

Removal of Dyes using Alginated, Calcinized and Hybrid Materials – A Comprehensive Review

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Abstract

Excessive and uncontrolled anthropogenic activities especially increased industrialization and rapid urbanization have become one of the major causes of severe water pollution. Dyes are the major contaminants in most of the water effluents especially, the wastewater collected from textile industries. These dyes pose a serious threat to the environment and human health. Many methods have previously been developed for the removal of dyes from water effluents but all these methods have their own pros and cons based on total cost, operation efficiency and environmental friendliness. In this review, process of adsorption using various alginated, calcinized and hybridized materials is discussed in detail as an efficient process for dye removal owing to being economical and ecofriendly in nature. Among various naturally existing and artificially manufactured adsorbents, adsorptive function of both raw and modified forms of clay and alginates along with their hybrids is also discussed here due to their significant adsorptive potential, easy availability, cost effectiveness and environmentally benign nature. By reviewing the extensive literature, it has been concluded that calcination is the most important parameter for the stabilization of clay material and adsorption capacity is found to be increased as the result of modification in raw adsorbent. Effect of various parameters such as temperature, pH, initial dye concentration, contact time and adsorbent dosage on the adsorption of dyes is described in this review article. Adsorption efficiency of clay, alginates and their hybrids is compiled in tabulated form. Hybrid consisting of clay-sodium alginate showed maximum adsorption efficiency for some dyes. Various characterization techniques such as UV-Visible, IR and EDX are also discussed in detail.

Keywords: Clay, Alginates, Calcination, Hybrid Materials, Dyes, Characterization, Adsorption Potentials

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

1. Introduction

Water is an essential component and an indispensable part of biosphere, it is important for the maintenance of all life forms on earth, pure water is not only used for drinking purpose but also for the completion of processes vital for life. At the same time, water has proved to be a potential source of spread of contagious diseases because water has ability to dissolve a vast variety of chemical compounds in it [1]. Pure water is colorless, clear, having normal taste and smell. Presence of organic compounds or inorganic chemicals and micro-organisms of any origin human or animal, hazardous chemical compounds, industrial and domestic wastes make water impure. Some physical and chemical characteristics of water determine its purity. Color, taste, smell, presence of organic matter, turbidity or transparency, temperature and pH are the important physical properties of water. Presence of some chemical substances within specified limit determines the

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chemical properties of water. Worldwide about 50 million deaths are caused by this polluted water each year. Africa and Asia are major contributor to this huge number of deaths [2]. Population of about 1.1 billion people don't have access to water reservoirs and polluted water has become the major cause of diseases in about half of the population of developing countries [3].

Water pollution is mainly caused by anthropogenic activities, increasing trends of urbanization and excessive industrialization. Sewage is the source of infectious agents and decomposable organic substances. Effluents of industries are the source of toxic contaminants that vary from simple metal salts to synthetic organic compounds of high complexity. Fertilizers and pesticides from the agriculture waste are also main contaminants of water. Physical pollutants include radioactive matter and heat. Pollution is also related to the increasing population. Both surface and ground water is being polluted due to the

pathogenic microbes. Organic waste is being accumulated in surface water due to human activities and these organic wastes are responsible for the proliferation of pathogenic organisms such as bacteria, fungi, virus and protozoans. It was considered that underground water is of high purity than surface water due to its staining potentials through rocks but recently it has been investigated that underground water is also being polluted due to percolation of contaminants through soil. Dumping of industrial and domestic waste can also interfere with the quality of ground water if dumping area is not properly protected from being in contact with water table [4].

There are various classes of coloring materials which are used for the dyeing purpose of various substrate such as acid dyes are used in dyeing of leather, silk, wool, acrylics, nylon, cosmetics, food, paper and ink-jet printing. Common examples of acid dyes include acid red 57, acid blue 2, orange (1 & 2) and methyl orange. Basic dyes are used in dyeing of polyacrylonitrile, modified nylons, modified polyester, medicines and paper. Basic dyes are water soluble and produced colored cations thus are called cationic dyes. Common examples of basic dyes are malachite green, methylene blue, crystal violet, basic brown, basic yellow 28, basic red 46 and basic red 9. Disperse dyes are applied in dyeing of nylon, cellulose fiber, cellulose acetate and acrylic fiber. These are non-ionic in nature and thus are not soluble in water. Common examples of this class includes disperse blue, disperse red, disperse orange and disperse yellow. Direct dyes are the class of dyes that can bind to cellulosic fibers only when dyeing takes place in electrolytic aqueous solution. Direct orange 34, direct blue, direct violet and direct black are some examples of direct dyes. Another class of dyes is reactive dyes which are used in wool, nylon, cotton fiber and cellulose. Some examples of this class are reactive red, reactive black 5, reactive yellow 2 and remazol. Vat dyes are the class of dyes that are used in cotton, rayon fibers, wool and flax wool. Indigo, Vat green 6 and Vat blue are some of its common examples [5].

Polluted water is the major source of number of diseases among human beings. Man is suffering from water-borne diseases by direct use of contaminated water or by getting pathogens indirectly in from of vegetables and fruits grown in unhygienic water. Many dangerous diseases such as cancer, neurological disorders, ulcerative colitis, respiratory and cardiovascular diseases are resulting from the use of contaminated water. Poor community is more likely to get water borne diseases due to unhygienic water supply and improper sanitation. Metals are present in water but excessive amount of these metals caused baldness, neural disorder, renal failure and liver diseases [1]. Along with these health issues to human beings, discharge of untreated wastewater into drinking water cause many environmental issues also. Organic matter in the wastewater will consume almost all the available oxygen and results in depletion of oxygen level required for the maintenance of

life in these water bodies [6]. Heavy metals such as iron in water bodies block the gills of fish and also known to has deleterious effects on fish and this fish proves harmful for human health when eaten [1]. Accumulation of phosphorous and nitrogen in water bodies promote the growth of aquatic plant species and these species form algal bloom that gives unpleasant taste, smell and color to the water [7].

Exposure to dyes over a long period of time can also causes detrimental effects on human health. Dyes particles on inhalation causes respiratory problems and also affects the immune system badly. In extreme conditions, respiratory sensitization causes the symptoms such as sneezing, itching, watery eyes and coughing and wheezing as evident in asthma. Exposure to the irritants during dyeing and finishing process causes skin irritation, sore eyes, blocked nose and sneezing. Azo dyes have complex nature and these are observed to have carcinogenic effect when it undergoes reductive cleavage. Azo dyes are mutagens and are toxic to environment [8]. Wastewater containing dyes pose hazardous effect on environment. Among water treatment techniques, photolysis and photocatalytic processes are chemical methods, while aerobic and anaerobic degradation are biological and ion exchange, adsorption, electro kinetic coagulation and membrane filtration are types of physiochemical methods. Depending on design, cost and efficiency of dye separation, these methods have certain limitations [5]. Electrocoagulation is a preferred technique over others due to its advantages such as easy handling, simple equipment, small retention time, small sludge amount, high velocities and no chemical additives [9].

In adsorption, constituents of adsorbate produce a thin film by adhering to the surface of the adsorbent. The adsorbate may be gaseous, liquid or solid. Adsorption process is classified into physical adsorption and chemical adsorption. The process of physical adsorption is affected by physical forces for example Van der Waals forces, polarity, hydrogen bonding, static interaction, hydrophobicity and dipole-dipole interactions. Due to these interactions, solutes are adsorbed on the surface of adsorbent. In chemical adsorption or chemisorption, adsorbate bound chemically to the surface of adsorbent by an electron exchange phenomenon. Adsorption depends on the properties of both adsorbate and adsorbent. Some properties of adsorbate that affects the adsorption include molecular size, molecular weight, molecular structure, polarity and concentration of solution. The properties of adsorbent for example surface area, charge on the surface and size of particles also affects the adsorption process. These physical and chemical properties of both adsorbate and adsorbent determine the efficiency of adsorption. Various factors like simplicity of design, ease of operation, initial cost and insensitivity towards toxic substances makes the adsorption most effective and favorable separation technique for the treatment of wastewater [5].

Clay is a fine grained material naturally found on the surface of earth and it is mainly composed of water, silica, alumina and weathered rock. Clay has been used as an adsorbent for the removal of heavy metals effectively. Clay has many advantages over other adsorbents such as low cost, high specific surface area, high ion exchange potential, harmless nature, marvelous adsorption characteristics and ease of availability [10]. Alginate is a bio-copolymer consisting of α -D-mannuronate (M) and β -L-guluronate (G) monomers linked through 1-4 linkage. Alginates form a gel system by crosslinking with divalent cations. Doping of this material is performed for the improvement of its functionality and network structure. Alginates are widely used in wastewater treatment and known to have various other fruitful applications [11].

2. Water Pollution

Pakistan is one of those countries which have abundant resources of natural water. But quality as well as quantity of that natural water is deteriorating with time. Pakistan is also included in the list of those thirty countries which are facing deficiency of water and severity of situation is going to increase day by day [12]. Water pollution is a physical process that occurs in various water resources such as lakes, ground water and rivers due to anthropogenic activities. In Pakistan, only 25% people have availability of pure drinking water. The quality of drinking water is determined by the quality of water source, efficiency of treatment process and condition of water supply lines. The quality of drinking water is determined by its chemical, physical and biological properties and minor changes in these parameters would affect the human health badly [13].

Water resources are being polluted due to discharge of municipal, agricultural and industrial effluents in open water system. In Pakistan, sewage of about 2000 million gallon is being expelled every 24 hours in the water bodies. Bigger industrial units such as paper and pulp, paint, plastic chemical, textile, pharmaceuticals, leather, pesticides, dairy, poultry, leather and tanneries are major contributor of pollution towards the surface as well as ground water. Fertilizers and pesticides also contribute to the water pollution when used excessively as they move to ground water in dissolved form and results in increased salinity and water logging thus fertility of soil decreases at irrigated land [3].

3. Organic Pollutants

Organic pollutants that persists in environment over long period of time and are not easily degraded, commonly categorized as persistent organic pollutants (POPs). These includes polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), dichlorodiphenyltrichloroethane (DDT), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Among organic pollutants, dichlorodiphenyltrichloroethane

(DDT) and polychlorinated biphenyls (PCBs) are released continuously from their deposits. These POPs are toxic to human and wildlife and are transported to wide range of areas. These pollutants undergo bioaccumulation in food web and by the use of fish and marine mammals accumulate in the human tissues [14].

3.1 Dyes

Dyes are the organic molecules of high structural complexity that are bound to the surface and impart color. Applications of dyes in various fields such as paper, plastics, food processing, leather tanning, cosmetics, printing, dye manufacturing and various kinds of the textile required them to be unaffected by numerous things for instance detergents. Wastewater of these industries if discharged into open water system without treatment, generally results in unusual coloration of natural water bodies thereby reducing the light penetration due to which biological and photochemical reactions are hindered. About more than 100,000 commercial dyes are produced at the rate of 7×10^5 tonnes per year. Out of this amount, approximately 10,000 tonnes of dyes are consumed by textile industry each year and 100 tonnes of dyes per year is discharged into open water system [15].

Regarding the number and volume of production, azo dyes accounts for 60 to 70% of all the organic dyes produced in industries worldwide. Reductive biotransformation of azo bond results in generation of the derivatives of aryl amine, these derivatives of aryl amine together with azo compounds itself are highly toxic. After entering the body of various microorganisms present in intestine, it produces enzymes azoreductase and nitroreductase and these enzymes catalyze the cleavage of azo bond and nitro group respectively. Such type of bond cleavage generally results in formation of N-hydroxylamines which can cause damage to DNA [16]. Aromatic amines are produced by the azo dyes and are carcinogenic, highly toxic and explosive in nature. Benzidine is one of the most commonly found carcinogens in dyes thus it must be removed from water. Wastewater also contains metals and other auxiliaries that are used in dye's manufacturing. These contaminants must be removed to maintain the water quality [17].

4. Inorganic Pollutants

Inorganic pollutants that are of serious environmental and human health concern include selenium, arsenic, fluoride, chromium and uranium. Globally arsenic is considered to have the maximum negative impact on human health. Chronic arsenic poisoning results in the accumulation of arsenic in hairs, skin and nails and this lead to the development of symptoms such as high blood pressure, neurological dysfunction and strong pigmentation of hands and feet (keratosis) [14].

4.1 Heavy Metals

According to a report of international agency on the cancer evaluation research compound of inorganic lead

are considered to be carcinogenic in humans. Safe limit for Pb set by WHO (World Health Organization) is 0.01 mg/L but its concentration has increased above this limit in ground water of many regions of Pakistan.

5. Techniques Used for Water Treatment

Synthetic dyes present in the wastewater pose a serious environmental hazard. Dyes in the wastewater must be removed by various separation techniques to avoid any health or environmental hazard. Methods used for the dye separation are divided into chemical, biological and physiochemical methods. On the basis of design, efficiency and total expanse, these methods have their own limitations [19].

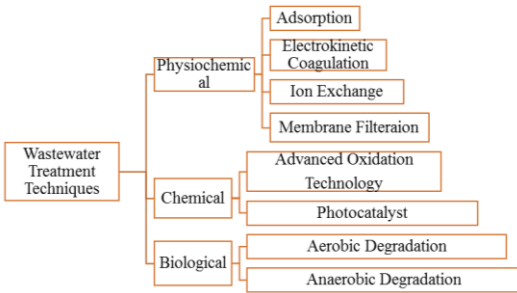


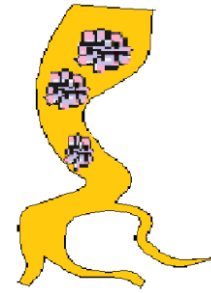
Fig 1 Types of wastewater treatment technique

5.1 Adsorption

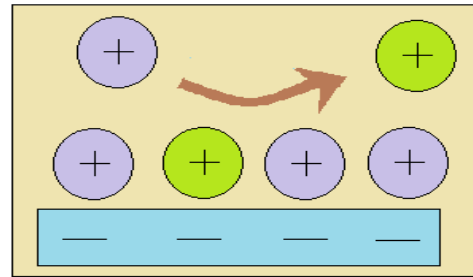
The term adsorption can be applied to all the processes that are involved in immobilization or uptake of contaminants on the adsorbents. The mechanisms responsible for this immobilization of contaminants by adsorbents are surface adsorption, surface precipitation, structural incorporation and partition. Surface adsorption is either physical or chemical adsorption. The phenomenon occurring onto or adjacent to the surface or pores involving London dispersion or van der Waals forces for the concentration of contaminants is called physical adsorption for example hydrophobic organic contaminants (HOCs) adsorbed on the activated carbon by physical adsorption while chemical bond formation is involved in chemisorption for example heavy metal cations adsorbed on the metal (hydr) oxides via chemisorption. Ion exchange is also a type of adsorption process in which ionic contaminants are exchanged with ions that are already adsorbed on the adsorbent. Electrostatic interaction is the most dominant interaction involved in adsorption of contaminants by the adsorbent. Adsorption of heavy metal cations by montmorillonite is an example of electrostatic interaction.

Partition is also an adsorption phenomenon in which contaminants are distributed between two phases and contaminants will be penetrated into the entire bulk phase instead of concentrating on the surface of adsorbent. Surface precipitation is the process in which contaminants are firstly adsorbed on the surface of adsorbent and then over saturation of cations and anions lead to the formation of precipitates. For example cations and oxyanions undergo co-adsorption on the surface of metal (hydr) oxides. Structural incorporation is also an adsorption process in which ions are

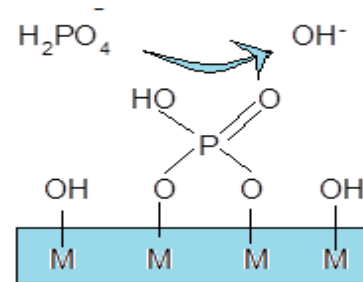
incorporated into the adsorbent's solid phase. For example isomorphous substitution lead to the metal cations incorporation into the minerals crystal structure [20].



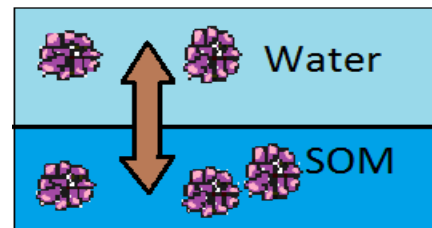
(a) HOC's adsorption on activated carbon



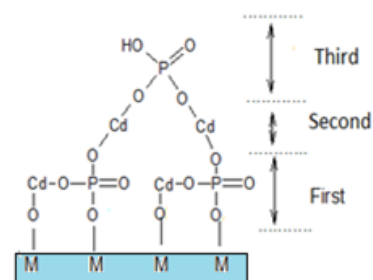
(b) Ion exchange process involving cationic pollutants uptake by negatively charged sorbent



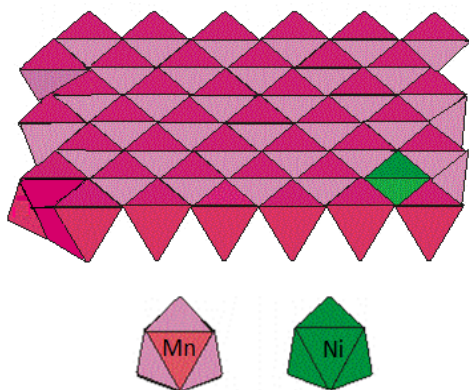
(c) Ligand exchange process involving phosphate uptake on the surface of metal hydroxides



(d) Partition process for the uptake of HOC to SOM



(e) Surface precipitation process involving phosphate and cadmium adsorption on metal hydroxide



(f) Structural incorporation process involving uptake of nickel on birnessite

Fig 2 Mechanism of uptake of pollutants by different adsorbents

Selectivity of adsorbent depends on its total cost, ease of use, surface area and adsorption capacity. A wide range of adsorbents such as agricultural solid waste, commercial activated carbon, activated carbon based on solid waste of agricultural origin, clay and minerals have been utilized for the removal of dye during wastewater treatment [19].

5.2 Activated Carbon

Activated carbon in both granular and powdered form can be used as adsorbent. The "granular activated carbon" also called GAC has ability to remove contaminants from wastewater by continuously contacting with them and activated carbon need not to be separated from the fluid. One of the limitations in the use of granular activated carbon is slow diffusion into the particles. Similarly, "powdered activated carbon" also known as PAC can also be used for the treatment of wastewater as it is low cost and requires less contact time but one of its limitation is that it will remain in the treated fluid and after the treatment its separation from the fluid pose a problem. Activated carbon pellet and activated carbon fiber are also available forms that are mostly obtained from coal and polymeric materials respectively. Certain limitations associated with the use of activated carbon are: it becomes more toxic after adsorption so its disposal cost increases and it cannot be regenerated easily. Furthermore, the technology required to produce good quality activated carbon is very expensive so it cannot be adopted in developing countries [21].

5.3 Agricultural Waste Based Activated Carbon

Activated carbon can be generated from any material that contains carbon in greater proportion and organics in low proportion. Agricultural wastes can be used as raw materials for the synthesis of activated carbon as these are low cost, easily available and require no expense during waste disposal. So agricultural solid waste based activated carbon has good adsorption capacity, promising mechanical strength and small ash content. Agricultural byproducts that can be used as raw material in the synthesis of activated carbon are sawdust, rice husks, corn cob, cotton silk, tobacco stem, nut palm fiber, oil palm shell, coconut

husk, bagasse and wheat straw. Activated carbon is prepared in two steps; in the first step the carbonaceous raw material is carbonated below 1000°C and in second step the carbonized product is activated by physical or chemical method [22].

5.4 Bio Sorbents

Biomaterials have been used for the removal of dyes during wastewater treatment by biodegradation and biosorption. Commonly used biomaterials as biosorbents are peat, fungi, yeast and bacterial biomass. Cell wall of these biomaterials has many functional groups due to the presence of polysaccharides, lipids and proteins. Different functional groups provide different binding sites to the dyes for example azo, hydroxyl and nitro groups which promote binding while sulfonic acid group hinders the binding. The phenomenon of ion exchange is mainly involved in binding of dyes to the biomaterial [23].

6. Clay

Lamellar structure of clay presents greater specific surface areas that increase the adsorption capacity of clay. When clay is compared with activated carbon under the same set of temperature and pH, its adsorption capacity is even greater than that of activated carbon [24]. Clays are naturally found aluminosilicates materials containing organic compound and metallic ions in small amount. Clays are usually present in water, soil, rocks and sediment as colloidal fraction. Clays have some important properties that make them a good adsorbent such as high surface area, chemical and mechanical stability, layered structure and greater cation exchange ability. Clays are also available abundantly in low cost as compared to other adsorbents. Natural clays have negative charges so these are able to remove cationic dyes for example methylene blue. The surface negative charge of clay can be changed to positive by surfactants. In this way, adsorption of anionic dyes can be enhanced. Different types of clays have been used for the removal of textile dyes and metal ions for example red clay for brilliant green dye, sodium bentonite for congo red, kaoline for zinc ions and montmorillonite clay for methylene blue dye [19].

6.1 Structure of Clay

Structure of clay and charge on its layers has an important impact on coordination of metal ions to the permanent charge sites and it is varied with the clay type being used. So, different clay minerals selected provide different arrangement of aluminol and silanol surface hydroxyl sites. Negative charge on silicate structure provides adsorption capabilities to the clay and this negative charge is neutralized by cationic dyes. Adsorption capacities of clay is also related to its large surface area of about 800m²/g [5].

6.2 Calcination of Clay

On calcination, some important properties of clay such as its structure, composition and physiochemical properties are changed. These changes depend on the type of

clay, the particle size and heating region. When temperature is raised up to dehydration level, adsorbed water is lost and it results in changes in porosity of clay along with loss of adsorption potential. Cation exchange capacity is reduced due to destruction of interlayer spaces. Hydrophilicity of clay is increased by partial escape of hydration and adsorbed water. At the end of this dehydration stage, the weight of clay is reduced and overall surface area available for adsorption is increased. Clay is stabilized and its useful permanent properties are maintained by calcination. Dehydroxylation occurs on further heating and after dihydroxylation if heating is still continued than alterations in the structure of clay and its surface functional groups are observed [26].

6.3 Natural and Modified Clay

There are various types of clays but montmorillonite clays have highest adsorption capacity than others. Modification of clay could be done to improve its ability of removal of contaminants from wastewater [5].

7. Alginates as Adsorbent

Alginates are polysaccharides obtained from some classes of brown algae for example *Laminaria hyperborea* and *lessonia* that globally exists in coastal water [36]. Soil bacteria for example *Azotobacter vinelandii* and species of *Pseudomonas* are also found to be the source of alginates. Alginates are linear copolymer with homopolymeric blocks of β -D-mannuronic acid and α -L-guluronic acid linked through 1,4-linkage. For the preparation of sodium or calcium alginate, alginate obtained from various sources is firstly washed than macerated and after that is extracted with sodium carbonate. After filtration, chlorides of sodium or calcium are added in the filtrate and thus alginate is converted to sodium alginate or calcium alginate respectively [37].

Alginate is naturally occurring carbohydrate polymer that has been used to remove dyes from wastewater due to its ability to remove pollutants. Several classes of brown algae are the source of alginate. Hydrogel formation is an important ability of alginate. When metallic divalent cations are added to an aqueous alginate solution it is readily converted to hydrogel. Calcium alginate beads with immobilized activated carbons have been used for the removal of dyes [38]. Alginates have been used as the most promising adsorbent in the form of coating on the surface of nanoparticles due its unique features of hydrophilicity, abundant resource availability, biocompatibility, inexpensiveness and eco-friendliness [39].

8. Clay and Alginate Hybrid

Hybrids consisting of clay and alginates have been synthesized to obtain better adsorption with increased surface area and high adsorption capacity [11].

9. Factors Effecting Adsorption

9.1 Effect of pH

Solution pH is one of the factors that affect the process of adsorption as it can change the chemistry of dye

solutions and adsorbent's functional groups. At low pH, adsorption of anionic dyes on the surface of negatively charged adsorbents generally increases. However, as the pH is increased, the adsorption of anionic dyes decreases but adsorption of cationic dyes on the surface of negatively charged adsorbents increases. Depending on the type of clay, modification of clay and dye nature, pH is optimized to achieve maximum adsorption [5].

In case of alginates for example Fe_3O_4 nanoparticles coated with alginates showed increase in adsorption of malachite green dye with increase in the pH of dye solution. Electrostatic interactions between dye molecules and adsorbents are influenced by this pH change. At high pH, ionization of hydroxyl and carboxyl groups of sodium alginates increases and interaction with cationic dye increases. At low pH, protonation of carboxylic groups occurs therefore adsorption of cationic dye decreases. Furthermore, due to electrostatic repulsion of carboxylate groups, volume expansion of polymer chains occurs and adsorption of cationic dyes is enhanced by penetration into structure of alginate [39].

9.2 Effect of Temperature

Adsorption process is affected by change of temperature in two ways; the rate of dye adsorption is affected by temperature change before the attainment of equilibrium and after the attainment of equilibrium. In short, equilibrium temperature affects the adsorption equilibrium of adsorbent for a particular adsorbate [30]. Dye adsorption may be endothermic or exothermic so for an endothermic adsorption process increase in temperature that results in increase in the adsorption capacity while for an exothermic adsorption process increase in temperature results in decrease in the adsorption capacity. For example adsorption of Congo red dye on the modified hectorite clay is favoured by increase in temperature while adsorption of methylene blue onto the montmorillonite clay is decreased with increase in temperature [19].

9.3 Effect of Initial Dye Concentration and Contact Time

Initial dye concentration has a significant influence on the quantity of adsorbed dye (mg/g) and percentage of dye removed. When initial dye concentration is increased, all adsorption sites become saturated and efficiency of dye removal is decreased. At all initial concentration of dye, amount of adsorbed dye (mg/g) increases with increase in contact time. Resistance in the mass transfer of dye between solution and adsorbent is overcome by the driving force provided by initial dye concentration [19].

9.4 Effect of Adsorbent Dosage

Efficiency of dye removal increases with increase in the mixture dosage. It is because of increase in the surface area and active sites available for adsorption. However, for some adsorbents such as clay and calcium hydroxide mixture, dosage of about 1gL^{-1} give dye removal efficiency of about 99% of Congo red as obtained from 8-23 gL^{-1} of other low cost adsorbents. So using small amount of

adsorbent having same dye removal efficiency as large amount of adsorbent is beneficial in terms of low cost and

small amount of sludge production [27].

Table 1 Heavy metals with safe limit (mg/L) by WHO and their impact above safe limit [18]

Type of Metals	Safe Limit in Drinking Water (mg/L) by WHO	Impact on Human Health above Safe Limit
Lead (Pb)	0.01	Carcinogenic in Humans
Cadmium (Cd)	0.003	Cancer of Lungs, Kidneys and Prostate
Nickel (Ni)	0.07	Cancer of Lungs, Nasal Cavity and Paranasal Sinuses
Copper (Cu)	2.0	-
Chromium (Cr)	No Safe Limit Provided	Cancer of Lungs, Nose and Nasal Sinuses
Zinc (Zn)	5	Chronic Intake Lead to Headache, Lipoprotein and Cholesterol Level Changes, Gastrointestinal Effects and Impaired Immune Function
Iron (Fe)	No Limit Provided	Gastrointestinal Distress
Arsenic (As)	10×10^{-3}	Skin, Bladder, Lung and Liver Cancer

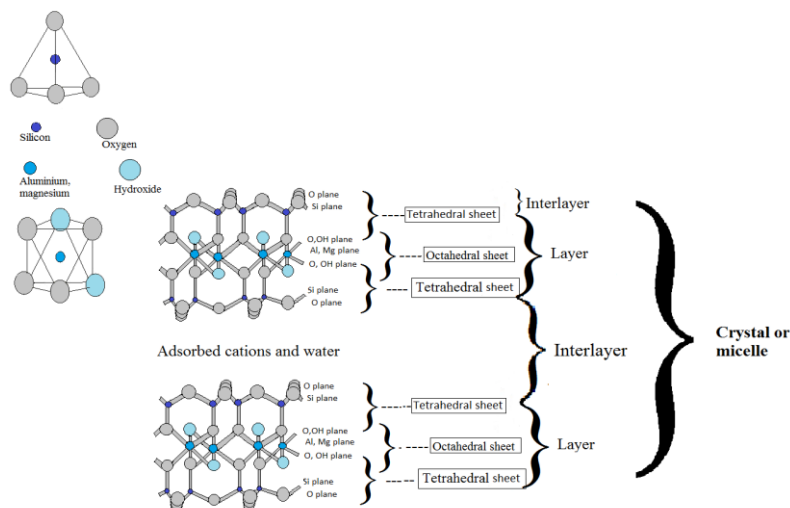


Fig 3 Structure of clay (2:1) [25]

Table 2 Clay type, its modification, type of dye removed and adsorption efficiency

Clay Type	Modification	Adsorbate Removed	Adsorption Capacity or Dye Removal Efficiency	References
Mixture of Sodium Bentonite, Kaolin and Zeolite	Treated with Ca(OH) ₂ and Calcination	Congo Red	95%	[27]
Kaolin	-	Basic Yellow 28, Malachite Green and Methylene Blue	65-99%	[28]
Local Clay	Treated with H ₂ SO ₄ and Al(OH) ₃ . Sodium Alginate (Binder)	Methylene Blue	Increased from 58.02 to 223.19 mg/g	[29]
Montmorillonite Clay	Modified with Fe ₂ O ₃	Methylene Blue	71.12 mg/g	[30]
Halloysite Rich Clay	-	Direct Orange 34	-	[31]
Clay	Modified with Red Mud Under Photo-Fenton Conditions	Acid Orange 7	>80%	[32]
Sepiolite Clay	-	Direct Blue 85	332 mg/g	[33]
Sepiolite Clay	-	Basic Red 46	110 mg/g (25°C)	[33]

			310 mg/g (35°C)	
Clay Based on ZnAl-r, molar ratio (3 and 4)	3 and Molar Ratio of Zn/Al Calcination	Indigo Carmine Dye	520.8 mg/g for CZnAl-4 > 358.4 mg/g for CZnAl-3 67.25 mg/g for ZnAl-3 > 21.65 mg/g for ZnAl-4	[34]
Smectite Rich Natural Clay	-	Acid Brown 75 Basic Yellow 28	8.33 mg/g 76.92 mg/g	[35]

Table 3 Alginate, its modification, contaminant removed and maximum adsorption efficiency

Adsorbent	Modification	Adsorbate	Adsorption Capacity or Maximum Absorption Efficiency	References
Sodium Alginate	Post-Crosslinking via Glutaraldehyde and Acetic Acid/HCl	Cu ²⁺ , Ag ⁺ , Fe ³⁺ and Methylene Blue	54.9 mg/g (Cu ²⁺), 82.8 mg/g (Ag ⁺) and 135.5 mg/g (Fe ³⁺) 572mg/g (Methylene blue)	[40]
Sodium Alginate	TiO ₂ Thin Film	Congo Red Dye	Increased >50%	[41]
Sodium Alginate	Ferrofluid as Magnetic Material , Activated Carbon	Methylene Blue	>34mmol/g of AC (Methylene Blue)	[42]
Alginic Acid Sodium Salt	Chitosan Powder	Direct Blue 78 Direct Yellow	97% (Direct Blue 78), 86% (Direct Yellow)	[43]
Alginates	Contains Ferrofluid and Activated Carbon, Cross Linked with Epichlorohydrin	Methyl Orange Methylene Blue	0.02 mmol/g (Methyl Orange) and 0.7 mmol/g (Methylene Blue)	[44]
Sodium Alginate	Cellulose Nano Crystal	Methylene Blue	256 mg/g 97%	[45]
Sodium Alginate	Cellulose Nano Crystal	Methylene Blue	255.5 mg/g	[46]
Alginate Beads	Immobilized Graphene Oxide	Acridine Orange	2.6 mmol/g	[47]

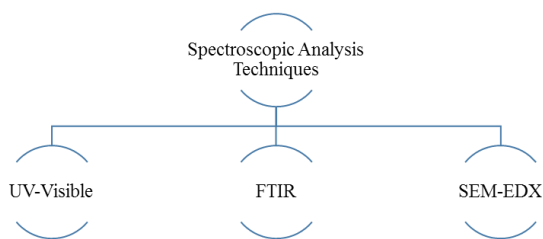
Table 4 Alginate-clay hybrid, dye removed and adsorption efficiency

Adsorbent	Adsorbate	Adsorption Capacity or Dye Removal Efficiency	References
Montmorillonite-Alginate Nano-biocomposite	Basic Red 46	85.07%	[48]
Ball Clay-Sodium Alginate	Methylene Blue	188.60%	[49]
Organobentonite-Sodium Alginate Composite 3:1 (AOBent/SA)	Methyl Orange	141.27 mg/g	[50]
Organobentonite-Sodium Alginate Composite 1:1 (AOBent/SA)	Methylene Blue	769 mg/g	[50]

10. Spectroscopic Analysis Techniques

UV-visible spectrometer has been used to determine the concentration of dyes in samples at their corresponding maximum absorption wavelength during the adsorption experiment. Functional groups present on the surface of adsorbents are studied via fourier-transform infrared spectroscopy (FTIR). The spectra were obtained from 400 cm⁻¹ to 4000 cm⁻¹. Information about the surface functional groups and surface sites that are responsible for adsorption is obtained by examining the surface of adsorbent before and after alteration [51]. Scanning electron

microscope provided with energy-dispersive X-ray analysis (SEM-EDX) has been utilized in determining surface morphology of clay (treated and untreated) and hybrid composites (before and after adsorption). During adsorption process EDX has been used for both semi-quantitative and qualitative analysis. It has been applied for determining the elemental composition of adsorbent after different levels of treatment [52].



11. Conclusion

Industrial wastewater contaminated with dyes is severely affecting environment and human health. According to the previous studies, clay and alginates are low cost adsorbents that can easily be obtained and their modification results in improved adsorption efficiency due to increased surface area and pore volume. Hybrids consisting of clay and alginates have better adsorption with increased surface area and high adsorption capacity. The adsorption process depends on various factors such as pH, temperature, contact time, dosage and initial concentration. Percentage of anionic dyes removal increased at low (acidic) pH while high pH favors the removal of cationic dyes due to electrostatic attraction. Adsorption process may be endothermic or exothermic, increase in temperature favors endothermic process and decrease in temperature favors exothermic process. Increasing the initial dye concentration leads to decrease in the percentage of dye removal as all available adsorption sites have been loaded. The amount of dye adsorption (mg/g) increases with increasing contact time at all initial dye concentrations. It was found that the removal efficiency increased with an increase in the amount of adsorbent.

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