]
Acid Activated Bentonite	Acid Red (AR57) Dye	416.3	2	EDX, XRD and FTIR	[49]
Acid Activated Bentonite	Acid Blue 294 Dye (AB294) Dye	119.1	2	EDX, FTIR and XRD	[49]

Magnesium Oxide Coated Bentonite (MCB)	Crystal Violet (CV+)	496	6.5	XRD	[50]
La (lll)-Modified Bentonite	Phosphate	14.0	6	SEM, EDX, XRD and XRF	[51]
CTAB Intercalated NA-Bentonite	Rhodamine B Dye	173.5	9	FTIR, Zeta Potential Analysis, XRD and SEM	[52]

Table 2 Maximum adsorption capacity and other features of zeolite based adsorbents

Adsorbent	**Pollutants Removed**	**Maximum Adsorption Efficiency mg/g**	**pH**	**Characterization of Adsorbent**	**References**
Magnetic Graphene Oxide Modified Zeolite	Methylene Blue Dye	97.346	10	SEM, XRD, FTIR, XPS and Magnetic Curves	[53]
Zeolite Based Hollow Fibre Ceramic Membrane	Cr (VI)	44%	4	SEM	[54]
3A Zeolite	Rhodamine B Dye	89.52%	9	FTIR and SEM	[55]
Mesoporous Zeolite-Activated Carbon Composite	Methylene Blue Dye	285.71	13	XRD, FTIR and SEM	[55]
Fe(lll)-Modified Zeolite-Alginate Beads	Pb^{+2}	136	4.7	XRD and FTIR	[56]
Natural Zeolite	Methylene Blue	29.18	7.5	XRD and FTIR	[57]
Natural Zeolite	Pb^{+2}	66-102	4	XRD and FTIR	[56]

Table 3 Pollutant removal efficiency of different composites as adsorbents

Composite	**Pollutants Removed**	**Maximum Adsorption Efficiency mg/g**	**pH**	**Characterization of Adsorbent**	**References**
Zeolite-Hydroxyapatite-Activated-Oil Palmash Composite	Tetracycline Antibiotic	244.63	3.3	XRD, SEM, FTIR and EDS	[58]
Crosslinked Quaternized Chitosan/Bentonite Composite	Amino Black 10B Dye	990.1	2-12	FTIR and XRD	[59]
Calcium Alginate-Bentonite Activated Carbon Composite Beads	Methylene Blue Dye	756.97	9	SEM, FTIR and BET Analysis	[43]
Bentonite/Alginate Composite	Crystal Violet Dye	36.3399	8.0	XRD, SEM and FTIR	[60]
Calcium Alginate-Bentonite-Activated Carbon Composite	Methylene Blue Dye	756.97	8.97	SEM, FTIR and BET Analysis	[43]

11. Factors Affecting Adsorption

Adsorption rate depends on some parameters such as pH, initial dye concentration, adsorbent dosage, contact time and temperature that severely affect the efficiency of adsorption. Changes in these factors will significantly affect the adsorption rate [6].

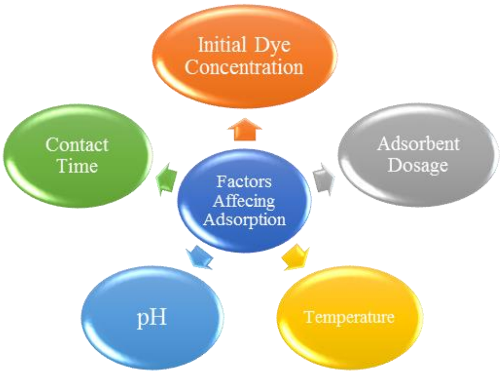

Fig 7 Factors affecting adsorption phenomenon

11.1 Effect of Initial Dye Concentration

Adsorption with the bentonite clay generally increases with increase of dye concentration till saturation is reached. Initial dye concentration generates significant driving gradient force to overwhelmed mass transfer resistance to the dyes between solid and aqueous phase. Zeolite also shows that increased dye concentration, increases the extent of degradation [61]. The adsorption uptake of zeolite activated carbon composite (Z-AC) material for methylene blue dye is 24.91-138.15 mg/g with increase in the initial dye concentration from 25 to 400 mg/g, which may be due to the pressure gradient. These findings indicated higher capacities of adsorption at higher initial concentration [62].

11.2 Effect of pH

Adsorption ability of dyes depends upon solution pH. Generally at low pH, the anionic dye removal percentage from solution increases because of electrostatic attraction between positive surface charge of anionic dye and adsorbent. Attraction is present between positively charged dye molecule and negatively charged adsorbent. When solution has high pH (basic), it decreases the removal percentage of anionic dye [63]. Optimized pH depends on type of clay used, nature of dye and modification of clay. Adsorption capacity of dyes using bentonite usually increases with increasing the pH. Removal percentage of methylene blue dye found to be lowest at the pH 3 (68.2%) and it gradually increases upto a certain pH range [43]. With modified zeolite, degradation of cationic dye, methylene blue increases with increase in pH value [61]. Under some acidic conditions, strong electrostatic attractions were found to be form in between acid (anionic) dye and positively charged surface of clay. When system's pH increases, adsorption decreases [64].

11.3 Effect of Contact Time

Dyes adsorption was found to increase with increase of time over bentonite adsorbent. For example, adsorption of acid blue 129 (AB129) dye over adsorbent in initial 20 minutes was rapid and then gradually increased. After about 55 minutes, equilibrium time was achieved [64]. The degradation of methylene blue dye increased from 22.08-52.65 percent for zeolite Y and further increased from 41.89-67.87 percent for Cu(II) incorporated zeolite Y, when reaction temperature was increased [61].

11.4 Effect of Adsorbent Dosage

Amount of adsorbent such as bentonite and zeolite dosage significantly affects the adsorption of dyes. With increasing the dosage, elimination efficiency was found to increase due to increase in available sorption surface sites resulting from increased adsorbent particles. Effect of the adsorbent dosage estimates the adsorption capacity of determined [45].

11.5 Effect of Temperature

With increase of temperature, percent degradation of cationic dyes such as methylene blue increased and for cationic dyes such as congo red dye also increased [65]. Using composite materials, effect of temperature was also studied. By increasing temperature, adsorption of dyes over composite material increased because of increased kinetic energy of molecules. When temperature of solution increased, volume of composite pores also increased with temperature and adsorption procedure is positively affected [13].

12. Analysis Techniques

12.1 Scanning Electron Microscopy (SEM)

SEM technique is mostly used for the structural analysis, ordering determination, morphologies (surface), cavities, cracks and fine particles which are attached to the surface of absorbent. Significant changes occurred on clay surface after the dyes adsorption [66].

12.2 X-Ray Diffraction Technique (XRD)

XRD is used for the determination of chemical arrangement and structure of absorbent before and after the adsorption [63]. XRD pattern of raw bentonite showed characteristic reflections associated to the presence of montmorillonite (Mt), muscovites (M) and quartz (Qt) [11].

12.3 Fourier Transform Infrared Spectroscopy (FTIR)

Functional groups are investigated using FTIR. This method also exhibits difference in the functional groups before and after the treatment. Some functional groups are common in different clays such as, Si-O is the functional group more commonly found in montmorillonite clay and Fe_3O_4/montmorillonite nano composites are the major part of bentonite clay.

13. Conclusion

Huge amount of industrial, domestic and agricultural wastewater needs to be treated before being released directly into the hydrosphere. Several different methods have been developed for water purification, but the process of adsorption has found to be most efficient and highly effective. The efficiency of adsorption of various wastewater pollutants specifically dyes was investigated using bentonite clay, zeolite and clay composite materials as adsorbents. In previous studies, naturally occurring raw clay and modified clay have shown good results for different types of dyes, metals and organic pollutants. Number of studies concluded that dye adsorption capacity of natural bentonite has tremendously been increased by incorporating different polymers and nanoparticles. Zeolite modified materials also gave best performance as an adsorbent to remove pollutants as compared to natural zeolite materials. Combined clay composites showed significant advantages over single-modified clays due to their high adsorption ability. Furthermore, non-toxic and environmentally compatible clay composites appeared to be an excellent alternative for removal of various pollutants of industrial wastewater. Previous studies concluded that different factors significantly influence the adsorption capacity. Such as, by increasing the reaction time and initial dye concentration, adsorption of dyes also increased. By increasing temperature, adsorption capacity of bentonite and zeolite materials on cationic dyes increased but efficiency of composite materials is far better than individual materials.

Referances

[1] A. Bhatnagar, M. Sillanpää. (2009). Applications of chitin-and chitosan-derivatives for the detoxification of water and wastewater—a short review. Advances in colloid and interface science. 152(1-2): 26-38.

[2] S.M. Shaheen, N.K. Niazi, N.E. Hassan, I. Bibi, H. Wang, D.C. Tsang, Y.S. Ok, N. Bolan, J. Rinklebe. (2018). Wood-based biochar for the removal of potentially toxic elements in water and wastewater: a critical review. International Materials Reviews. 1-32.

[3] F. Lu, D. Astruc. (2018). Nanomaterials for removal of toxic elements from water. Coordination Chemistry Reviews. 356: 147-164.

[4] K. Bharathi, S. Ramesh. (2013). Removal of dyes using agricultural waste as low-cost adsorbents: a review. Applied Water Science. 3(4): 773-790.

[5] W. Li, B. Mu, Y. Yang. (2019). Feasibility of industrial-scale treatment of dye wastewater via bio-adsorption technology. Bioresource technology.

[6] V. Katheresan, J. Kansedo, S.Y. Lau. (2018). Efficiency of various recent wastewater dye removal methods: A review. Journal of environmental chemical engineering.

[7] M. Vakili, M. Rafatullah, B. Salamatinia, A.Z. Abdullah, M.H. Ibrahim, K.B. Tan, Z. Gholami, P. Amouzgar. (2014). Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: A review. Carbohydrate polymers. 113: 115-130.

[8] S. Mishra, A. Maiti. (2018). The efficacy of bacterial species to decolourise reactive azo, anthroquinone and triphenylmethane dyes from wastewater: a review. Environmental Science and Pollution Research. 1-29.

[9] N. Singh, G. Nagpal, S. Agrawal. (2018). Water purification by using adsorbents: a review. Environmental Technology & Innovation.

[10] H. Han, M.K. Rafiq, T. Zhou, R. Xu, O. Mašek, X. Li. (2019). A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants. Journal of hazardous materials.

[11] L.N. Queiroga, M.B. Pereira, L.S. Silva, E.C. Silva Filho, I.M. Santos, M.G. Fonseca, T. Georgelin, M. Jaber. (2019). Microwave bentonite silylation for dye removal: Influence of the solvent. Applied Clay Science. 168: 478-487.

[12] N.M. Mahmoodi, M.H. Saffar-Dastgerdi. (2019). Zeolite nanoparticle as a superior adsorbent with high capacity: Synthesis, surface modification and pollutant adsorption ability from wastewater. Microchemical Journal. 145: 74-83.

[13] F. Şen, Ö. Demirbaş, M.H. Çalımlı, A. Aygün, M.H. Alma, M.S. Nas. (2018). The dye removal from aqueous solution using polymer composite films. Applied Water Science. 8(7): 206.

[14] S.A. Hamid, M. Shahadat, S. Ismail. (2017). Development of cost effective bentonite adsorbent coating for the removal of organic pollutant. Applied Clay Science. 149: 79-86.

[15] I. Michael, L. Rizzo, C. McArdell, C. Manaia, C. Merlin, T. Schwartz, C. Dagot, D. Fatta-Kassinos. (2013). Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: a review. Water Research. 47(3): 957-995.

[16] M.O. Barbosa, N.F. Moreira, A.R. Ribeiro, M.F. Pereira, A.M. Silva. (2016). Occurrence and removal of organic micropollutants: an overview of the watch list of EU Decision 2015/495. Water Research. 94: 257-279.

[17] S. Pandey. (2017). A comprehensive review on recent developments in bentonite-based materials used as adsorbents for wastewater treatment. Journal of Molecular Liquids. 241: 1091-1113.

[18] M. Stuart, D. Lapworth, E. Crane, A. Hart. (2012). Review of risk from potential emerging contaminants in UK groundwater. Science of the Total Environment. 416: 1-21.

[19] J. Davies, D. Davies. (2010). Origins and evolution of antibiotic resistance. Microbiol. Mol. Biol. Rev. 74(3): 417-433.

[20] R. Hirsch, T. Ternes, K. Haberer, K.-L. Kratz. (1999). Occurrence of antibiotics in the aquatic environment. Science of the Total Environment. 225(1-2): 109-118.

[21] R.V. Kandisa, K. Narayana Saibaba, K.B. Shaik, R. Gopinath. (2016). Dye removal by adsorption: a review. J Bioremed Biodegr. 7: 317.

[22] Z. Carmen, S. Daniela In *Textile organic dyes–characteristics, polluting effects and separation/elimination procedures from industrial effluents–a critical overview*, Organic pollutants ten years after the Stockholm convention-environmental and analytical update, 2012; IntechOpen: 2012.

[23] C. Pearce, J. Lloyd, J. Guthrie. (2003). The removal of colour from textile wastewater using whole bacterial cells: a review. Dyes and pigments. 58(3): 179-196.

[24] F. Rahman, M. Akter. (2016). Removal of dyes from textile wastewater by adsorption using shrimp shell. Int. J. Waste Resour. 6: 244.

[25] F.D. Ardejani, K. Badii, N.Y. Limaee, N. Mahmoodi, M. Arami, S. Shafaei, A. Mirhabibi. (2007). Numerical modelling and laboratory studies on the removal of Direct Red 23 and Direct Red 80 dyes from textile effluents using orange peel, a low-cost adsorbent. Dyes and pigments. 73(2): 178-185.

[26] M. Ahmad, M. Yousaf, A. Nasir, I.A. Bhatti, A. Mahmood, X. Fang, X. Jian, K. Kalantar-Zadeh, N. Mahmood. (2019). Porous Eleocharis@ MnPE Layered Hybrid for Synergistic Adsorption and Catalytic Biodegradation of Toxic Azo Dyes from Industrial Wastewater. Environmental science & technology.

[27] C.R. Holkar, A.J. Jadhav, D.V. Pinjari, N.M. Mahamuni, A.B. Pandit. (2016). A critical review on textile wastewater treatments: possible approaches. Journal of environmental management. 182: 351-366.

[28] D. Deng, J. Guo, G. Zeng, G. Sun. (2008). Decolorization of anthraquinone, triphenylmethane and azo dyes by a new isolated Bacillus cereus strain DC11. International Biodeterioration & Biodegradation. 62(3): 263-269.

[29] M. Kaykhaii, M. Sasani, S. Marghzari. (2018). Removal of dyes from the environment by adsorption process. Chemical and Materials Engineering. 6(2): 31-35.

[30] N.T. Thao, H.T.P. Nga, N.Q. Vo, H.D.K. Nguyen. (2017). Advanced oxidation of rhodamine B with hydrogen peroxide over ZnCr layered double hydroxide catalysts. Journal of Science: Advanced Materials and Devices. 2(3): 317-325.

[31] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke. (2001). Electrocoagulation (EC)—science and applications. Journal of hazardous materials. 84(1): 29-41.

[32] C.S. Lee, J. Robinson, M.F. Chong. (2014). A review on application of flocculants in wastewater treatment. Process Safety and Environmental Protection. 92(6): 489-508.

[33] A. Ahmad, S.H. Mohd-Setapar, C.S. Chuong, A. Khatoon, W.A. Wani, R. Kumar, M. Rafatullah. (2015). Recent advances in new generation dye removal technologies: novel search for approaches to reprocess wastewater. RSC Advances. 5(39): 30801-30818.

[34] I. Anastopoulos, A. Bhatnagar, D. Bikiaris, G. Kyzas. (2017). Chitin adsorbents for toxic metals: a review. International journal of molecular sciences. 18(1): 114.

[35] N.G. Paul. (1980). Some methods for the utilisation of waste from fibre crops and fibre wastes from other crops. Agricultural Wastes. 2(4): 313-318.

[36] M.K. Uddin. (2017). A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. Chemical Engineering Journal. 308: 438-462.

[37] T. Anirudhan, M. Ramachandran. (2015). Adsorptive removal of basic dyes from aqueous solutions by surfactant modified bentonite clay (organoclay): kinetic and competitive adsorption isotherm. Process Safety and Environmental Protection. 95: 215-225.

[38] A.A. Adeyemo, I.O. Adeoye, O.S. Bello. (2017). Adsorption of dyes using different types of clay: a review. Applied Water Science. 7(2): 543-568.

[39] M. Toor, B. Jin. (2012). Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing diazo dye. Chemical Engineering Journal. 187: 79-88.

[40] T. Chakraborty, A. Chakraborty, M. Shukla, Chattopadhyay, Tanmay. (2018). ZnO-Bentonite nanocomposite: An efficient catalyst for discharge of dyes, phenol and Cr (VI) from water. Journal of Coordination Chemistry. (just-accepted): 1-30.

[41] M. Shaban, M.R. Abukhadra, M. Shahien, S.S. Ibrahim. (2018). Novel bentonite/zeolite-NaP composite efficiently removes methylene blue and Congo red dyes. Environmental Chemistry Letters. 16(1): 275-280.

[42] K.Y. Foo, B.H. Hameed. (2011). The environmental applications of activated carbon/zeolite composite materials. Advances in colloid and interface science. 162(1-2): 22-28.

[43] A. Benhouria, M.A. Islam, H. Zaghouane-Boudiaf, M. Boutahala, B. Hameed. (2015). Calcium alginate–bentonite–activated carbon composite beads as highly effective adsorbent for methylene blue. Chemical Engineering Journal. 270: 621-630.

[44] M. Khan, R. Hegde, G. Venkatachalam. (2018). Removal of Cadmium from Aqueous Solution using Bentonite Clay. International Journal of Applied Environmental Sciences. 13(4): 353-364.

[45] D.F. Brito, E.C. da Silva Filho, M.G. Fonseca, M. Jaber. (2018). Organophilic bentonites obtained by microwave heating as adsorbents for anionic dyes. Journal of environmental chemical engineering. 6(6): 7080-7090.

[46] S. Hokkanen, B. Doshi, V. Srivastava, L. Puro, R. Koivula. (2019). Arsenic (III) removal from water by hydroxyapatite-bentonite clay-nanocrystalline cellulose. Environmental Progress & Sustainable Energy.

[47] S. Sadeghi, A.Z. Moghaddam, M. Massinaei. (2015). Novel tunable composites based on bentonite and modified tragacanth gum for removal of acid dyes from aqueous solutions. RSC Advances. 5(69): 55731-55745.

[48] M. Amin, A. Alazba, M. Shafiq. (2015). Adsorptive removal of reactive black 5 from wastewater using bentonite clay: isotherms, kinetics and thermodynamics. Sustainability. 7(11): 15302-15318.

[49] A.S. Özcan, A. Özcan. (2004). Adsorption of acid dyes from aqueous solutions onto acid-activated bentonite. Journal of colloid and interface science. 276(1): 39-46.

[50] E. Eren. (2009). Investigation of a basic dye removal from aqueous solution onto chemically modified Unye bentonite. Journal of Hazardous Materials. 166(1): 88-93.

[51] V. Kuroki, G.E. Bosco, P.S. Fadini, A.A. Mozeto, A.R. Cestari, W.A. Carvalho. (2014). Use of a La (III)-modified bentonite for effective phosphate removal from aqueous media. Journal of hazardous materials. 274: 124-131.

[52] Z. Huang, Y. Li, W. Chen, J. Shi, N. Zhang, X. Wang, Z. Li, L. Gao, Y. Zhang. (2017). Modified bentonite adsorption of organic pollutants of dye wastewater. Materials Chemistry and Physics. 202: 266-276.

[53] S. Bo, W. Ren, C. Lei, Y. Xie, Y. Cai, S. Wang, J. Gao, Q. Ni, J. Yao. (2018). Flexible and porous cellulose aerogels/zeolitic imidazolate framework (ZIF-8) hybrids for adsorption removal of Cr (IV) from water. Journal of Solid State Chemistry. 262: 135-141.

[54] M.R. Adam, N.M. Salleh, M.H.D. Othman, T. Matsuura, M.H. Ali, M.H. Puteh, A. Ismail, M.A. Rahman, J. Jaafar. (2018). The adsorptive removal of chromium (VI) in aqueous solution by novel natural zeolite based hollow fibre ceramic membrane. Journal of environmental management. 224: 252-262.

[55] M. Rahmani, M. Kaykhaii, M. Sasani. (2018). Application of Taguchi L16 design method for comparative study of ability of 3A zeolite in removal of Rhodamine B and Malachite green from environmental water samples. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 188: 164-169.

[56] M. Kragović, S. Pašalić, M. Marković, M. Petrović, B. Nedeljković, M. Momčilović, M. Stojmenović. (2018). Natural and Modified Zeolite—Alginate Composites. Application for Removal of Heavy Metal Cations from Contaminated Water Solutions. Minerals. 8(1): 11.

[57] R. Han, J. Zhang, P. Han, Y. Wang, Z. Zhao, M. Tang. (2009). Study of equilibrium, kinetic and thermodynamic parameters about methylene blue adsorption onto natural zeolite. Chemical engineering journal. 145(3): 496-504.

[58] W. Khanday, B. Hameed. (2018). Zeolite-hydroxyapatite-activated oil palm ash composite for antibiotic tetracycline adsorption. Fuel. 215: 499-505.

[59] L. Zhang, P. Hu, J. Wang, R. Huang. (2016). Crosslinked quaternized chitosan/bentonite composite for the removal of Amino black 10B from aqueous solutions. International journal of biological macromolecules. 93: 217-225.

[60] R. Fabryanty, C. Valencia, F.E. Soetaredjo, J.N. Putro, S.P. Santoso, A. Kurniawan, Y.-H. Ju, S. Ismadji. (2017). Removal of crystal violet dye by adsorption using bentonite–alginate composite. Journal of environmental chemical engineering. 5(6): 5677-5687.

[61] S. Chowdhury, K.G. Bhattacharyya. (2019). Use of Cu (II)-incorporated zeolite Y for decolourization of dyes in water: a case study with aqueous methylene blue and Congo red. SN Applied Sciences. 1(1): 87.

[62] W. Khanday, F. Marrakchi, M. Asif, B. Hameed. (2017). Mesoporous zeolite–activated carbon composite from oil palm ash as an effective adsorbent for methylene blue. Journal of the Taiwan Institute of Chemical Engineers. 70: 32-41.

[63] A. Kausar, M. Iqbal, A. Javed, K. Aftab, H.N. Bhatti, S. Nouren. (2018). Dyes adsorption using clay and modified clay: A review. Journal of Molecular Liquids. 256: 395-407.

[64] Z. Ullah, S. Hussain, S. Gul, S. Khan, F. Bangash. (2016). Use of HCl-modified bentonite clay for the adsorption of Acid Blue 129 from aqueous

solutions. Desalination and Water Treatment. 57(19): 8894-8903.

[65] G. Bhattacharya, R. Chowdhury, S. Metya. (2019). Residual factor as a variable in slope reliability analysis. Bulletin of Engineering Geology and the Environment. 78(1): 147-166.

[66] V. Vimonses, S. Lei, B. Jin, C.W. Chow, C. Saint. (2009). Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials. Chemical engineering journal. 148(2-3): 354-364.