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Research Paper

Development of Starch -Based Cationic Adsorbents for Removal of Anionic Dyes from Aqueous Systems

Science

KEYWORDS : Starch, cationized starch, quaternary ammonium salt, dye removal, acid dye

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ABSTRACT

Three cationic starch derivatives containing quaternary ammonium salt were prepared, including starch-2-hydroxy propyl-trimethyl ammonium chlorid , starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride. They having different chain length of the alkyl moiety. The essential target for such preparation is to bring into focus adsorbents which completely can remove anionic dyes, e.g., acid dyes from aqueous systems thereby improving the quality of water. Chemical changes in the molecular structure of starch by derivatization through cationization were monitored using FTIR, while morphological changes were detected using SEM. These derivatives were treated with four acid dyes: Methyl Orange, Yellow 2G, Acid red 27 and Methyl blue, which have different number of sulfonic group and different molecular weight. Factors affecting % of the dye removal were studied which, include structural nature of the dye (number of sulphonic group and molecular weight), chain length of the alkyl moiety of cationic starch, amine content, adsorbent dose, dye concentration, pH of the treating bath, duration of the treatment and agitation speed. According to the % of dye removal the starch-based adsorbents follow the order: Starch-2-hydroxy propyl-trimethyl ammonium chloride > Starch-2-hydroxy propyl-triethyl ammonium chloride > Starch-2-hydroxy propyl-tripropyl ammonium chloride and Methyl Orange > Yellow 2G > Acid red 27 > Methyl blue.

1 Introduction

Pollution of environment has become of a great concern over the last three decades world-wide. This was evidenced by the ever growing people`s worry about the present and future of the worlds. Such worry is; in particular, associated with the continuous enhancement and conferment effect of the environmental pollution which has very negative impact on distortion of the ecosystems.

One of the serious environmental pollution problems is the removal of dyes from water, which, is very important because the water quality is greatly affected by colour. Acid dyes are widely used in many industries such as textile, cosmetics, printing, paper, food processing, plastics, dye manufacturing, leather and pharmaceutical [1].

In dyeing processes 10–15% of all dyestuffs are lost directly to wastewater. The discharges of industrial wastewater containing dyes cause serious environmental problems because of its high toxicity and possible accumulation in the environment. Since the dyes are recalcitrant organic molecules, wastewater containing dyes is very difficult to be treated, where, they have a synthetic origin and complex aromatic molecular structures [2]. So they are resistant to aerobic digestion, and stable to light, heat and oxidizing agents [3,4]. Nowadays, the water pollution of organic has attracted a global concern because of its harmful impact on public health [5,6].

Adsorption is a process which, transfers the species from the water effluent to a solid phase thereby keeping the effluent volume to a minimum [7]. This process appears to be good for the treatment of effluents [8], due to low cost with high adsorption capacity, biodegradability [9,10], and also to control the biochemical oxygen demand [11].

In recent years, interest in finding an effective alternative adsorbances as starch [12], cellulose [1,13], chitin, chitosan [14-16] and lignin [17] is growing.

Various adsorbers have been used, including long-chain, amine-bearing primary, secondary, or tertiary amine groups to remove the anionic dyes e.g. reactive dyes and metal-complex acid dyes. The effect of pH and the structure of the amine has been studied [18]. Also studied were cationic starch derivatives containing primary, secondary, tertiary amino group, quaternary ammonium salt etherified and grafted that have been treated with three types of dyes i.e., acid dye, hydrolyzed reactive dye and direct dye [19], cationic starch derivatives bearing tertiary amine groups [20, 21] or cationized cellulose (quaternary ammonium salts) which, exhibited a much better adsorption capacity towards anionic dyes than cellulose. The results reveal: a) the adsorption capacity is dependent on nature of both adsorbent and dye as well as The temperature of the adsorption process [22], b) cationic starch-bearing quaternary ammonium salt are suitable, in principle, for the decolourisation of reactive dyestuff hydrolysates, and c) that they also display the desirable effect in the treatment of effluents containing direct dyestuffs [23].

The aim of this study was to compare all types of quaternary cationic starch derivatives bearing different amine groups chain length, as dye absorbers'. Also study the effect of dye molecular weight and active group numbers on the adsorption process.

2. EXPERIMENTAL

2.1. Materials

Methyl Orange, Yellow 2G, Acid red 27 and Methyl blue were used after purification. The structure of dyes, their chemical name and molecular size are shown in table 1.

Quat-188 (3-chloro-2-hydroxypropyl) tri-methyl ammonium chloride, triethylamine, tripropylamine were supplied by Fluka, Germany. Starch was supplied by Cairo Company for starch and glucose, Cairo, Egypt. Sodium hydroxide, epichlorohydrin, ethanol, isopropanol, hydrochloric acid, acetic acid, dimethyl sulphoxide, n-butanol, ethylether were among laboratory grade chemicals.

N-(3-chloro-2-hydroxypropyl) triethylammonium chloride and *N*-(3-chloro-2-hydroxypropyl) tripropylammonium chloride were prepared in accordance with the literature [24].

2.2 Preparation of cationic starch bearing quaternary ammonium salt

Starch-2-hydroxy propyl-trimethyl ammonium chloride (SHPTMAC) was prepared via reacting starch with Quat-188 (3-chloro-2-hydroxypropyl) tri-methyl ammonium chloride) in presence of sodium hydroxide as catalyst according to Hebeish et al [25]. Starch-2-hydroxy propyl-triethyl ammonium chloride

(SHPTEAC), and starch-2-hydroxy propyl-tripropyl ammonium chloride (SHPTPAC) were prepared via reacting starch with, *N*-(3-chloro-2-hydroxypropyl) triethylammonium chloride and *N*-(3-chloro-2-hydroxypropyl) tripropylammonium chloride respectively, in presence of sodium hydroxide as catalyst using the semi-dry process according to Khalil et al [24].

2.3 Dye purification

This was done by dissolving 10 g sample of dye in 10 ml dimethyl sulphoxide at 60°C, the solution so obtained was filtered and the dye was precipitated in 500 ml n-butanol at room temperature for 15 min. The dye was filtered and washed twice with ethanol, then with ethylether. The purified dyes were dried at 60 °C [19].

2.4 Adsorption of dyes

Adsorption experiments were carried out by shaking the adsorbent with 100 ml aqueous dye solution of required concentration at 30 °C in a thermostatic shaker operated at different rpm (0-300). The samples were withdrawn from the shaker and the dye solution was separated from the adsorbent by centrifugation. Dye concentration in the supernatant solution was estimated by measuring absorbance at a suitable λmax for each dye using SHTMADZU UV-Visspestrophptometer and computing concentration from the calibration curve.

The amount of dye adsorbed onto the adsorbent, q_e (mg/g) was calculated by mass balance relationship [Eq. 1].

$$q_e = (C_o - C_e)\ V/W \qquad (1)$$

Where C_o and C_e are the initial and equilibrium liquid-phase concentrations of dye (mg/l), V the volume of solution (L), and W the weight of the adsorbent (g).

$$\%\ \text{of dye removal} = 100\ X\ q_e / C_o \qquad (2)$$

2.5 Analysis

2.5.1 Nitrogen Content

The amine content of the prepared cationic starch derivatives was estimated via determination of nitrogen content by ASTM Method E258-67 as follows:

$$\text{Amine content} = \frac{\text{Nitrogen \%} \quad X\ 1000}{14} (\text{m mole / 100 g sample})$$

2.5.2 FT-IR Spectra

Infrared spectra of starches were taken on a Nicolet Nexus 470 Fourier transform infrared

spectra (FTIR) spectrophotometer (Thermo Electron Corporation, USA) between 4000 and 400 cm^{-1} at a resolution of 4 cm^{-1} for 32 scans using KBr pellets.

2.5.3 Scanning electron micrographs

Scanning electron micrographs were taken with a scanning electron probe micro analyzer (JXA-840A JEOL, Tokyo, Japan). The specimen in the form of films were mounted on the specimen stabs and sputtered with thin gold films. The micrographs were taken at magnification of 10006 using 10 kV accelerating voltage.

3. RESULTS AND DISCUSSION

3.1 Characterization of The Quaternary Starch

3.1.1 Infra red spectra

The FTIR spectra is a useful tool for investigating the structure of quaternary starches and native starch were taken to examine the changes in chemical structure, as shown in Figure 1.

Compared with the spectrum of native starch at curve (a), new peaks were observed in 1481-1484 cm^{-1} the spectra of starch-2-hydroxy propyl-trimethyl ammonium chloride at curve (b) at 1481cm-1, starch-2-hydroxy propyl-triethyl ammonium chloride at curve at1483 cm^{-1} (c), and starch-2-hydroxy propyl-tripropyl ammonium chloride at curve (d) at 1484 cm^{-1} . The peaks were assigned to stretching vibration of C-N [26-28] in quaternary starch substituents. The peaks proved successful introduction of starch-2-hydroxy propyl-trimethyl ammonium chloride, starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride substituents onto starch chains, respectively.

3.1.2 Scanning electron micrographs

The changes in morphology of the native and cationic starch granules were studied by using the scanning electron microscopy (SEM).

The native corn starch granules (Fig. 2a) are round and polygonal in shape with well-defined integrity, whereas the cationization process considerably changes the starch granule morphology; being dependent upon the chain length of the quaternary group in the molecular structure of starch. This state affairs is low with starch-2-hydroxy propyl-trimethyl ammonium chloride (Fig. 2b); the cationic reagent penetrates the interior of the starch molecule, and the starch granules are markedly enlarged and begin to disintegrate.

With a further increase in chain length as in starch-2-hydroxy propyl-triethyl ammonium chloride (Fig. 2c), the surfaces of the starch granules completely disintegrate, and their edges drastically lose definition. Destroying the structure of the corn granule and reducing hydrogen bonding apparently occur with starch-2-hydroxy propyl-tripropyl ammonium chloride (Fig. 2d). The latter quaternary starch acquires the longest chain length within the range studied.

3.2 Factors Affecting Dye Adsorption

3.2.1 Structural nature of the dye (number of sulphonic group and molecular weight)

Table 2 depicts the relationship between the number of sulfonic group of the dye and its molecular weight and maximum decolorization efficiency expressed as percent of dye removal. The latter was monitored when different dyes (Methyl Orange, Yellow 2G, Acid red 27 and Methyl blue) were used. As is evident the maximum % of dye removal depends on number of sulphonic group and molecular weight of the dye and follows the order:

Methyl Orange > Yellow 2G > Acid red 27 > Methyl blue

It is also evident (table 2) that at the same amine content the maximum dye sorption efficiency percent (i.e. maximum % of dye removal) relies on the dye molecular weight e.g. with starch-2-hydroxy propyl-trimethyl ammonium chloride (amine content 100 m mole/100 g sample) the dye sorption efficiency percent were 100, 95.9, 87 and 75 for the Methyl Orange, Yellow 2G, Acid red 27 and Methyl blue respectively. In case of starch-2-hydroxy propyl-triethyl ammonium chloride (amine content 128 m mole/100 g sample), the dye sorption efficiency percent were 92, 83, 72 and 64 for the Methyl Orange, Yellow 2G, Acid red 27 and Methyl blue respectively, with quaternary ammonium salt derivative of starch-2-hydroxy propyl-tripropyl ammonium chloride (amine content 100 m mole/100 g sample) the dye sorption efficiency percent were 83, 71, 60.9 and 47 for the Methyl Orange, Yellow 2G, Acid red 27 and Methyl blue respectively. The superiority of Methyl Orange is due to its highest reactivity which is associated with the presence of basic group and lower molecular size of this dye (see table 1).

Methyl Orange has only one sulfonic group, therefore, the electrostatic force of which is less than that of Yellow 2G which has two sulfonic groups. Indication of this is that the electrolytes reduce the extent of binding of the dye with the quaternary starch and, therefore, the binding energy decreases. That is, the binding energy, probably because of a diminished electrostatic interaction between the dye anion and the oppositely charged group on the polymer decreases. This could be explained in terms of stiric hindrance effect. However, decrement in the capacity of dye sorption by decrement in total absorbent surface area in the sorbent cannot be ruled out. It is logical that, the decrease in the capacity of dye sorption may be attributed to overlapping or aggregation of adsorption sites resulting in a decrease in total adsorbent surface area available to the dye and an increase in diffusion path length. Here, the remaining vacant surface sites were difficult to occupy because of the repulsive forces between the dye molecules on the cationized starch and the bulk phase [29].

Table 2 shows also that, the binding extent of Acid red 27 by cationized starch is higher than that of Methyl blue although both have the same number of sulfonic groups and the only difference between them is the parent structure or the molecular weight. Therefore it seems reasonable to attribute the difference in the binding affinity of these dyes to the electrostatic force between dye and cationized starch.

3.2.2 Chain length of the alkyl cationic starch

We have prepared three cationic starch derivatives, namely, starch-2-hydroxy propyl-trimethyl ammonium chloride, starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride. These derivatives bear the same amine group but having different chain length of the alkyl. The essential reason for such preparation is to clarify the effect of chain length of the alkyl in these cationic starch derivatives on % of the dye removal. Figure 3 shows the effect of the alkyl cationic starch on the percent of dye removal for the dye Methyl Orange.

Results of % of dye removal shown in Figure 3 and table 2 signify that:

The % of dye removal increases with increasing the amine content to reach maximum value then decreases. This is observed irrespective of the cationic starch derivatives used or dyes employed within the range studied.

The % of dye removal values of starch-2-hydroxy propyl-trimethyl ammonium chloride samples are higher than those of starch-2-hydroxy propyl-triethyl ammonium chloride, and starch-2-hydroxy propyl-tripropyl ammonium chloride samples.

The maximum % of dye removal values of the starch-2-hydroxy propyl-trimethyl ammonium chloride samples are higher than those of the starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride samples. Those samples of quaternary starch exhibit maximum % of dye removal values of 100, 92 and 83% respectively when Methyl Orange dye was used.

The maximum % of dye removal values of the starch-2-hydroxy propyl-trimethyl ammonium chloride samples are higher than those of starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride samples; the latter display values of 95.9, 83 and 71%, respectively, when Yellow 2G dye was used .

The maximum % of dye removal values obtained with the starch-2-hydroxy propyl-trimethyl ammonium chloride samples are higher than those of the starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride samples. These values are 87, 72 and 63.8% for starch-2-hydroxy propyl-trimethyl ammonium chloride, starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride compounds respectively when Acid red 27 dye was used.

The maximum % of dye removal values obtained with starch-2-hydroxy propyl-trimethyl ammonium chloride samples are higher than those of the starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride samples. The latter exhibit values of 75, 64 and 50% for starch-2-hydroxy propyl-trimethyl ammonium chloride, starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride compounds, respectively, using Methyl blue dye.

The maximum % of dye removal is determined by chain length of the alkyl cationic group in the molecular structure of starch and follows the order:

Starch-2-hydroxy propyl-trimethyl ammonium chloride > Starch-2-hydroxy propyl-triethyl ammonium chloride > Starch-2-hydroxy propyl-tripropyl ammonium chloride.

It is understandable that the quaternary ammonium salt has very high basisity. Starch-2-hydroxy propyl-tripropyl ammonium chloride has very high stirric hindirance due to the highest substitutions chain length whereas starch-2-hydroxy propyl-trimethyl ammonium chloride has the lowest stirric hindirance. Meanwhile starch-2-hydroxy propyl-triethyl ammonium chloride acquires stirric hindirance in between which makes it stands in mid-way position in affecting its dye sorption value and bring into focus the aforementioned order which is, indeed, the same order reported previously [19].

3.2.3 Amine content

Table 2 shows the effect of amine contents (within a range of (25-170) m mole/100 g sample) on the % of dye removal brought about using the three cationic starch derivatives under investigation. It is obvious that:

(a) the % of dye removal increases with increasing the amine content to attain maximum value and then decreases thereafter. This is observed regardless of the four dyes used (Methyl Orange, Yellow 2G, Acid red 27 and Methyl blue) and;

(b) the maximum % of dye removal is a manifestation of the chain length of the alkyl amine. The maximum dye sorption values obtained with the three cationic starches in question are 100, 92 and 83 for Methyl Orange, 95.9, 85 and 71 for Yellow 2G, 87, 72 and 63.8 for Acid red 27 and, 64 and 50, m mole dye/100 g sample) for 74Methyl blue

With the above ends in view, it is clear that they need a plausible explanation which may be drawn as given under.

Anionic dye sorption by making use of cationic starch depends on: (a) the amine type, (b) amine content (the distance between every functional group) and (c) the dye molecular size. At low amine content, the distance between the functional groups is lower than the dye molecular size. Therefore the dye sorption increases by increasing the amine content up to a distance equal to the dye molecular size to get the maximum dye sorption. On increasing the amine content the distance between the functional groups became lower than the dye molecular size which cause stirric hindirance, leading to lower utilization for the functional group for dye sorption [19].

The maximum % of dye removal attain values of 100% (at amine content 100 m mole/100 g sample), 92% (at amine content 128 m mole/100 g sample), 83% (at amine content 133 m mole/100 g sample) for starch-2-hydroxy propyl-trimethyl ammonium chloride, starch-2- hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride, respectively, when Methy Orange was employed (see table 2).

This order is not obtained at the same amine content i.e., the starch-2-hydroxy propyl-trimethyl ammonium chloride acquires the highest % of dye removal at amine content (100 mmole/100 g sample) while the starch-2-hydroxy propyl-triethyl ammonium chloride acquire the lower % of dye removal at amine content (128 m mole/100 g sample). On the other hand, starch-2-hydroxy propyl-tripropyl ammonium chloride displays the lowest % of dye removal at amine content (133 m mole/100 g sample).

3.2.4 Adsorbent dose

Adsorbent dose is an important parameter in determination of adsorption capacity and adsorption percent. Table 3a shows the % dye removal as function of adsorbent concentration. The adsorption of the dye on starch-2-hydroxy propyl-trimethyl ammonium chloride, starch-2-hydroxy propyl-triethyl ammonium chloride, and starch-2-hydroxy propyl-tripropyl ammonium chloride, at different concentrations (50 – 500 mg/L) was investigated, for a duration of 75 min. Dye concentration (150 ppm) with amine content 100 mmole/100 g sample and at pH 2 were employed for performing dye adsorption. Results of table 3 shows that % of dye removal increases by increasing the adsorbent contents from (50 – 300 mg/L) for all dyes and all cationized starches and then levels off at an adsorbent dose (400 - 500 mg/L). This is the case with all dyes and all cationized starch. Nevertheless Methyl orange is an exception since the % of dye removal increases by increasing absorbent concentration. Most probably the increase in the number of ions competing for the available binding sites on the surface of the adsorbent cause almost complete decolorization of dyes by virtue of higher cationicity of the adsorbent. Crini [30] observed that the increase in adsorption with adsorbent dosage can be attributed to increasing the adsorbent surface and availability of more adsorption sites. Also, higher molecular weight of the dye and longer chain length of the amine decrease the % of dye removal. This destabilization can be attributed to the electrostatic repulsion among the anions of dye already bound with polycations when the optimal range is exceeded [31].

3.2.5 Dye concentration

Table 3b shows the effect of dye concentration on the % of dye removal using different acid dyes and cationized starches. The latter include three cationic starch derivatives, namely, starch-2-hydroxy propyl-trimethyl ammonium chloride, starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride, bearing amine content of 100 mmole/100 g sample. Treatment of the dye solution with cationized starch was performed at room temperature for 75 min. at pH 2 and adsorbent (300 mg/L) while shaking at 175 rpm using the acid dye at different concentrations (50 – 500 mg /L).

It is observed (table 3b) that, the % of dye removal is determined by the dye concentration and structural nature of the dye embracing the functional group of the dye and its molecular weight in addition to the chain length of the alkyl cationic starch. The % of dye removal attains a value of 100 % with all dyes and with all types of cationized starch provided that the dye concentration is equal to 50 ppm. Nevertheless, starch-2-hydroxy propyl-trimethyl ammonium chloride attains 100 % of dye removal when higher dye concentrations were employed. For example a dye concentration range of 50-200 ppm and of 50-100 ppm for Methyl Orange and Yellow 2G respectively. On the other hand, 100 % of dye removal could be achieved only at a dye concentration of 50 ppm in case of Acid red 27 and Methyl blue. It is logical that increasing the acid dye concentration would increase the number of collisions between acid dye anions and adsorbent, which enhances the sorption process. It is also logical that a large number of vacant surface sites are available for dye adsorption during the initial stage of interaction of the dye with the adsorbent when dye concentration of 50 ppm is used [32].

Starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride achieve the goal by through attaining 100% of dye sorption using at Methyl Orange at a concentration range of 50-100 ppm, while, the other dyes attain 100% dye removal at concentration of 50 ppm only. It is believed that the increase in dye adsorption is direct consequence of both the adsorbent surface and the structure matter of the dye with all dyes and all cationized substrate, higher concentrations of the dyes is accompanied by lower % of dye removal, because higher concentration of acid dye leads to an increase in the mass gradient between the solution and the cationized starch. Then this mass gradient functions as a driving force for the transfer of acid dye molecules from bulk solution to the cationized starch surface.

It is further postulated that the decrement in the capacity of dye sorption may be attributed to overlapping or aggregation of adsorption sites. As a result, there will be a decrease in total adsorbent surface area available to the dye and an increase in diffusion path length. Once this the case, the remaining vacant surface sites are difficult to occupy because of the repulsive forces between the dye molecules on the cationized starch and the bulk phase [29]. By and large, current results may be regarded as indication of the suitability of starch-2-hydroxy propyl-trimethyl ammonium chloride for the adsorptive treatment of textile effluents.

3.2.6 pH of the reacting bath

Table 4a shows the effect of pH of the treating bath in the % of dye removal when different acid dyes and different cationized starches were used. As a function of pH, % of dye removal of four acid dyes via adsorption onto cationic starch-2-hydroxy propyl-trimethyl ammonium chloride, starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride was determined. These cationized starches bear amine content of 100 mmole/100 g sample. The treatment was carried out at room temperature for 75 min., adsorbent at a concentration of 300 mg/L while, shaking at 175 rpm with a dye concentration of 150 mg/L. The treatment of the cationized starches with the acid dye was conducted at different pH`s (1-8) in order to establish the optimum pH value for each dye. The pH solutions were adjusted by 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH as set out in table (4a)

Table 4a shows the % of dye removal using the different cationized starches. The results imply that:

(1) With all acid dyes, % of dye removal increases by increasing the pH till maximum values are attained and then decreases. The decrease in adsorption capacity at $pH < 2$ is attributed to the amino group as being closed to the sulfonic group of the acid dyes. Also the access of nitrogen molecules becomes difficult due to the small size of the pores at very low pH [32].

(2) The maximum % of dye removal of all acid dyes occurs at pH 2.

(3) Although, the maximum dye sorption of all acid dyes occurs at pH 2 yet it has different

values being dependent upon molecular weight and number of sulphonic groups of the acid dye. Values of maximum dye sorption amount to 100, 95.5, 87 and 75 for the dyes: Methyl Orange, Yellow 2G, Acid red 27 and Methyl blue respectively.

It is as well to report that, adsorption behavior of each of the said dyes onto starch-2-hydroxy propyl-triethyl ammonium chloride, and starch-2-hydroxy propyl-tripropyl ammonium chloride was monitored for comparison (table 4a). Clearly the adsorption capacity for each kind of dye onto starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride is much less than that of the starch-2-hydroxy propyl-trimethyl ammonium chloride. This means that, maximum % of dye removal depends on chain length of the alkyl cationic starch type and follows the order:

Starch-2-hydroxy propyl-trimethyl ammonium chloride > Starch-2-hydroxy propyl-triethyl ammonium chloride > Starch-2-hydroxy propyl-tripropyl ammonium chloride.

The adsorption of the acid dye onto cationic starch could be associated with a combination of electrostatic interaction, hydrogen bond and van der Waals force. Logically, the pH of the solution affects the surface charge of the adsorbent and also the degree of ionization of the materials (essentially the acid dye) present in the solution. Increase in the solution pH causes the dissociation of the functional groups on the adsorbent surface active sites which, in turn, affects the adsorptive process. Acid dyes are also called anionic dyes because they usually exist in the sulphate form. Therefore, at a lower pH, the cationic starch bearing quaternary ammonium salt surface will be positively charged via protonation process, which increases the electrostatic attractions between acid dye molecules and cationic starch bearing quaternary ammonium salt surface. At higher pH, the number of positively charged sites are reduced and raise the number of negatively charged sites, creating electrostatic repulsion between the negatively charged surface of the cationic starch bearing quaternary ammonium salt and the anionic acid dyes molecules where the sulfonic group of the dye molecules present negative charge even at strong acidic solutions since their pKa values are lower than zero [33,34]. On the other hand, the lower adsorption of acid dyes, in alkaline pH is because of the presence of excess OH ions competing with the dye anions for the adsorption sites. As a result, there was no significant reduction in the adsorption of acid dyes from the solution. A similar behavior was observed for the adsorption of anionic dye onto native and modified fungus biomass [35].

3.2.7 Duration of treating bath

Table 4b shows the effect of duration (time allowed for interaction of the acid dye with cationized starches, on % of dye removal of four acid dyes under their interaction with cationic starch-2-hydroxy propyl-trimethyl ammonium chloride, starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride. These cationized starches bear amine content of 100 mmole/100 g sample. The treatment was carried out at room temperature while shaking at 175 rpm with absorbent concentration of 300 mg/L and dye concentration of 150 mg /L at pH2 for various periods of time (15-210 min) in order to establish the optimum duration for each dye.

Results of table 4b bring into focus the following:
The % of dye removal increases by increasing the adsorption duration (irrespective) regardless of the acid dye and cationic starches used. However, with Methyl Orange the dye sorption increases till reaching 100% with all types of cationic starches. It is certain, however, that % dye removal of 100% could be achieved under the effect of different durations 75, 90 and 120 min were recorded for starch-2-hydroxy propyl-trimethyl ammonium chloride, starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride, respectively.

With the acid dye Yellow 2G, 100% dye removal could be achieved within durations of 90, 120 and 150 min for starch-2-hydroxy propyl-trimethyl ammonium chloride, starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride, respectively.

With Acid red 27 and Methyl blue, the % of dye removal increases by time up to 180 and 210 min. respectively. Further prolongation of time is also accompanied by increment in dye sorption value but to lower extent and there is no 100% dye removal.

With the above ends in view, the results reflect the effect of chain length of the alkyl group and also the molecular weight and number of sulphonic group of the dyes on % of dye removal. The initial dye adsorption is rapid because the adsorption of the dye occurs initially onto the exterior surface, after that the dye molecules enter into pores (interior surface), a relatively slow process [36], indicating the effect of repulsive forces between the dye molecules on the cationized starch and the bulk phase.

3.2.8 Agitation speed

Agitation speed is an important parameter in adsorption phenomena, where, it is influencing the distribution of the solute in the bulk. This effect was studied on starch-2-hydroxy propyl-trimethyl ammonium chloride, bearing (amine content 100 mmole/100 g sample) at room temperature for 75 min. and at pH 2 and adsorbent (300 mg/L) with dye concentrations (150 mg/L) and different speed of agitation from 0 (without shaking) to 300 rpm using the four dyes: Methyl Orange, Yellow 2G, Acid red 27 and Methyl blue.

Figure 4 shows the % of dye removal versus the speed of agitation. Obviously, increasing the speed of agitation from 0 rpm to 175 rpm is accompanied by enhancement in the % of dye removal which attains the highest values irrespective of the dye used. No increasing in % of dye removal is observed when the speed of agitation is increased to more than rpm value of 175 rpm. This could be ascribed to the point that increasing the agitation rate causes the film resistance to mass transfer surrounding the adsorbent particles to decrees. As a result, an increase in the adsorption of the dye molecules occurs. At any event, however, optimum agitation speed calls for175 rpm.

4 Conclusions

Results of the present study signified that chain length of the alkyl moiety of the prepared cationic starch derivatives, namely, starch-2-hydroxy propyl-trimethyl ammonium chloride, starch-2-hydroxy propyl-triethyl ammonium chloride and starch-2-hydroxy propyl-tripropyl ammonium chloride exerted a marked influence on acid dye removal and followed the order:

Starch-2-hydroxy propyl-trimethyl ammonium chloride > Starch-2-hydroxy propyl-triethyl ammonium chloride > Starch-2-hydroxy propyl-tripropyl ammonium chloride.

This order was valid for the four acid dyes: Methyl Orange, Yellow 2G, Acid red 27 and Methyl blue. Meanwhile the structural nature of the dye (number of sulphonic group and molecular weight) had a substantial effect on the % of dye removal and followed the order:

Methyl Orange > Yellow 2G > Acid red 27 > Methyl blue

FTIR Spectroscopy and Scanning Electron Microscope (SEM) confirmed the changes in the molecular structure and morphological characteristics of the starch granules, respectively, by derivatization via cationization.

Current results may be regarded as indication of the suitability of starch-2-hydroxy propyl-trimethyl ammonium chloride for the adsorptive treatment of textile effluents where, this starch derivative achieved the goal (i.e.100% dye removal) at an amine content of 100 mmole/100 g sample and room temperature for 75 min. at pH 2 and adsorbent (300 mg/L) while shaking at 175 rpm using the acid dye concentrations (150 mg /L) especially when the dye Methyl Orange, was used .

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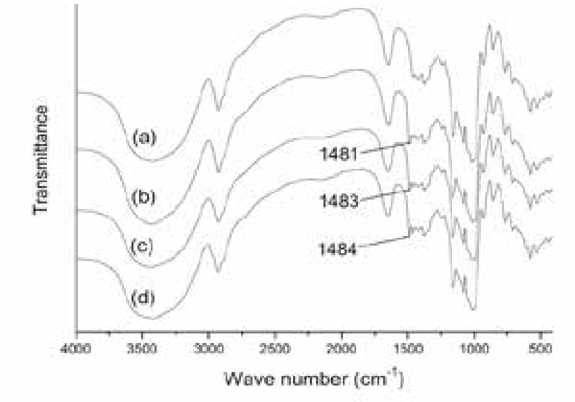
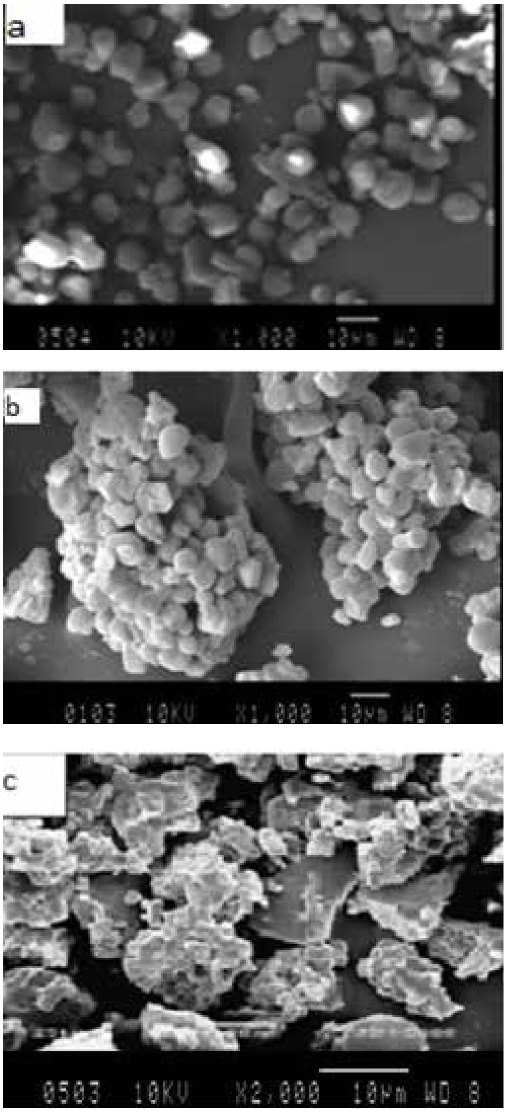


Figure 1: FTIR of native starch (a); trimethyl ammonium chloride hydroxypropyl starch (b); triethyl ammonium chloride hydroxypropyl starch(c); tripropyl ammonium chloride hydroxypropyl starch (d).



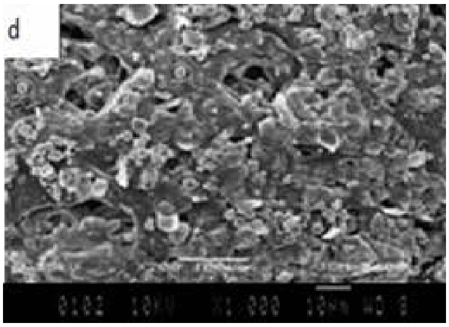


Figure 2: SEM pictures of starch granules: (a) native starch; (b) trimethyl ammonium chloride hydroxypropyl starch; (c) triethyl ammonium chloride hydroxypropyl starch; (d) tripropyl ammonium chloride hydroxypropyl starch.

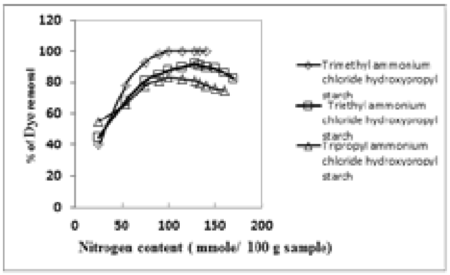


Figure 3: Effect of chain length of the alkyl cationic starch on the % of dye removal for Methyl Orange dye

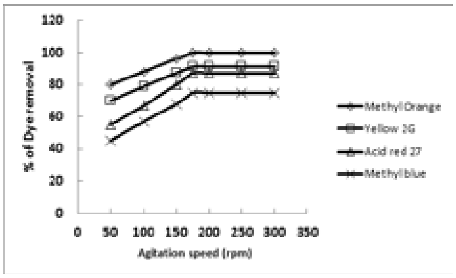


Fig. 4: Effect of agitation speed on % of dye removal of acid dyes

trimethyl ammonium chloride hydroxypropyl starch (amine content 100 mmole/100 g sample); at room temperature, adsorbent (300 mg/L); at 75 min. ; dye concentrations (150 mg /L) a; pH2 .

Table 1: Dyes structure and molecular weight.

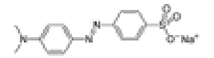
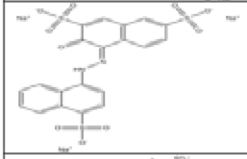
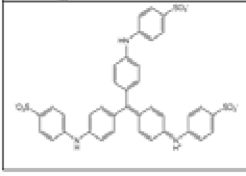
Dye formula	Dye name	Molecular weight	Molecular formula
	Methyl Orange	327.33	$C_{14}H_{14}N_3NaO_3S$
	Yellow 2G	551.29	$C_{16}H_{10}Na_2N_4O_7S_2$
	Acid red 27	604.47305	$C_{20}H_{11}N_2Na_3O_{10}S_3$
	Methyl blue	799.814	$C_{37}H_{27}N_3Na_2O_9S_3$

Table 2 : Effect of type of dye , amine type and content on the % of dye removal at pH 2.

Dye type	Trimethyl ammonium chloride hydroxypropyl starch		Triethyl ammonium chloride hydroxypropyl starch		Tripropyl ammonium chloride hydroxypropyl starch	
	Amine content mmole/100 g sample	% of dye removal	Amine content mmole/100 g sample	% of dye removal	Amine content mmole/100 g sample	% of dye removal
Methyl Orange	54	78.0	50	68	25	60
	75	90	75	81	50	76
	90	97	100	88	100	83
	100	100	128	92	133	80
	115	100	150	90	160	75
	140	100	170	85	---	---
Yellow 2G	54	70.0	50	62	25	56
	75	83.0	75	75	50	68
	90	91.0	100	80	100	71
	100	95.9	128	83	133	69
	115	95.9	142	79	160	60
	140	90.0	170	68	---	--
Acid red 27	54	65	50	55	25	36.0
	75	76	75	65	50	51.0
	90	83	100	70	100	60.9
	100	87	128	72	133	63.8
	115	83	142	65	160	55.0
	140	72	170	60	---	---
Methyl blue	54	55	50	51.0	25	25
	75	63	75	58.0	50	40.0
	90	70	100	63.0	100	47
	100	75	128	64.0	133	50.0
	115	71	142	60.0	160	47.6
	140	65	170	55.0	---	----

At room temperature, ; dye concentrations (150 mg /L) ; shaking at 175 rpm ; pH2 ; 75 min.; adsorbent (300 mg/L).

Table 3a: Effect of adsorbent dose on % of dye removal using different acid dyes and different cationized starch substrate.

Dye type	adsorbent concentration mg/L	Trimethyl ammonium chloride hydroxypropyl starch	Triethyl ammonium chloride hydroxypropyl starch	Tripropyl ammonium chloride hydroxypropyl starch
		% of dye removal		
Methyl Orange	50	78.0	62	55
	100	90	68	60
	200	97	81	76
	300	100	88	83
	400	100	92	80
	500	100	90	85
Yellow 2G	50	70.0	62	56
	100	83.0	70	63
	200	91.0	78	69
	300	95.9	80	71
	400	93.0	79	60
	500	90.0	68	55
Acid red 27	50	65	55	36.0
	100	76	61	45.0
	200	83	67	51.5
	300	87	70	60.9
	400	83	65	55.0
	500	72	60	50
Methyl blue	50	55	51.0	25.0
	100	63	58.0	35.0
	200	70	61.0	40.0
	300	75	63.0	47.0
	400	71	60.0	44.6
	500	65	55.0	40.0

Cationic starch (amine content 100 mmole/100 g sample); at room temperature, ; dye concentrations (150 mg /L) ; shaking at 175 rpm ; pH 2 ; 75 min. .

Table 3b: Effect of dye concentration on the % of dye removal using different acid dyes and different cationized starch substrate.

Dye type	Dye concentration (ppm)	% of dye removal		
		Trimethyl ammonium chloride hydroxypropyl starch	Triethyl ammonium chloride hydroxypropyl starch	Tripropyl ammonium chloride hydroxypropyl starch
Methyl Orange	50	100	100	100
	100	100	100	100
	150	100	88	83
	200	100	82	73
	250	92	70	62
	300	80	62	60
Yellow 2G	50	100	100	100
	100	100	92	88
	150	95.5	80	71
	200	85	71	69
	250	69	64	56
	300	50	49	41

Acid red 27	50	100	100	100
	100	90	82	75
	150	87	70	61
	200	79	67	54
	250	61	53	46
	300	42	32	22
Methyl blue	50	100	100	100
	100	80	73	63
	150	75	63	47
	200	67	57	40
	250	53	42	36
	300	35	25	15

Cationic starch (amine content 100 mmole/100 g sample); at room temperature, adsorbent (300 mg/L); shaking at 175 rpm ; pH 2 ; 75 min.

Table 4a: Effect of pH of the medium on the % of dye removal using different acid dyes and different cationized starch substrate.

Dye type	pH	% of dye removal		
		Trimethyl ammonium chloride hydroxypropyl starch	Triethyl ammonium chloride hydroxypropyl starch	Tripropyl ammonium chloride hydroxypropyl starch
Methyl Orange	1	88	79	68
	2	100	88	83
	3	92	82	77
	4	72.9	78	62
	5	58	48	40
	6	50	42	35
	7	44	39	30
	8	35	33	25
Yellow 2G	1	77	68	59
	2	95.5	80	71
	3	85	71	69
	4	69	64	56
	5	50	39	31
	6	44	34	24
	7	40	29	20
	8	33	22	17
Acid red 27	1	70	60	50
	2	87	70	61
	3	79	67	54
	4	61	53	46
	5	42	32	22
	6	39	26	18
	7	30	21	14
	8	23	17	12
Methyl blue	1	65	52	41
	2	75.0	63	47
	3	67	57	40
	4	53	42	36
	5	35	25	15
	6	30	20	10
	7	23	13	7
	8	16	10	5

Cationic starch (amine content 100 mmole/100 g sample); at room temperature, adsorbent (300 mg/L); shaking at 175 rpm ; dye concentrations (150 mg /L) ; 75 min. .

Table 4b : Effect of duration of the medium on the % of dye removal using different acid dyes and different cationized starch substrate.

Dye type	**Duration (min)**	% of dye removal		
		Trimethyl ammonium chloride hydroxypropyl starch	Triethyl ammonium chloride hydroxypropyl starch	Tripropyl ammonium chloride hydroxypropyl starch
Methyl Orange	30	78.0	55	60
	45	90	68	71
	60	97	81	79
	75	100	88	83
	90	100	92	95
	120	100	100	100
Yellow 2G	30	65	62	56
	45	70.0	70	60
	60	83.0	77	67
	75	95.9	80	71
	90	100	96	83
	120	98	100	95
	150	90	97	100
Acid red 27	30	65	55	36.0
	45	76	60	47.0
	60	83	67	52.9
	75	87	70	60.8
	90	87	70	62
	120	88	71	63
	150	88	72	63
	180	89	73	64
	210	90	73	65
	240	91	74	66
Methyl blue	30	55	51	30
	45	63	58	38
	60	70	60	42
	75	75	63	47
	90	76	64	51
	120	76	65	51
	150	77	66	52
	180	77	67	53
	210	78	68	54
	240	79	69	55

Cationic starch (amine content 100 mmole/100 g sample); at room temperature, adsorbent (300 mg/L); shaking at 175 rpm ; dye concentrations (150 mg /L) a; pH2 .

REFERENCE

[1] Genlin Zhang, Lijuan Yi, Hui Deng, Ping Sun, Dyes adsorption using a synthetic | carboxymethyl cellulose-acrylic acid adsorbent. Journal of Environmental Sciences | 2014, 26, 1203–1211. | [2] Ai L., Zhang C., Meng L., Adsorption of methyl orange from aqueous solution on | hydrothermal synthesized Mg–Al layered double hydroxide, J. Chem. Eng. Data | 2011, 56, 4217–4225. | [3] Kyzas G., Lazaridis N.K., Mitropoulos A.C., Removal of dyes from aqueous solutions | with untreated coffee residues as potential low-cost adsorbents: Equilibrium, reuse and | thermodynamic approach, Chem. Eng. J. 2012, 189–190 148–159. | [4] Ma J., Cui B., Dai J., Mechanism of adsorption of anionic dye from aqueous solutions | onto organobentonite, J. Hazard. Mater. 2011, 186, 1758–1765. | [5] Li S.F., Removal of crystal violet from aqueous solution by sorption into semi interpenetrated | networks hydrogels constituted of poly (acrylic acid–acrylamide–methacrylate) and amylase, | Bioresour. Technol. 2010 , 101, 2197–2202. | [6] Bao N., Li Y., Wei Z., Yin G., Niu J.J., Adsorption of dyes on hierarchical mesoporous TiO | fibers and its enhanced photocatalytic properties, J. Phys.Chem. C. 2011, 115, 5708–5719. | [7 Mall I.D., Srivastava V.C., Agarwal N.K., Removal of Orange-G and Methyl Violet dyes by | adsorption onto bagasse fly ash-kinetic study and equilibrium isotherm analyses, Dyes Pigm. | 2006, 69, 210–223 | [8] Sananmuang, R., Cha-un, N., Physical characteristics and adsorption properties | for reactive dyes of char and activated carbon prepared mangosteen peel and tamarind | seed. Naresuan Univ. J. 2007, 15 (1), 9–16. | [9] Iqbal, J., Tirmizi, S.A., Mirza, M.L., Iqbal, J., Adsorption status of some transition | metal ions on pretreated fish scales. J. Chem. Soc. Pak. 2005, 27 (1), 77–81. | [10] Dong-Peng Li, Yan-Ru Zhang, Xuan-Xuan Zhao, Bao-Xiang Zh ., Magnetic nanoparticles | coated by aminoguanidine for selective adsorption of acid dyes from aqueous solution | Chem. Eng. J 2013, 232, 425–433. | [11] Cooper P., Colour in Dye House Effluent, in: Society of Dyers and Colorists, | Alden Press, Oxford, 1995. | [12] Wang, Z., Xiang, B., Cheng, R., Li, Y., Behaviors and mechanism of acid dyes | sorption onto diethylenetriamine-modified native and enzymatic hydrolysis starch. | J. Hazard. Mater. 2010, 183(1-3), 224–232. | [13] Wojn arovits, L., F Oldv ary, C.M., Tak acs, E., Radiation-induced grafting of | cellulose for adsorption of hazardous water pollutants: A review. Radiat. Phys. Chem. | 2010, 79(8), 848–862. | [14] Sheau-Ming Chen , Ming-Shien Yen, Yun-Hwei Shen, Effect of chitosan biopolymer | and UV/TiO2 method for the de-coloration of acid blue 40 simulated textile wastewater. | African Journal of Biotechnology 2010, 9(34), 5575-5580. | [15] Chatterjee S., Lee D.S., Lee M.W., Woo S.H., Congo red adsorption from aqueous solutions by using chitosan hydrogel beads impregnated with nonionic or anionic surfactant. Bioresour. Technol. 2009, 100, 3862. | [16] Wang, L., Zhang, J., Wang, A., Fast removal of methylene blue from aqueous | solution by adsorption onto chitosan-g-poly (acrylic acid)/attapulgite composite. | Desalination 2011, 266(1-3), 33–39. | [17] Silva, L.G., Ruggiero, R., Gontijo, P.M., Pinto, R.B., Royer, B., Lima, E.C. et al., | Adsorption of Brilliant Red 2BE dye from water solutions by a chemically modified | sugarcane bagasse lignin. Chem. Eng. J 2011, 168, 620–628. | [18] Steenken-Richter, I.; Kermer, W. D., Decolorising textile effluents. Journal | Society of Dyers and Colouists, 1992, 108, 182. | [19] Khalil M.I., Aly A.A., Use of cationic starch derivatives for the removal of anionic dyes from textile effluents. Journal of applied polymer science 2004, 93 (1), 227-234. | [20] Joseph A. Laszlo, Removing acid dyes from textile wastewater using biomass for | decolorization. Am Dyest Rep, 1994, 83, 17-21,48. | [21] El- Hilw Z.H., Synthesis of cotton-bearing DEAE, carbamoyethyl, carboxyethyl, | and poly(acrylamide) graft for utilization in dye removal. Journal of applied polymer | science 1999, 73 (6), 1007-1014. | [22] Hashem, A.; El-Shishtawy, R. M., Preparation and characterization of cationized cellulose for the removal of anionic dyes adsorption. Sci Technol 2001, 19(3), 197-210. | [23] Nechwatal, A.; Nicolai, M.; Mieck, K.-P., Use of absorbers based on starch for the effluent | treatment of dyeing liquors. Starch/Staerke 1999, 51, 286. | [24] Khalil M.I and Farag S., Preparation of Some Cationic Starches Using the Dry Process Starch/Staerke 1998, 50(6), 267–271. | [25] Hebeish, A., Aly, A.A., El-Shafei, A.M., Zaghloui, S., Innovative starch derivatives as textile auxiliaries for application in sizing, finishing and flocculation, Starch/Staerke | 2008, 60(2), 97 – 109. | [26] Chang YJ, Choi HW, Kim HS, Lee H, Kim W, Kim DO, Kim BY, Baik MY., | Physicochemical properties of granular and non-granular cationic starches prepared under | ultra high pressure. Carbohydr. Polym. 2014, 99, 385-393. | [27] Wang YB, Xie WL., Synthesis of cationic starch with a high degree of substitution in an | ionic liquid. Carbohydr. Polym. 2010, 80, 1172-1177. | [28] Xing GX, Zhang SF, Ju BZ, Yang JZ., Study on adsorption behavior of crosslinked cationic | starch maleate for chromium (VI). Carbohydr. Polym., 2006, 66, 246-251. | [29] Absalan G., Asadi M., Kamran S., Sheikhian L., Goltz D.M., Removal of reactive red- | 120 and 4-(2-pyridylazo) resorcinol from aqueous samples by Fe3O4 magnetic | nanoparticles using ionic liquid as modifier, J. Hazard. Mater. 2011, 192, 476–484. | [30] Crini, G., Non-conventional low-cost adsorbents for dye removal: a review. | Bioresour. Technol. 2006, 97 (9), 1061–1085. | [31] Izumi T., Takahashi K., Hirata M., Interactions of water-soluble polymers | with small molecules I: poly(2-diethylaminoethyl methacylate)orange II and | ethyl orange systems, Colloid Polym. Sci. 1986, 264, 748–755. | [32] Javed Iqbala, Feroza Hamid Wattoo ,Rukhsana Malika, Syed Ahmad Tirmizib, Muhammad | Hamid Sarwar Wattooc, Muhammad Imran,Allah Bux Ghangro, Adsorption of acid yellow | dye on flakes of chitosan prepared from fishery wastes. Arabian Journal of Chemistry | 2011, 4, 389–395. | [33] Wojciech Konicki, Daniel Sibera, Ewa Mijowska, Zofia Lendzion-Bielu- , Urszula Narkiewicz, Equilibrium and kinetic studies on acid dye Acid Red 88 adsorption by | Magnetic ZnFe2O4 spinel ferrite nanoparticles. Journal of Colloid and Interface Science 2013, 398, 152– 160. | [34] Eder C. Lima , Betina Royer, Julio C.P. Vaghetti, Nathalia M. Simon, Bruna M. da Cunh | Flavio A. Pavan, Edilson V. Benvenutti, Renato Cataluña-Veses, Claudio Airoldi, | Application of Brazilian pine-fruit shell as a biosorbent to removal of reactive red 194 | textile dye from aqueous solution: Kinetics and equilibrium study. J Hazard Mater 2008 , 155, 536–550. | [35] Gulay Bayramoglu, Biosorption of benzidine based textile dyes "Direct Blue 1 and Direct | Red 128" using native and heat-treated biomass of Trametes versicolor. J Hazard | Mater 2007, 143, 135-43. | [36] Mall, I.D., Srivastava V.C. & Agarwal N.K., Removal of orange-G and methyl violet dyes by adsorption onto bagasse fly ash kinetic study and equilibrium isotherm analyses. Dyes Pigments 2006, 69(3), 210-223. |