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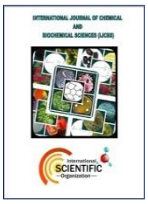

Wastewater treatment and dyes removal using electrocoagulation aided by natural Biosorbents – A review

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Abstract

Natural water reservoirs are found to be under intense pressure owing to the continuous population growth, rapid urbanization and excessive industrialization more specifically in developing countries of the world. Production of wastewater is a rising problem whose probable outcomes are further intensified because of inadequate infrastructure and improper management. According to some estimations approximately two million tons of agricultural waste and sewage material is annually discharge into natural waterways and this addition is completely illegal and fully unregulated. Several methods and techniques have commonly been employed in order to overcome this water pollution but each method has its own limitations. Among all methods, adsorption techniques proved to be rather more eco-friendly, cheap, cost effective and practically efficient when coupled with electrocoagulation. Use of natural bio-sorbents is known to have good adsorption potential and is abundantly available for agricultural country like Pakistan. This review article is compiled to explore the efficiency of different bio-sorbents for wastewater treatment. The objective of review is to recognise the use of different bio-sorbents such as fruit peels, husk, bagasse, straw, cotton waste, chitin chitosan, different seeds and water melon rind. This article reviews the optimum efficacy under optimum conditions of different types of bio-sorbents and natural inorganic adsorbents like clays, bentonite, sepiolite and zeolites. Different physical and chemical parameters are evaluated in order to estimate the efficacy of removal of contaminants in wastewater. Metals separation, regeneration and recycling are also studied in this review.

Key words: Biosorbents, Bagasse, Chitin and Chitosan, Bentonite, Sepiolite, Zeolite, Wastewater, Agricultural Waste

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1. Introduction

Water pollution is alarming product of rapid urbanization and excess industrialization thereby becoming a serious problem for almost all the countries of the world. Millions of different manufacturing units and agricultural industries are producing thousands of toxic pollutants like heavy metal ions, dyes or coloured impurities, complex organic compounds such as phenols, pesticides and other persistent organic pollutants. Wastewater that is being used for numerous agricultural applications and domestic purposes are posing serious threats to human life and biological components of entire ecosystem. Due to water pollution, world is facing thousands of water-borne diseases including cancer [1].

Economic development mainly relies on water all over the world. Water is being used in almost every sector like manufacturing industries, agriculture based livestock, agronomic wastes, horticultural by products, domestic residues, urban connections and rural supplies that had reduced the water quality and led to severe water scarceness. Water scarcity is one of the major issues, the world is facing today. According to UNESCO, reduction in water quality is the main cause of water scarcity. In present scenario, world is trying to achieve the efficient water recycling methods in order to meet the water supply challenges [2]. In water scarcity facing countries, Pakistan is at the top in facing serious water shortage since last two decades. The economy of Pakistan is agricultural based thus facing a huge pressure of water shortage. To overcome the water scarcity, untreated water is used for agricultural purposes that is resulting serious health problems and a variety of environmental problems in Pakistan. In Pakistan, the situation become very critical due lack of appropriate number of wastewater treatment plants [3].

Out of numerous water contaminants, hazardous dyes and coloured compounds are the most important toxic pollutants that are severely degrading the environment and aquatic ecosystem. Paper industry, pulp material, textile wastes and dyeing residues, leather by-products, printing equipments, tannery wastes and food processing units, cosmetics and paint industries are the main contributors of such kind of toxic dyes in water. Before leaving in natural water, these dyes should be pre-treated because it causes several diseases of skin such as strong irritation, intense mutations, lethal cancer, severe gastrointestinal infections and painful food poisoning. Hence, such kinds of dyes effluents should be removed in order to avoid the contamination of natural water resources.

Various methods and number of techniques are commonly used to treat the dyes waste from wastewater resources. Many cost-effective adsorbents are investigated for the treatment of dyes wastewater. These adsorbents were derived from agricultural wastes, industrial by-products and natural materials. Such kind of adsorbents got great attention because of their high pore ratio as well as cost effectiveness along with high fixed carbon content percentage [4].

Rapid industrial progress has been observed in last few decades, which resulted in release of large amount of toxic metals into environment. These metals showed extraordinary impacts on life and environment. Metals like cadmium, zinc, copper, nickel, lead, mercury and chromium are commonly found in industrial wastewaters that have showed drastic effects on water quality, human health and biodiversity of entire ecosystems [5].

In order to treat metals contaminated wastewaters, various techniques like chemical precipitation, adsorption, co-precipitation, carbon adsorption, ion exchange and membrane filtration have commonly been employed and extensively been investigated among which adsorption technique proved to be good owing to its cost effectiveness, simple design and ease of operation [6].

Nonconventional adsorbents are classified into five different categories (a) bio-adsorbents from living and non-living biomass (b) natural inorganic materials (c) agricultural and industrial wastes (d) fruit wastes and (e) plant wastes [7]. In last few years, many alternative, cheaper and easily available useful materials are tested to maintain the pollutant content level allowed by various legislative authorities. Biosorption showed excellent results in removing heavy metals from aqueous solution of industrial wastewater [8].

A large number of materials like maize bran, grape stalk waste, sugar beet pulp, tree fern, red sea-wood, carrot residues, olive pomace, bone char, *Aspergillus niger*, wheat bran, baggage fly ash, cassava waste, black locust, oak saw dust, sugarcane bagasse, almond shell carbon, carboxy methyl cellulose, spent grain, sunflower stalks and olive stone carbon are found to be potential natural adsorbents [9].

2. Biosorption

Removal of heavy metal contaminants from dilute aqueous wastewater by biosorption process has been investigated and showed promising results. This process has proven to be advantageous because of its efficiency and cheapness for reducing the heavy metal ions from wastewaters. The process of biosorption is effective and inexpensive which made it better process as compared to other techniques and processes. But it is only suitable to treat dilute solutions of contaminants. Typical sources of bio-sorbents are (1) microbial biomass like bacteria, fungi and yeast (2) algal biomass and (3) dead biomass like bark, lignin, shrimp, krill, squid and crab shell etc.

Biosorbents showed various characteristics like vast resource, cost effectiveness and potential adsorption. Various low cost and cheap adsorbents like potato peels, sawdust, black gram husk, eggshells, seed shells, coffee husk, sugar beet, pectin gels and citrus peels has been investigated for their potential of biosorption. In biosorption, techniques required a lot of work to be done because most of the work done is in theoretical or in experimental phases. Another main problem to be solved is the difficulty of separation of biosorbent after adsorption and removal of coloured impurities [10].

2.1 Agriculture Waste Based Biosorbents

Agriculture waste based biosorbents (AWBs) has shown strong affinity and high selectivity for heavy metals due to availability of large number of binding sites present on its surface. AWBs are cheaper, easily available, abundant and agricultural in origin. The application and processing of AWBs are easy and recovery has almost no effect on the end product and environment. On the basis of their characteristics, AWBs can be used in various industrial applications more preferably in comparison with numerous other conventional adsorbents, because it is eco-friendly, cheap and effective in nature [11].

2.1.1 Chitin and Chitosan

Naturally occurring polysaccharide more specifically chitin is found in crustaceans, crabs and shrimps and cuticles of insects and cell wall of fungi. In naturally occurring polysaccharides, chitin is the second most abundant polysaccharide after cellulose. It has showed a great adsorption capacity with respect to dyes and heavy metal ions in different fields of environmental biotechnology. In some recent scientific investigations, various physio-chemical parameters are being investigated for the adsorption of reactive yellow 2 (RY2) and reactive black 5 (RB5) [12].

Physical and chemical parameters of chitosan hydro-beads are being investigated for the adsorption of azo based dye congo-red by some recent researchers. Optimum activity of adsorption process has been investigated at 30°C. Both ionic and physical forces are identified in binding of chitosan with dyes. Many other affecting parameters like optimum pH range of 3.0-12 and optimum contact time of

10h has been found to be more efficient. Additionally, chitosan flakes and swollen tyrosinase chitosan bead's adsorptive abilities are investigated and being compared. Chitosan beads swollen with tyrosinase proved more efficient than chitosan flakes [13].

Adsorption capacity of chitosan swollen beads is five times more than the chitosan flakes. Higher yield of about 3.4 is found in case of dihydroxy phenyl alanine that is even lower than tyrosinase swollen chitosan beads that is 14 times as compared to chitosan flakes experimentally. Optimum temperature in case of chitosan tyrosinase beads is 30°C. The absorption of R222 dye, acid phosphate and glucosidase by chitosan beads are being investigated and showed higher efficiency in results [14].

In an experimental investigation, chitosan beads were prepared from cuttlebone waste. Crosslinking chemical regents like epichlorohydrin (ECH), gluteraldehyde, ethylene glycol and diglycidyl was used. These chemicals also contributed for the stabilization of beads in acid solutions and enhanced adsorption capacity. Adsorption capacity of single layer beads was found to be quiet higher that is 1,802-1,840gkg^{-1}at pH 3.0 and 30°C. Effects of initial dye concentrations, pH, temperature, ionic strength, beads wetness and dryness are the kinetics being investigated. With the decrease in pH and increase in dye initial concentration, huge increase in adsorption capacity was being reported. The adsorption capacity of chitosan beads were being investigated for different type of dyes such as Reactive Blue 2, Reactive Yellow 2, Reactive Red 2, Reactive Red 189 and various acid dyes like Acid Red 14, Acid Orange 7, Acid Orange 12 and one direct dye Red 81 that showed astonishing results with huge yield value of about 1.911-2.498 gkg^{-1}at pH 3-4 and temperature 30°C. Hence, chitosan was investigated and proved as potential low cost adsorbents as compared to commercially available activated carbon based adsorbents [15].

2.1.2 Cotton Waste

Cotton is a pure cellulose fiber that is extensively used all over the world. Physical and chemical properties of cotton proved that it has great adsorption capacity. Dyes like Reactive Yellow 23, Acid Yellow 99 and Acid Blue 25 were treated with cotton waste in 1.25 percent nitrogen solution which showed results in 302, 448 and 589 mg of adsorption at 293K. Cotton waste was being investigated for the adsorption of direct dye by reverse micellar process and high adsorption potential [16].

2.1.3 Garlic Peel

Garlic is used worldwide in cooking. The garlic peel is an agricultural based waste product that is reported to be a good biosorbent. Methylene blue dye adsorption by garlic peel was optimized with following parameters like contact time and initial concentration. For the efficient adsorption of MB by garlic peel, pH range was found to be optimum in between 4-12, initial concentration was 25-200 mgL^{-1} and temperature was 303, 313 and 323 Kelvin. The adsorption capacities of about 82.64, 123.45 and 142.86 mgL^{-1} were reported for monolayer of garlic peel. Reported results proved that garlic peel waste is a good substitute for costly adsorbents available now-a-days in market [17].

2.1.4 Tea Waste

Tea waste has proved to be an efficient adsorbent because of large surface area. Tea waste was being investigated for the adsorption of methylene blue dye in aqueous solution. Various parameters were investigated that affects adsorption capacity of tea waste including initial concentration of dye, pH, contact time and amount of dye adsorbed. Contact time of 5h, initial concentration of 20-50 mgL^{-1} and pH range of about 4.3 to 4.1 were found to be optimum for adsorption of methylene blue by tea waste. Tea waste showed great adsorption capacity of 85.16 mg g^{-1} for methylene blue dye [18].

2.1.5 Oil Palm Wood

Palm wood is an agricultural waste that has proved to be an excellent adsorbent. The wood was being investigated for adsorption by modifying it into activated carbon by pyrolysis for methylene blue dye. Physical and chemical parameters were investigated like optimum contact time was 1.5 hours, optimum pH was 7 and 298 K temperature showed 90.9 mg g^{-1} adsorption capacity of biomass activated wood of oil palm [19].

2.2 Fruit Peel Wastes as Biosorbents

Fruit peel wastes (FPW) are being investigated for the treatment of wastewater in recent few years. Food processing and agricultural industries are producing a huge amount of fruit peel waste which became a major environmental concern now-a-days. So FWP can be used for the treatment of wastewater effluents. FPW are natural bio-materials. Characteristics of FPW like (a) abundant availability (b) cost effectiveness (c) efficient adsorption capacity (d) easy chemical modification (e) easy regeneration and (f) least disposal problem after adsorption made them highly useful biosorbents. Physical characteristics of FPW depends on various parameters like (i) location of source (ii) geological conditions (iii) season (iv) ripening conditions and (v) quality or type of fruit [7]. Banana is the common and most consumed fruit all over the world. Many tons of banana peels are being produced on daily basis which causes environmental and disposal problems. Banana peel is investigated as useful and efficient adsorbent due to the presence of several chemical groups like carboxyl, hydroxyl and amides thus proved to play an effective role in the processes of biosorption [5].

2.2.1 Bagasse

Bagasse is the waste of sugar industry and it contains cellulose, lignin and pentose as a major chemical constituent. Bagasse has several functional groups like carboxyl, hydroxyl, carboxylic and amines which provides binding sites for metal ions through cation exchange on adsorptive sites [20]. Sugar cane bagasse is common agricultural waste and its excessive consumption as biosorbent can be economically feasible. After extracting the juice from sugar cane stalks, remaining biomass is 42% cellulose, 25% hemicellulose and 23% lignin that have numerous different carboxyl and hydroxyl groups which sturdily binds with metal cations during the process of adsorption. Bagasse has proved to be a potential biosorbent [5].

Bagasse was tested for removal of Methylene Blue dye and proved that chemically processed bagasse showed better results as compared to raw bagasse waste. Several affecting variables like concentration of dye, contact time, temperature, dose and pH was being investigated for the adsorption capacity of activated bagasse. It was reported that chemically processed bagasse showed 20% better results than raw waste bagasse in varied conditions. Activated bagasse was also investigated for the adsorption of Methylene Red from aqueous solution and many industries are known to use activated bagasse for the efficient adsorption of Methylene Red. Excellent adsorption of basic dyes like Basic Green 4, Basic Violet 1 and Basic Violet 10 were being investigated and showed effective results. For the adsorption capacity of activated bagasse, optimum pH 5.6-5.9, optimum contact time 12h and optimum temperature of 323 K were reported. Under optimum conditions, activated bagasse showed adsorption capacity of 34.20 mg g^{-1} [21].

2.2.2 Watermelon Rind

Watermelon rind is the most common source of non-essential amino acid such as citrulline as it has abundant amount of carboxyl and amino groups which has strong binding sites for heavy metals in aqueous solution of wastewater. Hence watermelon rind is an efficient biosorbent [5]. Watermelon is summer fruit and the red spongy material inside is used as fruit or juice but outer green rind is useless waste. Cellulose, lignin and pectin are two main components in watermelon rind. Cellulose, lignin and pectin contain hydroxyl and carboxyl functional groups which provide binding sites for heavy metal ions. Watermelon constitute 6-7% of the summer fruit production and in recent researches watermelon rind has shown an efficient economical adsorbent in removing cationic dyes and heavy metal cations like cadmium, nickle and cobalt from aqueous solution [22].

2.2.3 Husk

Husk is an agricultural residue that is basically a seed covering and a waste. Various types of husks like rice husk, bengal husk, hazelnut husk and coffee husk have commonly been investigated to treat the metal contaminated wastewater [20]. Rice husk is a cheap and inexpensive adsorbent and is abundantly studied for the treatment of various heavy metals and metalloids (like lead, cadmium, zinc, nickle and arsenic) removal from both ground and wastewaters. For the treatment of drinking water, treated rice husk is used as compared to untreated adsorbent in order to avoid low adsorption capacity, high COD and BOD and organic component released in water [23].

2.2.4 Straw

Straw is an agricultural by product and a waste material. Straw is mainly used as raw material in paper industry and animal fodder. Different types of straws like wheat straw, barley straw and rape straw are being investigated in recent years and showed good results and efficient adsorption from wastewater [20]. Wheat (*Triticum aestivum*) is commonly cultivated all over the world and is known to be a main food item. Consumption of wheat straws is more common in paper industry or for animals feed. On the other hand, wheat straw showed good metal sorption power in recent scientific researches [24].

2.2.5 *Passiflora ligularis* (Yellow Passion Fruit)

For the adsorption of methylene blue (MB) dye, powdered waste of yellow passion fruit waste (YPFW) was investigated as an efficient adsorbent. Adsorption capacity of YPFW for the MB was studied with various physiochemical parameters to optimize the conditions. The experiment was done in batch form. Suggested optimum physiochemical parameters were 303 K temperature, 42.5-43.5 hours of shaking time, 8.5-9.5 pH range and dosage of 3.2 mgL^{-1}. Out of two different sets of 23 experiments, the maximum reported yield of YPFW was 44.65-44.70 mg g^{-1} [25].

2.3 Seeds as Biosorbent

Different seeds such as *Moringa oleifera*, *Ocimum basilicum* L. and sawdust have commonly been used as natural and cost efficient biosorbents for adsorption of various coloured compounds and hazardous heavy metal ions from wastewater [26].

2.3.1 *Moringa oleifera* (MO)

Moringa oleifera is an all season plant that is famous for its many aspects like drought tolerance, analgesic activity, anti-hypertensive effects and anti-inflammatory actions. It is found in almost all tropical regions of the world. Seeds of *Moringa oleifera* has coagulating potential as finely grinded seeds were investigated for many features like turbidity, alkalinity, total dissolved solids and hardness for wastewater treatment [27].

2.3.2 *Ocimum basilicum* L. (Basil)

Ocimum basilicum L. is a traditional herbaceous plant that is found in tropical regions of Central and South America, Africa and Asia. The leaves and essential oil of this plant has long been used for fragrance in food and other traditions. It is reported that basil is used in dental formulations and oral products. Basil plant contains various bioactive compounds like flavonoids and has been reported for its anti-oxidant potentials and anti-microbial activities. Basil has been traditionally used in medicines to treat ulcer, dyspepsia, diarrhoea, migraine, insomnia, depression, acne, insect stings and skin infections. Basil seeds are the natural source of exopolysaccharides as it swells on wetting. There is a pectin matrix on the seed surface which becomes mucilaginous on wetting and swelling, and seeds have great capacity of hydration. The polysaccharide of basil consists of two main components glucomannan (1→4) xylan and a small amount of glucan. Glucomannan is comprised of polysaccharide chain of β-D-glucose and β-D-mannose with acetyl group attached in molar ratio 1:16 and β 1→4 linkage. Basil seeds were also tested for biosorption in order to ensure the removal of copper, hexavalent chromium, radionuclides of caesium-137 and strontium-90 from aqueous solution. Yet there are only few reports of basil seeds usage in treatment of wastewater [28].

2.3.3 Sawdust

Sawdust has been investigated as adsorbent and showed good adsorption potential as an alternative adsorbent. Sawdust contains phenolic, hydroxyl and carboxyl functional groups responsible for metal binding as metal ions hoard in secondary layer of wood where lignin is in less amount [29].

2.4 Fungi as Biosorbent

A large variety of fungi are being investigated to decolorize various dyes. Several genera of fungi have been investigated both in living as well as in in-active form to treat the wastewater contaminated with dyes. Some fungi genera like *Aspergillus niger*, *Rhizopus arrhizus* and *Rhizopus oryzae* are also investigated for decolorizing and absorbing a large variety of dyes along with white rot fungi. Fungi are widely used in biosorption. The mechanism involved in biosorption is both physical and chemical interactions like adsorption, deposition and ion exchange. Both carboxylic and amino groups of *Aspergillus niger* are the binding sites in the treatment of Basic Blue 9 dye. While in biosorption of Acid Blue 29, the electrostatic binding sites are primarily amino groups of *Aspergillus niger*. For biosorption of Congo red amino group, carboxyl group and phosphate groups are the binding sites along with the electrostatic attraction. Lipid fraction and amino group are the main binding sites along with physical, chemical and electrostatic attractions [43].

2.5 Algae as Biosorbent

Algae are found both in fresh as well as marine salt water. Algae are reported as potential adsorbents owing to their wide availability. Algae have relatively greater surface area and strong bonding affinity so it has great biosorption potentials. In algal biosorption mechanism, cell wall play major role in electrostatic attraction and adsorption. On the surface of cell wall, carboxyl, amino and phosphate groups are reported to be present which play major role in biosorption mechanism. These groups provide binding sites for contaminants in wastewater treatment. In the reported mechanism, dyes from wastewater diffused to solid biopolymer surface of algal cell wall [43].

2.6 Bacteria as Biosorbent

The mode of solute uptake by dead/inactive bacterial cells is extracellular and the chemical functional groups of the cell wall plays vital role in biosorption. Functional groups present on the bacterial cell wall include carboxyl, phosphonate, amine and hydroxyl groups. Several dye molecules, which exist as dye cations in solutions are also attracted towards carboxyl and other negatively charged groups. Also, amino groups adsorb anionic dyes via electrostatic interactions or hydrogen bonding. It was observed that the amine groups of *Corynebacterium glutamicum* were responsible for the binding of reactive dye anions via electrostatic attraction. Carboxyl, amine, phosphonate, sulfonate and hydroxyl groups have become well established as being responsible for dye binding [43].

3. Regeneration and Recovery of Loaded Metals and Dyes

The loaded metals and dyes can be recovered by physical or chemical treatments. Physical method involves microwaving and heating whereas chemical method involves the use of eluents as acid, alkali and organic solvent. NaOH, KOH, H_2SO_4, HCl, HNO_3, $NaNO_3$, $Ca(NO_3)_2$, EDTA, self-emulsifying drug delivery systems (S-EDDS) and Na-citrate etc. are the chemicals commonly employed for desorption. Even trace amount of valuable metals such as Cu^{2+}, Cr^{2+}, Cd^{2+}, Ni^{2+} and Au^{1+} have been recovered by standardizing the operating protocols and parameters. Furthermore, metal-stripped adsorbents proved amenable resources to regeneration and fit to be recycled and reused. Regeneration of the adsorbent after eluting the metals is easier and cheaper due to the abundance of hydroxyl and carboxyl groups on their surfaces [47]. It was suggested that gold can be eluted from biosorbents by improved striping method that involves alkali treatment followed by use of organic solvents [48]. It was reported that incineration of the gold-loaded sorbents is superior over gold-cyanide complex solution in metallic gold recovery [49].

3.1 Effect of pH

The pH of the solution is the most important parameter as it controls the sorption at the biomass–solution interface. It not only influences the charges on the sorption sites of biomass type but also the speciation of metal ions. So it is very important to consider the ionic states of the functional groups of the biosorbent as well as the metal solution chemistry at different pH values. A decrease in pH means there are more H^+ ions in the solution and the biomass is thus protonated. Thus the sorption sites are occupied by H+ ions before metal ions can attack them. The biosorbent now behaves as a positively charged species. When the pH is raised from highly acidic pH, this positive character decreases. FTIR analyses of simple and modified wheat straw (WS and MWS) showed that the biomass types contain a variety of functional groups namely carboxyl, hydroxyl, sulfhydryl, amino and amido, etc. With the change in pH of solution, the behaviour of each of these functional groups changes. For example, carboxyl groups are protonated in highly acidic pH (pH less than 3) and act as positively charged species and thus can attract negatively charged ions. On increasing the pH, de-protonation (ionization) of these functional groups occurs and they become negatively charged moieties. At this stage, they can attach positive cations with them. Generally, it can be inferred that at highly acidic pH, binding of positively charged metal ions is reduced due to electrostatic repulsions because of the positive nature of the adsorbent and the binding increases with the increase in pH because the adsorbent becomes negatively charged [24].

3.2 Effect of Contact Time

The studies of contact time are very important as these provide the minimum time required to remove maximum amount of metal ions from solution and thus help scaling up the entire process [24].

4. Natural Inorganic Materials

Soil contains several inorganic materials which were proved to be efficient, cheap and substitutive adsorbents like clay, zeolites, bentonites and sepiolites. Greater surface to volume ratio were reported for these adsorbents. Due to huge resources of adsorbents, these materials were used without renewal. Most of the soil adsorbents were reported to be efficient with layered structures. Needle like structure of soil adsorbents were also reported in some studies which proved that clay adsorbents have huge surface area and cost effectiveness as compared to commercially available activated carbon [50].

4.1 Clay

Clay is a major component of soil and it is known to have various types like sepiolite, vermiculite, serpentine, kalonite and smectites. Adsorption of Acid Blue 9, Methylene Blue, Basic Red 18 and other cationic dyes were investigated along with various other parameters strongly affecting the adsorption efficiency. The contact time of one hour and pH range of 1-11 were found to be optimum for wastewater treatment by using these materials as potential adsorbents. Mica, kaolinite, montmorillonite and smectite are the subgroups of clay that were investigated for their adsorption efficiency. Clay was also investigated as metal adsorbent. Clay polymer composites were proved to be good and efficient adsorbents for heavy metal ions. Results showed that when the solution concentration of metal increases the adsorption capacity of clay increases from 0.95-9.4 mgg^{-1}. The optimum adsorption capacity was found at the pH of about 5.5, temperature 308-318 K and adsorbent dose of 30 g L^{-1} [51].

4.2 Sepiolite

Sepiolite is one of the clay contents of soil that was proved to be potential adsorbent in previous studies. Sepiolite was proved as cheap and non-renewing adsorbent. Layered structures with canals and lumps were reported for sepiolite. Sepiolite contains sheets of silica and magnesium. Sepiolite was investigated for the treatment of different dyes like Acid Blue 62, Methylene Blue, Methylene Violet and Reactive Blue 221 and Acid Red dye. Different parameter like 473 K temperature, 5.5-11 pH range and 3h contact time was reported to be optimum having maximum adsorption capacities for sepiolite. Sepiolite was also investigated for the adsorption of Basic Red 9 triarylmethane dye. Various reaction parameters like temperature, contact time, initial concentration and pH were optimized. Contact time of 40 min was required to establish adsorption equilibrium. It was reported that by increasing initial concentration of dye, the efficiency of adsorption increases. For the adsorption of Basic Red 9, negative surface charge of sepiolite is required. Maximum initial concentration of 180×10^{-6} $molL^{-1}$ of Basic Red 9 dye was reported sufficient for its efficient adsorption. Three different temperatures 298K, 308K and 318K were reported for the treatment of Basic Red 9 by sepiolite with lower temperature favouring the adsorption. Adsorption capacity of sepiolite depends on the iso-electric pH which was reported to be 3.27 for sepiolite where its negative and positive sites were found to be equal. Results showed that adsorption capacity of sepiolite increases with the increase in pH as negative sites increases for cationic dyes [52].

4.3 Bentonite

Bentonite is extensively found in earth crust. Main components of bentonite are aluminium phyllosilicates and montmorillonite that were investigated as potential adsorbents. Bentonite was investigated for the adsorption of colloidal solutions, coloured dyes and other impurities abundantly found in wastewater. Modified bentonite dodecyl trimethyl ammonium bromide (DTMA-bentonite) was investigated for the adsorption of Acid Blue 193, Methylene Blue, Malachite Green and Basic Blue 9 from aqueous solution. Parameters affecting the adsorptivity of modified bentonite were reported to be optimum at pH ranging from 1.5-7, temperature 293K and adsorption capacity of about 740.5 mgg^{-1} [53].

4.4 Zeolites

Various parameters for the maximum adsorption capacity of Ramazol Yellow and Ramazol Brilliant Blue dyes were investigated. Zeolite adsorbent dosage of 10 gL^{-1}, contact time of about 3-5h, initial dyes concentration of about 100 mgL^{-1} and 24h for 1000 mgL^{-1} dyes concentration and solid to liquid ratio 10 gL^{-1} were reported to be optimum with maximum dye removal efficiency. Optimum contact time for both dyes was reported to be in between 10 to 11 hours. Optimum dosage of zeolite was found to be 10 gL^{-1} with 150 rpm and 12h of reaction time. Optimum adsorption capacities of Ramazol Yellow and Ramazol Brilliant Blue were 38.311 and 13.4952 mgg^{-1}. Experiments proved that there was slight change in adsorption capacity of surface modified zeolites from 30°C to 600°C. So, optimum temperature for adsorption of Ramazol Yellow and Ramazol Brilliant Blue was 25-30°C [54].

Table 1 Natural biosorbents and their adsorption capacities

Biosorbent	Contaminants Removed	Max. Adsorption Capacity	pH	Particle Size	References
Lemon Peel	Cobalt (Co)	22 mg/g	6.0	BSS 150–200	[6]
Watermelon Rind	Chromium (Cr^{3+})	172.6 mg/g	3.0	100 Mesh Size	[22]
Watermelon Rind	Nickel (Ni^{2+}) and Cobalt (Co^{2+})	35.5 mg/g for Ni^{2+} 23.3 mg/g for Co^{2+}	5.0	100 Mesh Size	[30]
Banana Peel	Copper (Cu)	8.24 mg/g	6.48	<150 µm	[5]
Sugarcane Bagasse	Copper (Cu)	9.48 mg/g	6.48	<150 µm	[5]
Watermelon Rind	Copper (Cu)	5.73 mg/g	6.48	<150 µm	[5]
Orange Peel	Lead Ions (Pb^{2+})	46.61 mg/g	5.0	20 Mesh	[31]
Coffee Husk	Cyanide Ions	90.6%	8.0	-	[32]
Saw Dust	Zn (II) and Cd (II)	14.10 mg/g(Zn) and 26.73 mg/g(Cd)	5.0(Zn) and 6.0(Cd)	250–350 µm	[9]
Neem Bark	Zn (II) and Cd (II)	13.29 mg/g (Zn) and 25.57 mg/g (Cd)	5.0 (Zn) and 6.0 (Cd)	250–350 µm	[9]
Moringa Oleifera Seeds	Cu, Cd and Pd	98% (Cu and Cd) and 78.1% (Pb)	600 µm	-	[27]
Ocimum basilicum L.	Congo Red Dye	68.5%	6.0-8.5	-	[28]
Wheat Straw	Cd (II)	39.22 mg/g	6.0	<100 µm	[33]
Walnut Shell	Hg (II) Ion	151.5 mg/g	5.0	0.088 mm	[34]
Passiflora ligularis	Methylene Blue	44.70 mg g^{-1}	8.5-9.5	<100 µm	[35]
Bagasse	Basic Green 4, Basic Violet 1 and Basic Violet 10	34.20 mg g^{-1}	5.6-5.9	<100 µm	[36]
Oil Palm Wood	Methylene Blue	90.90 mg g^{-1}	7.0	<100 µm	[37]
Tea Waste	Methylene Blue	85.16 mg g^{-1}	4.3	<100 µm	[38]
Garlic Peel	Methylene Blue	142.86 mg g^{-1}	6.0	<100 µm	[39]
Cotton Waste	Reactive Yellow 23	0.37 mmol g^{-1}	7.0	-	[40]
	Acid Yellow 99	0.36 mmol g^{-1}	7.0	-	
	Acid Blue 25	0.59 mmol g^{-1}	7.0	-	
Chitin	Reactive Yellow 2 and Reactive Yellow Black 5	2.83 mgg^{-1} and 1.88 mgg^{-1}	8.0 and 6.0	-	[41]
	Acid Red 73	782.2 mgg^{-1}	7.0		
Chitosan	Reactive Red 189, Acid Red 14, Acid Orange 7, Acid Orange 12, Direct Red 81, Direct Red 28	1936 mgg^{-1} 1940 mgg^{-1} 1940 mgg^{-1} 1954 mgg^{-1} 2383 mgg^{-1} 81.23 mgg^{-1}	3.0 3.0 4.0 3.0 4.0 7	-	[42]

Table 2 Microorganisms as effective biosorbents for removal of toxicants

Biosorbents	Contaminant Removed	Adsorption Capacity	pH	Particle Size	References
Dead Fungi (*Aspergillus niger)*	Direct Red 28	14.7 mg/g	6.0	Less than or equal	[44]

				to 300 µm	
Alga	Reactive Red 5	196.1 mg/g	2.0	-	[45]
Corynebacterium glutamicum	Reactive Black 5 at 500 mg/L	350 mg/g	1.0	0.4–0.6 mm	[46]

Table 3 Natural inorganic materials as potential adsorbents for removal of dye

Natural Inorganic Adsorbent	**Contaminants Removed**	**pH**	**Contact Time**	**Adsorption Capacity**	**Reference**
Clay	Basic Red 22	7.0	1h	488.40 mgg^{-1}	[55-57]
	Basic Blue 69	7.0	1h	585 mgg^{-1}	
	Basic Red 18	3.0	1h	157 mgg^{-1}	
	Acid Blue 9	3.0	1.5h	57.80 mgg^{-1}	
	Methylene Blue	7.0	1.5h	6.30 mgg^{-1}	
Sepiolite	Reactive Yellow 176	11.0	3h	169.1mgg^{-1}	[58-62]
	Reactive Black 5	11.0	3h	120.5 mgg^{-1}	
	Reactive Red 239	11.0	3h	108.8 mgg^{-1}	
	Methylene Blue	6.6	3h	$1.87\times10^{-4}molg^{-1}$	
	Acid Blue 62	6.7	3h	$32.9\times10^{-4}molg^{-1}$	
	Reactive Blue 221	6.7	3h	$55.9\times10^{-4}molg^{-1}$	
	Methyl Violet	6.6	4h	$1.76\times10^{-4}molg^{-1}$	
	Basic Red 9	>3.27	40min	$180\times10^{-6}molL^{-1}$	
Bentonite	Malchite Green	7	3h	7.2 mgg^{-1}	[63-66]
	Acid Blue 193	1.5	3h	740 mgg^{-1}	
	Basic Blue 9	7.9	3h	1667 mgg^{-1}	
	Methylene Blue	6.8	3h	33.0 mgg^{-1}	
Zeolite	Ramazol Yellow	7.0	12h	38.311 mgg^{-1}	[67]
	Ramazol Brilliant Blue	7.0	12h	13.50 mgg^{-1}	

Conclusions

Biosorbents are most efficient adsorbents for removal of various toxic contaminants such as dyes and heavy metals from wastewater. These biosorbents are abundantly available in low cost and can be easily regenerated and recycled. Due to these benefits along with various other advantages, such types of materials are rather more demanding adsorbents for wastewater treatment in comparison with other objects. Biosorbents can be obtained easily from agricultural wastes such as fruit peels, bagasse, husks, seeds and many others. By determining the optimum conditions, maximum advantages can be obtained from these natural biosorbents. Various factors such as particle size, contact time, pH and temperature are controlled to obtain maximum output. Highly basic pH promotes binding of positively charged metal ions.

References

[1] I. Anastopoulos, G.Z. Kyzas. (2015). Composts as Biosorbents for Decontamination of Various Pollutants: a Review. Water, Air, & Soil Pollution. 226(3): 61.

[2] D.L. Villasenor-Basulto, P.D. Astudillo-Sanchez, J. del Real-Olvera, E.R. Bandala. (2018). Wastewater treatment using Moringa oleifera Lam seeds: a review. Journal of Water Process Engineering. 23: 151-164.

[3] M.A. Khan, S.S. Shaukat, M.A. Khan. (2009). Growth, yield and nutrient content of sunflower (Helianthus annuus L.) using treated wastewater from waste stabilization ponds. Pak. J. Bot. 41(3): 1391-1399.

[4] A. Bhatnagar, E. Kumar, A. Minocha, B.-H. Jeon, H. Song, Y.-C. Seo. (2009). Removal of anionic dyes from water using Citrus limonum (lemon) peel: equilibrium studies and kinetic modeling. Separation Science and Technology. 44(2): 316-334.

[5] C. Liu, H.H. Ngo, W. Guo, K.-L. Tung. (2012). Optimal conditions for preparation of banana peels, sugarcane bagasse and watermelon rind in removing copper from water. Bioresource technology. 119: 349-354.

[6] A. Bhatnagar, A. Minocha, M. Sillanpää. (2010). Adsorptive removal of cobalt from aqueous solution by utilizing lemon peel as biosorbent. Biochemical Engineering Journal. 48(2): 181-186.

[7] P.D. Pathak, S.A. Mandavgane, B.D. Kulkarni. (2015). Fruit peel waste as a novel low-cost bio adsorbent. Reviews in Chemical Engineering. 31(4): 361-381.

[8] S. Ahmady-Asbchin, Y. Andres, C. Gerente, P.L. Cloirec. (2009). Natural seaweed waste as sorbent

for heavy metal removal from solution. Environmental technology. 30(7): 755-762.

[9] T.K. Naiya, P. Chowdhury, A.K. Bhattacharya, S.K. Das. (2009). Saw dust and neem bark as low-cost natural biosorbent for adsorptive removal of Zn (II) and Cd (II) ions from aqueous solutions. Chemical Engineering Journal. 148(1): 68-79.

[10] F. Fu, Q. Wang. (2011). Removal of heavy metal ions from wastewaters: a review. Journal of environmental management. 92(3): 407-418.

[11] T. Nguyen, H. Ngo, W. Guo, J. Zhang, S. Liang, Q. Yue, Q. Li, T. Nguyen. (2013). Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. Bioresource technology. 148: 574-585.

[12] M. Bilal, M. Asgher, R. Parra-Saldivar, H. Hu, W. Wang, X. Zhang, H.M. Iqbal. (2017). Immobilized ligninolytic enzymes: an innovative and environmental responsive technology to tackle dye-based industrial pollutants–a review. Science of the Total Environment. 576: 646-659.

[13] E. El-Sayed, T. Tamer, A. Omer, M. Mohy Eldin. (2016). Development of novel chitosan schiff base derivatives for cationic dye removal: methyl orange model. Desalination and Water Treatment. 57(47): 22632-22645.

[14] L. Li, Y. Li, L. Cao, C. Yang. (2015). Enhanced chromium (VI) adsorption using nanosized chitosan fibers tailored by electrospinning. Carbohydrate polymers. 125: 206-213.

[15] S. Olivera, H.B. Muralidhara, K. Venkatesh, V.K. Guna, K. Gopalakrishna, Y. Kumar. (2016). Potential applications of cellulose and chitosan nanoparticles/composites in wastewater treatment: a review. Carbohydrate polymers. 153: 600-618.

[16] S. Hokkanen, A. Bhatnagar, M. Sillanpää. (2016). A review on modification methods to cellulose-based adsorbents to improve adsorption capacity. Water research. 91: 156-173.

[17] A. Asfaram, M. Fathi, S. Khodadoust, M. Naraki. (2014). Removal of Direct Red 12B by garlic peel as a cheap adsorbent: kinetics, thermodynamic and equilibrium isotherms study of removal. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 127: 415-421.

[18] L.S. Thakur, M. Parmar. (2013). Adsorption of heavy metal (Cu2+, Ni2+ and Zn2+) from synthetic waste water by tea waste adsorbent. International Journal of Chemical and Physical Sciences. 2(6): 6-19.

[19] T. Ahmad, M. Rafatullah, A. Ghazali, O. Sulaiman, R. Hashim. (2011). Oil palm biomass–Based adsorbents for the removal of water pollutants—A review. Journal of Environmental Science and Health, Part C. 29(3): 177-222.

[20] C.K. Jain, D.S. Malik, A.K. Yadav. (2016). Applicability of plant based biosorbents in the removal of heavy metals: a review. Environmental Processes. 3(2): 495-523.

[21] C. Dalai, R. Jha, V. Desai. (2015). Rice husk and sugarcane baggase based activated carbon for iron and manganese removal. Aquatic Procedia. 4: 1126-1133.

[22] N.A. Reddy, R. Lakshmipathy, N. Sarada. (2014). Application of Citrullus lanatus rind as biosorbent for removal of trivalent chromium from aqueous solution. Alexandria Engineering Journal. 53(4): 969-975.

[23] S. Lata, S. Samadder. (2014). Removal of heavy metals using rice husk: a review. International Journal of Environmental Research and Development. 4(2): 165-170.

[24] U. Farooq, M.A. Khan, M. Athar, J.A. Kozinski. (2011). Effect of modification of environmentally friendly biosorbent wheat (Triticum aestivum) on the biosorptive removal of cadmium (II) ions from aqueous solution. Chemical Engineering Journal. 171(2): 400-410.

[25] G.P. Gerola, N.V. Boas, J. Caetano, C.R.T. Tarley, A.C. Gonçalves, D.C. Dragunski. (2013). Utilization of passion fruit skin by-product as lead (II) ion biosorbent. Water, Air, & Soil Pollution. 224(2): 1446.

[26] A.C. Gonçalves Jr, F. Rubio, A.P. Meneghel, G.F. Coelho, D.C. Dragunski, L. Strey. (2013). The use of Crambe abyssinica seeds as adsorbent in the removal of metals from waters. Revista Brasileira de Engenharia Agrícola e Ambiental. 17(3): 306-311.

[27] T.C. Shan, M. Al Matar, E.A. Makky, E.N. Ali. (2017). The use of Moringa oleifera seed as a natural coagulant for wastewater treatment and heavy metals removal. Applied Water Science. 7(3): 1369-1376.

[28] S. Shamsnejati, N. Chaibakhsh, A.R. Pendashteh, S. Hayeripour. (2015). Mucilaginous seed of Ocimum basilicum as a natural coagulant for textile wastewater treatment. Industrial Crops and Products. 69: 40-47.

[29] A. Abdolali, W. Guo, H.H. Ngo, S.-S. Chen, N.C. Nguyen, K.L. Tung. (2014). Typical lignocellulosic wastes and by-products for biosorption process in water and wastewater treatment: a critical review. Bioresource technology. 160: 57-66.

[30] R. Lakshmipathy, N. Sarada. (2013). Application of watermelon rind as sorbent for removal of nickel

and cobalt from aqueous solution. International Journal of Mineral Processing. 122: 63-65.

[31] V. Lugo-Lugo, S. Hernández-López, C. Barrera-Díaz, F. Ureña-Núñez, B. Bilyeu. (2009). A comparative study of natural, formaldehyde-treated and copolymer-grafted orange peel for Pb (II) adsorption under batch and continuous mode. Journal of Hazardous Materials. 161(2-3): 1255-1264.

[32] M. Gebresemati, N. Gabbiye, O. Sahu. (2017). Sorption of cyanide from aqueous medium by coffee husk: Response surface methodology. Journal of applied research and technology. 15(1): 27-35.

[33] A. CO, K.A. El-Latif, R. Abdullah, M. Yusoff. (2011). Rice production and water use efficiency for self-sufficiency in Malaysia: a review. Trends in Applied Sciences Research. 6(10): 1127-1140.

[34] M. Zabihi, A. Ahmadpour, A.H. Asl. (2009). Removal of mercury from water by carbonaceous sorbents derived from walnut shell. Journal of Hazardous Materials. 167(1-3): 230-236.

[35] B. Hameed, R. Krishni, S. Sata. (2009). A novel agricultural waste adsorbent for the removal of cationic dye from aqueous solutions. Journal of hazardous materials. 162(1): 305-311.

[36] N. Consolin Filho, E. Venancio, M. Barriquello, A. Hechenleitner, E. Pineda. (2007). Methylene blue adsorption onto modified lignin from sugar cane bagasse. Eclética Química. 32(4): 63-70.

[37] A. Ahmad, M. Loh, J. Aziz. (2007). Preparation and characterization of activated carbon from oil palm wood and its evaluation on methylene blue adsorption. Dyes and Pigments. 75(2): 263-272.

[38] M.T. Uddin, M.A. Islam, S. Mahmud, M. Rukanuzzaman. (2009). Adsorptive removal of methylene blue by tea waste. Journal of hazardous materials. 164(1): 53-60.

[39] B. Hameed, A. Ahmad. (2009). Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass. Journal of hazardous materials. 164(2-3): 870-875.

[40] P. Sharma, H. Kaur, M. Sharma, V. Sahore. (2011). A review on applicability of naturally available adsorbents for the removal of hazardous dyes from aqueous waste. Environmental monitoring and assessment. 183(1-4): 151-195.

[41] G. Akkaya, İ. Uzun, F. Güzel. (2007). Kinetics of the adsorption of reactive dyes by chitin. Dyes and Pigments. 73(2): 168-177.

[42] Y. Wong, Y. Szeto, W. Cheung, G. McKay. (2004). Adsorption of acid dyes on chitosan—equilibrium isotherm analyses. Process Biochemistry. 39(6): 695-704.

[43] A. Srinivasan, T. Viraraghavan. (2010). Decolorization of dye wastewaters by biosorbents: a review. Journal of environmental management. 91(10): 1915-1929.

[44] Y. Fu, T. Viraraghavan. (2002). Removal of Congo Red from an aqueous solution by fungus Aspergillus niger. Advances in Environmental Research. 7(1): 239-247.

[45] Z. Aksu, S. Tezer. (2005). Biosorption of reactive dyes on the green alga Chlorella vulgaris. Process Biochemistry. 40(3-4): 1347-1361.

[46] K. Vijayaraghavan, Y.-S. Yun. (2007). Utilization of fermentation waste (Corynebacterium glutamicum) for biosorption of Reactive Black 5 from aqueous solution. Journal of Hazardous Materials. 141(1): 45-52.

[47] S. Patel. (2012). Potential of fruit and vegetable wastes as novel biosorbents: summarizing the recent studies. Reviews in Environmental Science and Bio/Technology. 11(4): 365-380.

[48] M. Soleimani, T. Kaghazchi. (2008). Activated hard shell of apricot stones: a promising adsorbent in gold recovery. Chinese Journal of Chemical Engineering. 16(1): 112-118.

[49] I.S. Kwak, M.A. Bae, S.W. Won, J. Mao, K. Sneha, J. Park, M. Sathishkumar, Y.-S. Yun. (2010). Sequential process of sorption and incineration for recovery of gold from cyanide solutions: Comparison of ion exchange resin, activated carbon and biosorbent. Chemical Engineering Journal. 165(2): 440-446.

[50] Y. Zhao, X. Zhao, A. Babatunde. (2009). Use of dewatered alum sludge as main substrate in treatment reed bed receiving agricultural wastewater: Long-term trial. Bioresource technology. 100(2): 644-648.

[51] B.I. Olu-Owolabi, A.H. Alabi, E.I. Unuabonah, P.N. Diagboya, L. Böhm, R.-A. Düring. (2016). Calcined biomass-modified bentonite clay for removal of aqueous metal ions. Journal of Environmental Chemical Engineering. 4(1): 1376-1382.

[52] D. Yildiz, I. Kula, N. Şahin. (2013). Preconcentration and determination of Cd, Zn and Ni by flame atomic absorption spectrophotometry by using microorganism Streptomyces albus immobilized on sepiolite. Eurasian Journal of Analytical Chemistry. 8(3): 112-122.

[53] W.S. Tan, A.S.Y. Ting. (2014). Alginate-immobilized bentonite clay: adsorption efficacy and reusability for Cu (II) removal from aqueous solution. Bioresource technology. 160: 115-118.

[54] H. Figueiredo, B. Silva, C. Quintelas, M.M.M. Raposo, P. Parpot, A. Fonseca, A. Lewandowska,

M. Bañares, I.C. Neves, T. Tavares. (2010). Immobilization of chromium complexes in zeolite Y obtained from biosorbents: synthesis, characterization and catalytic behaviour. Applied Catalysis B: Environmental. 94(1-2): 1-7.

[55] P. Waranusantigul, P. Pokethitiyook, M. Kruatrachue, E. Upatham. (2003). Kinetics of basic dye (methylene blue) biosorption by giant duckweed (Spirodela polyrrhiza). Environmental pollution. 125(3): 385-392.

[56] Y. Bulut, Z. Baysal. (2006). Removal of Pb (II) from wastewater using wheat bran. Journal of environmental management. 78(2): 107-113.

[57] J.-w. Feng, Y.-b. Sun, Z. Zheng, J.-b. Zhang, L. Shu, Y.-c. Tian. (2007). Treatment of tannery wastewater by electrocoagulation. Journal of Environmental Sciences. 19(12): 1409-1415.

[58] O. Ozdemir, B. Armagan, M. Turan, M.S. Celik. (2004). Comparison of the adsorption characteristics of azo-reactive dyes on mezoporous minerals. Dyes and Pigments. 62(1): 49-60.

[59] M. Doğan, Y. Özdemir, M. Alkan. (2007). Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite. Dyes and Pigments. 75(3): 701-713.

[60] M. Alkan, S. Çelikçapa, Ö. Demirbaş, M. Doğan. (2005). Removal of reactive blue 221 and acid blue 62 anionic dyes from aqueous solutions by sepiolite. Dyes and Pigments. 65(3): 251-259.

[61] D. Karadag, M. Turan, E. Akgul, S. Tok, A. Faki. (2007). Adsorption equilibrium and kinetics of reactive black 5 and reactive red 239 in aqueous solution onto surfactant-modified zeolite. Journal of Chemical & Engineering Data. 52(5): 1615-1620.

[62] J. Kyzioł-Komosińska, C. Rosik-Dulewska, A. Dzieniszewska, M. Pająk, I. Krzyżewska. (2014). Removal of Cr (III) ions from water and wastewater by sorption onto peats and clays occurring in an overburden of lignite beds in central Poland. Environment Protection Engineering. 40(1).

[63] H. Tahir, M. Sultan, Z. Qadir. (2013). Physiochemical modification and characterization of bentonite clay and its application for the removal of reactive dyes. International Journal of Chemistry. 5(3): 19.

[64] H. Chen, J. Zhao. (2009). Adsorption study for removal of Congo red anionic dye using organo-attapulgite. Adsorption. 15(4): 381-389.

[65] G. Crini. (2006). Non-conventional low-cost adsorbents for dye removal: a review. Bioresource technology. 97(9): 1061-1085.

[66] N. Al-Bastaki. (2004). Removal of methyl orange dye and Na2SO4 salt from synthetic waste water using reverse osmosis. Chemical engineering and processing: Process intensification. 43(12): 1561-1567.

[67] A. Kuleyin, F. Aydin. (2011). Removal of reactive textile dyes (Remazol Brillant Blue R and Remazol Yellow) by surfactant-modified natural zeolite. Environmental Progress & Sustainable Energy. 30(2): 141-151.