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Journal of
Applied
Chemical
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jacr.kiau.ac.ir

Journal of Applied Chemical Research, 13, 4, 93-105 (2019)

Removal of C.I. Acid red 1 (AR1) Dye Pollutant from Contaminated Waters by Adsorption Method using Sunflower Seed Shells and Pine cone as Agro-waste Materials

Samira Alizadeh[1,2], **Kambiz Seyyedi***[1,2]

Department of Chemistry, Tabriz branch, Islamic Azad University, Tabriz, Iran.

[2]*Department of Chemistry, East Azarbaijan Science and Research branch, Islamic Azad University, Tabriz, Iran*

(Received 09 Feb. 2019; Final revised received 23 May 2019)

Abstract

Dyes are widely used in various industries, since their direct discharge to nature can cause many biological and environmental problems. Some of these dyes are toxic, carcinogenic and can cause skin and eye irritation. There are various dye removal techniques, but Adsorption was found to be very effective and cheap method among the all available dye removal methods. The purpose of this study was to investigate the adsorption of C.I. Acid Red 1 (AR1) dye pollutant to sunflower seed shells (SSS) and pine cones (PC) as agro waste materials, to find out the optimal conditions for major operational parameters such as contact time, adsorbent dosage, initial dye concentration and pH. The results showed that the optimal conditions for decolorization of the solution containing 40 mg/L AR1,by SSS and PC adsorbents with removal efficiency of 84.2% and 74.47%, respectively, were obtained at100 min of contact time and pH= 2 at room temperature. Optimal value of adsorbent dosage for SSS and PC was determined 2.6 and 3.2 g/L, respectively. The physicochemical properties of the adsorbent were studied using various descriptive techniques such as FTIR, SEM, and BET. The adsorption process of both adsorbents was best fitted to Freundlich model and followed pseudo-second-order rate kinetics.

Keywords: C.I. Acid Red 1, Adsorption, Skin sunflower seeds, Pine cones.

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[*] ***Corresponding author:*** *Kambiz Seyyedi, Department of Chemistry, Tabriz branch, Islamic Azad University, Tabriz, Iran. Department of Chemistry, East Azarbaijan Science and Research branch, Islamic Azad University, Tabriz, Iran. E-mail: k.seyyedi@iaut.ac.ir.*

Introduction

Out of all contaminants found in industrial sewage, dyes are the most undesired ones, as the direct discharge of dye effluents can cause serious problems to the environment due to high organic loading, rather high toxicity and aesthetic pollution from dyes [1].Due to their aromatic structures, these compounds are rather stable, non- biodegradable, and difficult to remove from wastewaters. Dyes usually have a synthetic origin and complex aromatic molecular structures, which make them rather stable and more difficult to biodegrade [2]. The dyeing effluents from different industries, contain low levels of dyes, which cause serious problems meanwhile due to their possible toxicity and carcinogenicity. This is even exacerbated by the fact that many dyes formerly were made of known carcinogens. Moreover, dyes can significantly affect photosynthesis and can lead to lower penetration of light, thus affecting the growth of plants as well as the invertebrate and other forms of wildlife; dyes can cause allergy, dermatitis, skin irritation, cancer, and mutations in human body[3].

Several treatment methods have been developed for removing dyes from wastewater, such as coagulation/flocculation [4], reverse osmosis [5], biodegradation [6], electrocoagulation [7], advanced oxidation process, photocatalysis [8], ion exchange and adsorption [9]. However, some of these processes have proved to suffer from many disadvantages such as high energy demand in photo-degradation process, formation of flocs together with dye stuff and production of large amounts of sludge in Electrocoagulation method, short half-life and high operational cost in ozonation and degradation of some pollutants into toxic by-products in photocatalytic method [10]. The removal of organic dyes by adsorption onto low-cost materials has recently became the subject of considerable interest. Some of the advantages of adsorption process are possible regeneration at low cost, availability of known process equipment, sludge-free operation and recovery of the sorbate. One of the advantages of this method is reflected in the possibility of using large and different categories of available adsorbents as well as consideration of dye structure.

In addition to the above-mentioned advantages, adsorption is also able to recover adsorbents for reuse and to prevent secondary problems with dye-bearing sludge which is very difficult to dispose [11, 12]. Agricultural waste materials are inexpensive, easily available, abundant, easily applied, highly efficient and usable according to green chemistry principles. Then developing countries are eager to use them in order to treat industrial wastewaters. Harmless adsorption by agricultural wastes, led us use a novel adsorbent for removing pollutants from waste water. Thus, it is a good choice to remove synthetic dyes before they discharge downstream bodies of water [13].

Pine tree belongs to Pinaceae family and is an evergreen plant, which is extensively raised in Iran, leading to the production of a large amount of pine cone waste. Since sunflower grows abundantly in Iran to produce oil, sunflower seed shell waste is being produced annually at a high scale.

It should be mentioned that, over the past decades, sunflower oil has become popular worldwide (14- 16). Most of the agricultural waste from this plant is traditionally discarded or set on fire. However, right manipulation and exploitation of this bio-resource may bring obvious economic and social benefits for us [17].In this paper, the feasibility of using pine cones (PC) and sunflower seed shells (SSS) as adsorbents to remove AR1 dye pollutant from aqueous solutions were investigated. The influence of process variables such as contact time, adsorbent dosage, initial pH solution, temperature, stirring speed, and initial dye concentration were studied under batch mode and the optimal experimental conditions were determined. Evaluation of the isotherm models and kinetics of the process was one of the aims of this study.

Experimental

Preparation of adsorbents

Raw pine cones were obtained from Tabriz, North West of Iran. Sunflower seed shell wastes were obtained from a local oil-pressing factory in Tabriz. The collected biomaterials were completely washed with distilled water, they were, then, dried in an oven at a temperature of 70 °C with a fixed weight. Later, they were crushed into powder and sieved to obtain a particle size range of 80 μm. The obtained particles were, then, preserved in the desiccator for later use. No other chemical or physical treatments were performed.

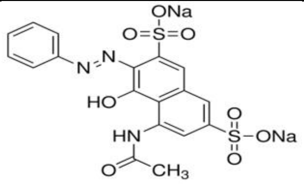
Analysis of characteristics of adsorbents

The morphology of the adsorbents was evaluated using scanning electron microscopy (SEM) (Cam Scan, MV2300, Canada) instrument. Meanwhile Fourier transform infrared (FTIR) (Bruker Tensor 27, Germany) and Brunauer Emmett Teller (BET) (Belsorp- mini 2, Japan) instruments were used to study the functional groups and surface properties, respectively.

Preparation of dye solution

The dye used in this study was AR1 which was obtained from Sigma–Aldrich Corporation. The characteristics of the dye are presented in Table 1. The stock solution (1000 mg/L) of AR1 was prepared by dissolving pre-specified given amount of dye in distilled water, and the other concentrations were obtained by diluting this stock solution.

Table 1. Characteristics of AR1.

Formula	
Color Index Name	C. I. Acid Red 1 (AR1)
Molecular Class	Single Anionic Azo Dye
Molecular Formula	$C_{18} H_{13} N_3 Na_2 O_8 S_2$
Color Index Number	11805
M_W (g/mol)	509.42
$_{max}\lambda$	507

Experimental methods and measurements

A batch equilibrium experiment was carried out to study the effectiveness of SSS and PC adsorbents on the removal of AR1 dye and also to investigate the variation of process parameters such as contact time, adsorbent dosage, initial pH of the solution, and initial dye concentration in the adsorption process. Different values of the adsorbent (0.4- 4.8 g/l) were placed in contact (10-120 min) with dye solution samples. The initial dye concentration range varied between (10-50 mg/l) and solution pH was (2-10) in a 250 ml flask. The initial pH values of the solutions were previously adjusted with 0.1 M HCl or NaOH using a pH meter (Hanna- 211). Afterwards, the samples were filtered in order to analyze the residual dye concentration in the filtrate. As it was observed in UV-Vis spectrum (Shimadzu, UV mini- 1240) the maximum absorbance wavelength (λ_{max}) was at 507 nm, so the amount of remaining dye was analyzed at this wavelength. Finally, the removal efficiency (R%), and for kinetic and isothermic studies the equilibrium adsorption capacity (q_e) and the time-dependent amount of dye adsorbed per unit mass of adsorbent(q_t) were calculated, respectively.

Results and discussion

Surface characteristics of adsorbents

SEM micrograph of SSS and PC (Figure 1) shows that the samples have a considerable number of heterogeneous pores where there is a good possibility for the dye to trap and be adsorbed.

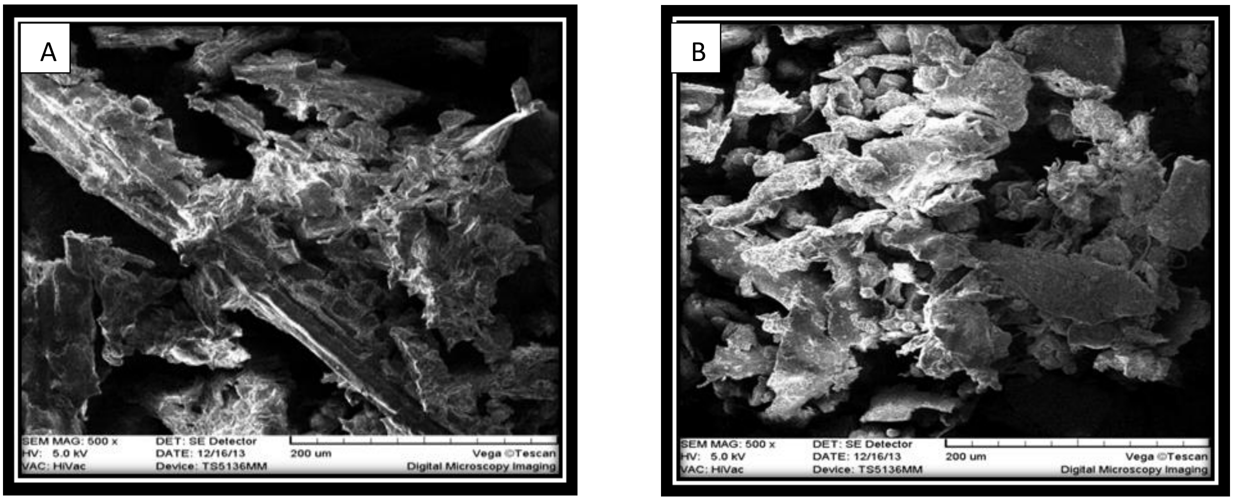


Figure 1. SEM images of adsorbents: (A) SSS, (B) PC.

PC and SSS are lignocellulosic materials with a chemical composition consisting of hemicelluloses, lignin, celluloses, and extractive. Based on the analysis of both adsorbent powders using FITR (Figure 2); it was observed that the sample's spectral bands can be divided into four main sections: (i) the section covering 3100–3600 cm^{-1} which is a broadband indicative of unbounded –OH group, (ii) the section covering between 2700 and 2900 cm^{-1}which is a peak attributed to aliphatic C–H stretching, (iii) the section between 1500 and 1750 cm^{-1}which represents the carbonyl group stretching and (iv) the finger print region which covers wave numbers below 1500 cm^{-1}. Prominent peaks in the spectra happen at 3334.19 cm^{-1}representing unbounded hydroxyl group (– OH), 2700–2900 cm^{-1}which comprises the majority of the aliphatic fraction of waxes, 1026.93 cm^{-1}associated with C–O–C functionalities, and 1511.41 cm^{-1}which results from aromatic ring vibrations which may come from the lignin fraction of the plant material [15, 18].

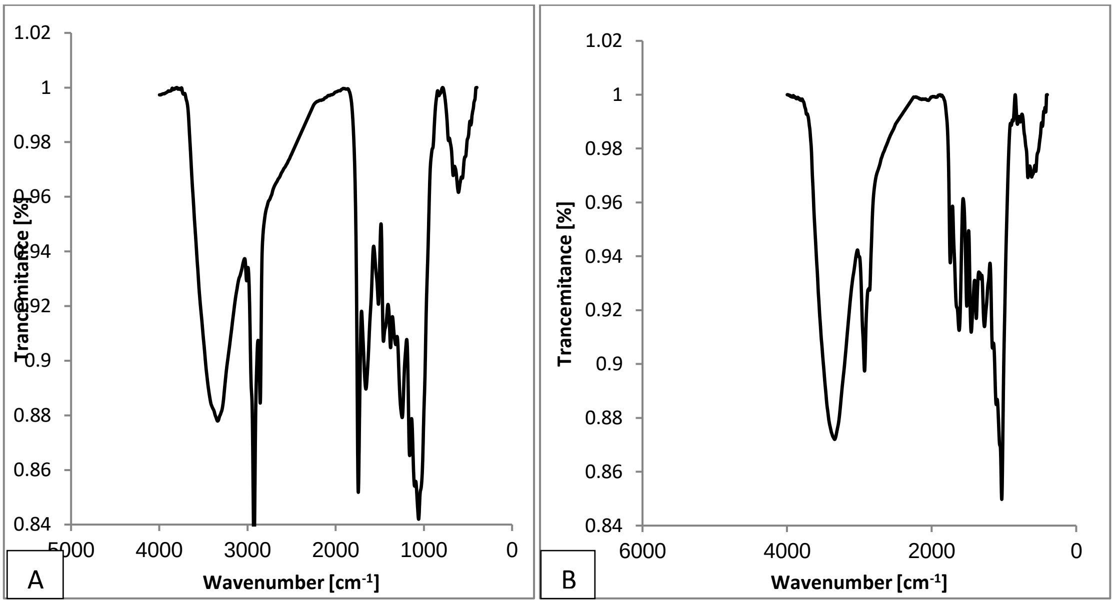


Figure 2. FTIR spectrum of adsorbents: (A) SSS, (B) PC.

The BET surface area, pore volume, and average pore diameter of the SSS were: 0.17 m^2/g, 0.011 cm^3/g, and 12.17 nm respectively; and of the PC were: 0.68 m^2/g, 0.005 cm^3/g, and 3.07 nm, respectively.

The effect of contact time

The effect of contact time on adsorption of dye can be studied by preparing an adsorbent–adsorbate solution with a fixed adsorbent dose and initial dye concentration at pH=4 for different time intervals and shaken to the point of equilibrium. According to Figure 3, generally the dye removal efficiency rises with an increase in contact time to a certain value. Further increase in contact time does not lead to higher uptake, since dyes are deposited on the available adsorption site in the adsorbent material. At this point, the amount of the dye desorbing from the adsorbent is in dynamic equilibrium with the amount of the dye being adsorbed into the adsorbent. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under these operating conditions [19, 20].The obtained results showed that, the equilibrium time for the adsorption of AR1 by SSS and PC was obtained 100min with color removal efficiency of 26.44% and 33.78%, respectively.

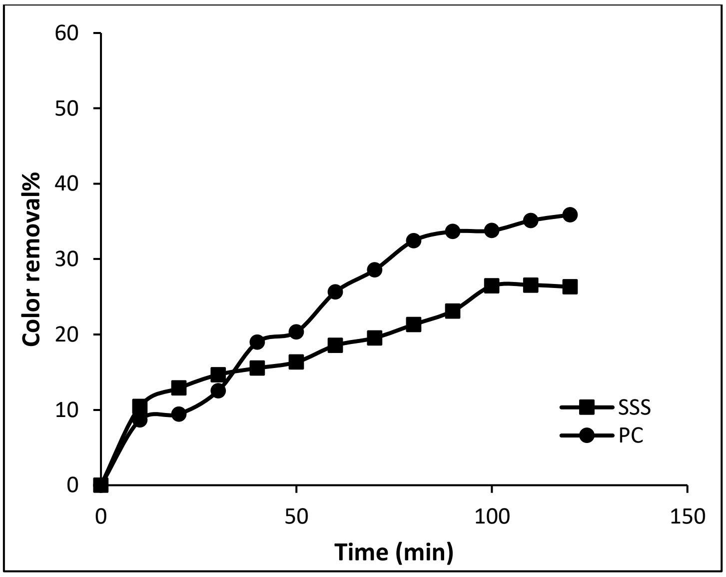


Figure 3. Effect of contact time on the color removal efficiency: pH=2, Adsorbent dosage=2g/L, [AR1]=40mg/L.

The effect of pH

Dye adsorption depends highly on the pH of the solution since it determines whether dissociation and ionization of the dye molecule will take place on the surface of the adsorbent. Figure 4 displays the effect of pH on the removal of AR1 onto SSS and PC adsorbents with pH of 2-10. The results revealed that dye removal efficiency gradually decreases with an increase in pH of solution, this could be attributed to the fact that at lower pH, the adsorbent surface is highly positively charged due to the protonated amino groups of adsorbents allowing electrostatic attraction between positively charged adsorbent and negatively charged sulfonate groups of anionic dye AR1 [21]. The results also indicated that, dye removal rate of about58% and 78% were attained at pH = 2 for SSS and PC adsorbents respectively. Therefore, it was found that the optimal pH for both adsorbents was 2.

In order to establish the behavior of the studied materials in contact with aqueous media containing dye and the optimal pH range for a high dye adsorption efficiency and to confirm the results mentioned above, the pH_{PZC} value (pH of zero charge) was determined. The results also showed that, the value of pH_{PZC} for SSS and PC are 3.9 and 2.4, respectively. With $pH < pH_{PZC}$ the surface charges of the sorbents are positive and susceptible to electrostatic interactions with anionic dye molecule; at $pH > pH_{PZC}$ the sorbent surface is negatively charged and it may bind cationic dye such as AR1 [22].

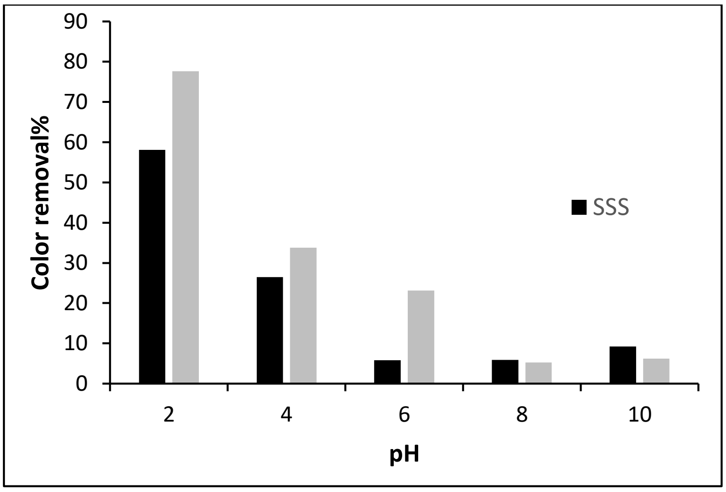


Figure 4. Effect of pH of solution on the color removal efficiency: Contact time=100min, Adsorbent dosage=2g/L, [AR1]=40mg/L.

The effect of adsorbent dosage

The effects of sorbent dose on the removal of dyes are shown in Figure 5.Dye removal efficiency increased from 59 to 84% with an increase in SSS dose within the range of 0.6-2.6 g/L, and about PC adsorbent, it increased from 41 to 74% within the range 0.6-3.2 g/L, resulting from the increasing number of available sorption sites. The adsorption equilibrium of dye decreased above the range of1.6 and 3.2 g/L for SSS and PC adsorbents respectively. This, in turn, results from increasing collision of adsorbent particles in the solution and desorption of the dye molecules from the surface of adsorbents. Therefore, the SSS biomass value of 2.6 g/L and the PC biomass value of 3.2 g/L were chosen as the optimal values for subsequent experiments.

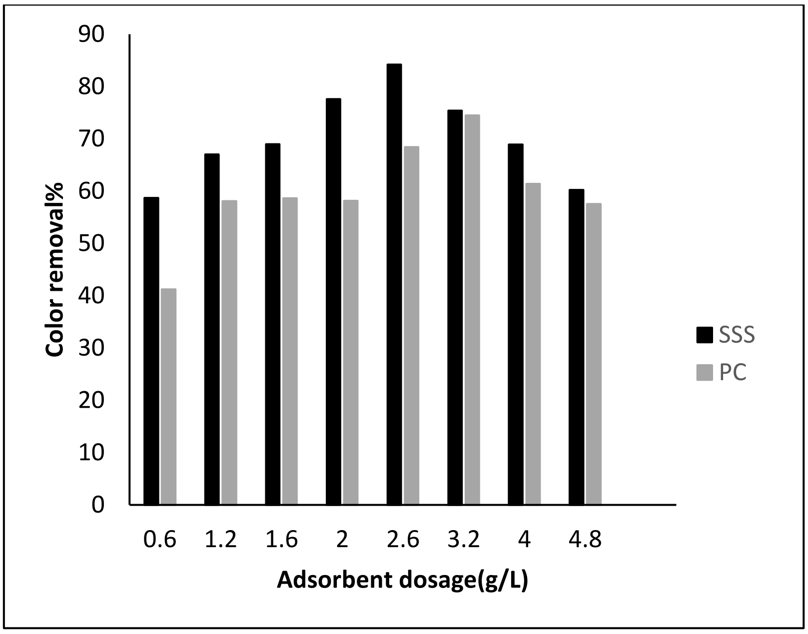


Figure 5. Effect of adsorbent dosage on the color removal efficiency: pH=2, Contact time= 100min, [AR1]=40mg/L.

The effect of initial dye concentration

Initial concentration provides an important driving force to overcome all mass transfer resistance of dye anions between the aqueous and solid phases. Adsorption of dye on adsorbent surface was determined for different concentrations of AR1 on 2.6 g/l of SSS and 3.2 g/l of PC. According to the obtained results, due to constant adsorbent dosage in the solution and limited adsorption capacity of adsorbents, increasing the initial dye concentration reduced dye removal efficiency over the same time interval (Figure 6).

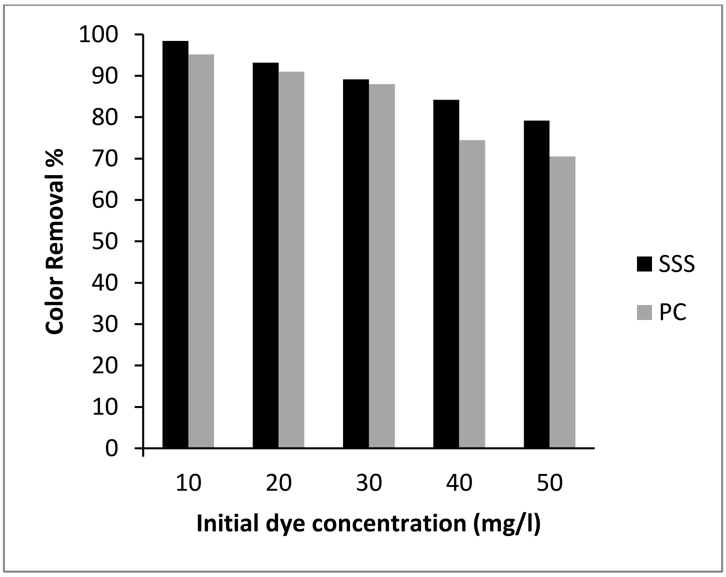


Figure 6. Effect of initial dye concentration on the color removal efficiency: pH=2, Adsorbent dosage of SSS=2.6 and PC=3.2 g/L, Contact time= 100 min.

The equilibrium adsorption isotherms

Langmuir isotherm

The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface. The basic assumption is the fact that, adsorption takes place at specific homogeneous sites within the adsorbent. Once a dye molecule occupies a site, no further adsorption can take place in that site [23]. The regression results for Langmuir model coefficient are plotted in Figure 7 with an excellent correlation coefficient for PC adsorbent (R^2 = 0.9759 and 0.991 for SSS and PC adsorbents, respectively). This suggests that Langmuir isotherm provides a good model of the sorption system for PC adsorbent. According to Table 2, the maximum monolayer capacity (Q) obtained from Langmuir model is 11.9 mg/g for PC.

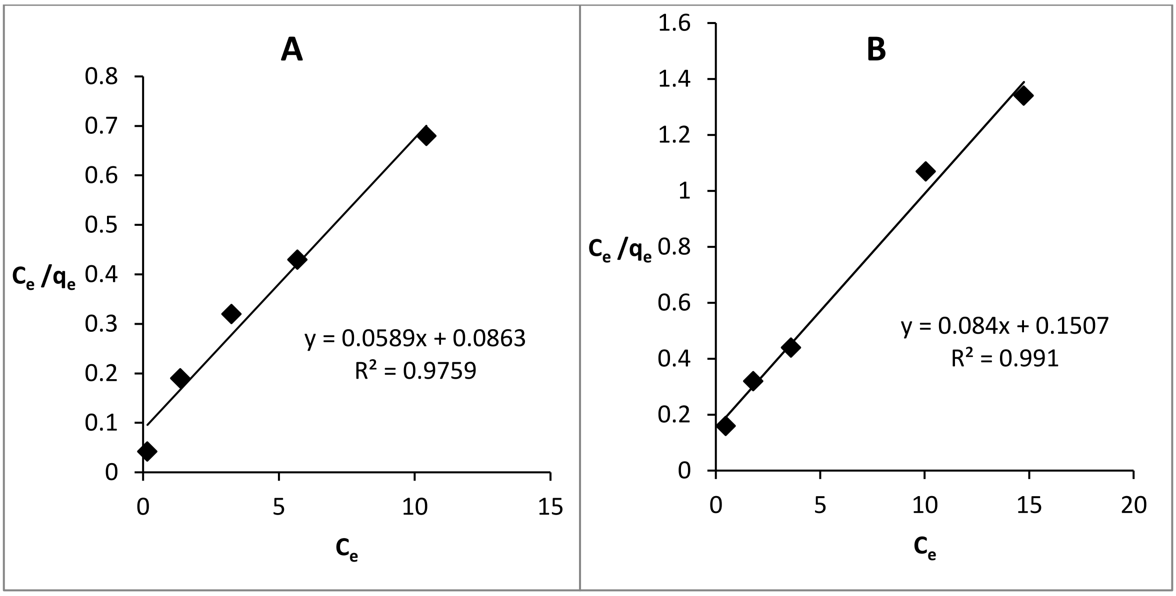


Figure 7. Fit of Langmuir isotherm data for the adsorption of AR1on to (A) SSS and (B) PC.

Table 2. Langmuir Isotherm parameters for the adsorption of AR1on to SSS and PC.

Adsorbent	**K_L (L/mg)**	**Q_m (mg/g)**	**R^2**
SSS	0.68	16.97	0.9759
PC	0.56	11.9	0.991

Freundlich isotherm

The Freundlich isotherm can be applied to non-ideal adsorption on heterogeneous surfaces as well as multilayer sorption. The magnitude of the exponent (1/n) gives an indication of the favorability of adsorption. Value of 1/n < 1 represents the favorable adsorption condition [23]. As shown in Figure 8, the comparability of the Freundlich model to the Langmuir model was demonstrated by R^2 = 0.9921 and 0.9455 for SSS and PC adsorbents, respectively, showing a good correlation coefficient for SSS adsorbent in Freundlich model. As shown in Table 3, the 1/n value is 0.35 for SSS adsorbent.

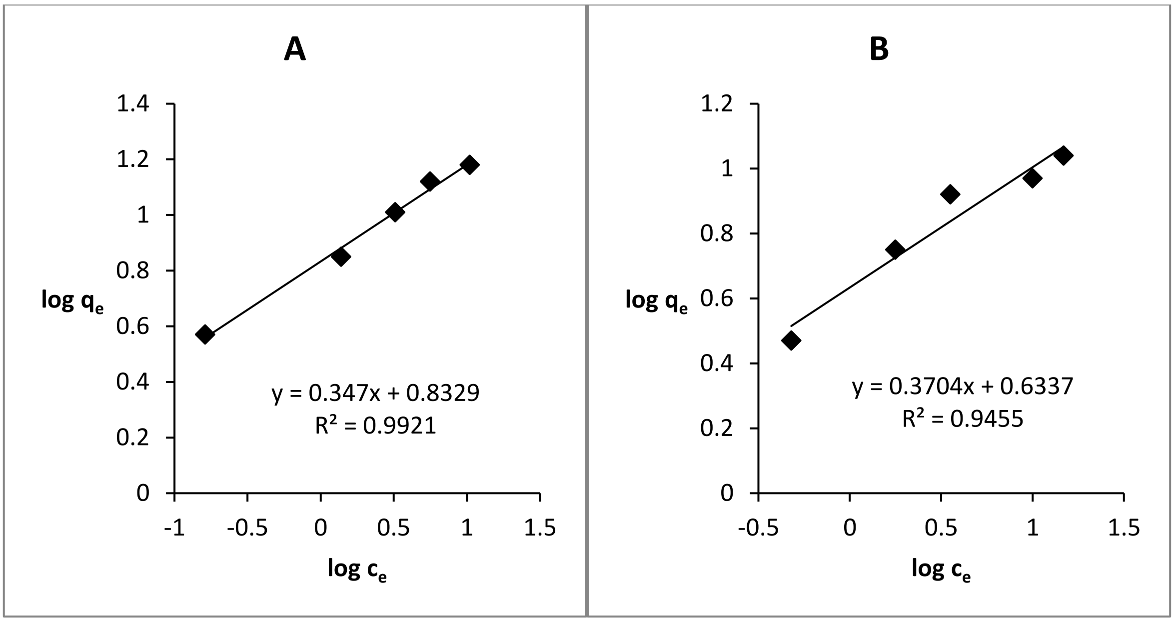


Figure 8. Fit of Freundlich isotherm data for the adsorption of AR1on to (A) SSS and (B) PC.

Table 3. Freundlich Isotherm parameters for the adsorption of AR1on to SSS and PC.

Adsorbent	**K_f (mg/g)(L/g)$^{1/n}$**	**n**	**1/n**	**R^2**
SSS	6.81	2.88	0.35	0.9921
PC	4.3	2.7	0.37	0.9455

Tempkin isotherm

As Figure 9 shows, the Tempkin adsorption data were analyzed according to the linear form of Temkin isotherm [23].According to Table 4, the heat of adsorption of AR1 onto SSS and PC adsorbent was found to be 2.76 and 2.28J/mol, respectively. The R^2values obtained from Tempkin model were comparable to those obtained for Langmuir and Freundlich equations. It can be observed that the Langmuir isotherm for PC and the Freundlich isotherm for SSS better fit the data than the Tempkin isotherms because of their higher R^2values (Table 5).

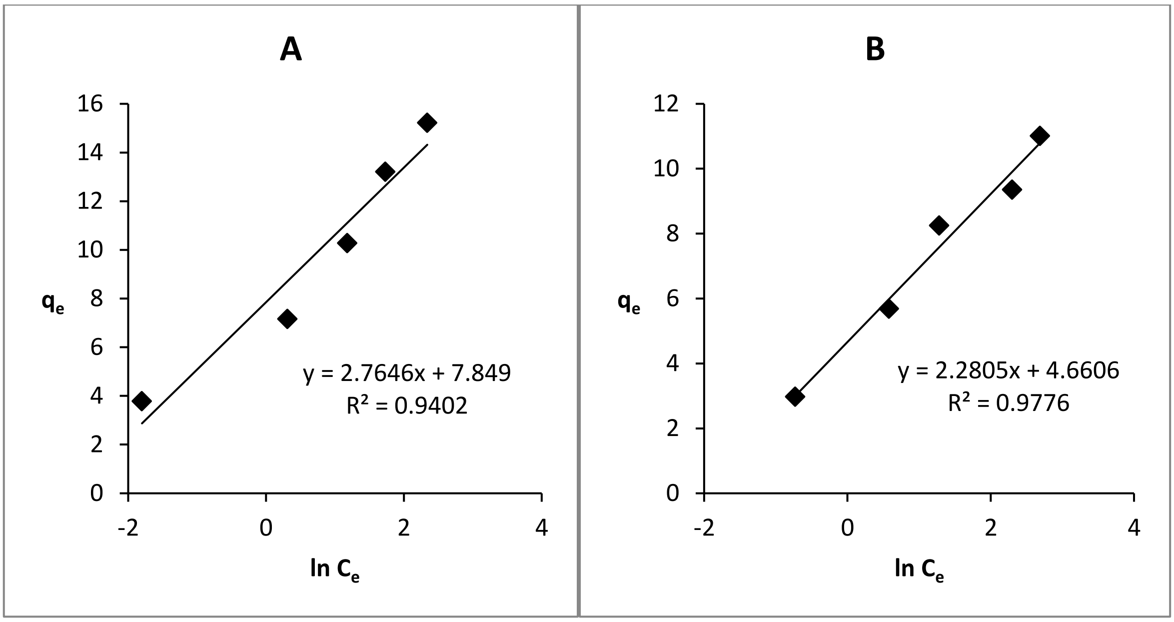


Figure 9. Fit of Tempkin isotherm data for the adsorption of AR1on to (A) SSS and (B) PC.

Table 4. Tempkin Isotherm parameters for the adsorption of AR1on to SSS and PC.

Adsorbent	**B(J/mol)**	**A(L/g)**	**R^2**
SSS	2.76	17.2	0.9402
PC	2.28	7.7	0.9776

Table 5. Comparison of Isotherm fitting for the adsorption of AR1on to SSS and PC.

Adsorbent	**Langmuir**	**Freundlich**	**Tempkin**
SSS	0.9759	0.9921	0.9402
PC	0.991	0.9455	0.9776

Adsorption kinetics

The rate as well as the mechanism of adsorption process can be elucidated on the basis of kinetic study. To determine the rate controlling and mass transfer mechanism, experimental kinetic data was correlated to linear form of the pseudo first-order (Lagergren model) and second-order (Ho model) rate models. The R^2 values obtained from Figure 10suggested that Lagergren model was not well fitted to the modelling of kinetic data.According to Figure 10, the extremely high value of the correlation coefficient about both adsorbents shows a good compliance of the data with the pseudo-second order kinetic. As Fig. 10(C) shows, The intra-particle diffusion model (Webber and Morris model) assumes that the sorption of AR1 by SSS and PC adsorbents is a multi-step process involving; (a) transport of adsorbate from the aqueous solution to the sorption sites of the sorbent (surface sorption),(b) diffusion into pores (intra-particle diffusion) and (c) rapid binding of dye molecules on the adsorbent sites [15]. The validity of the model is confirmed by linear plots of the Weber and Morris Equation. It can be concluded that the sorption of the dye AR1 onto SSS and PC adsorbents is a complex process, and intra-particle diffusion stage is the rate limiting step.

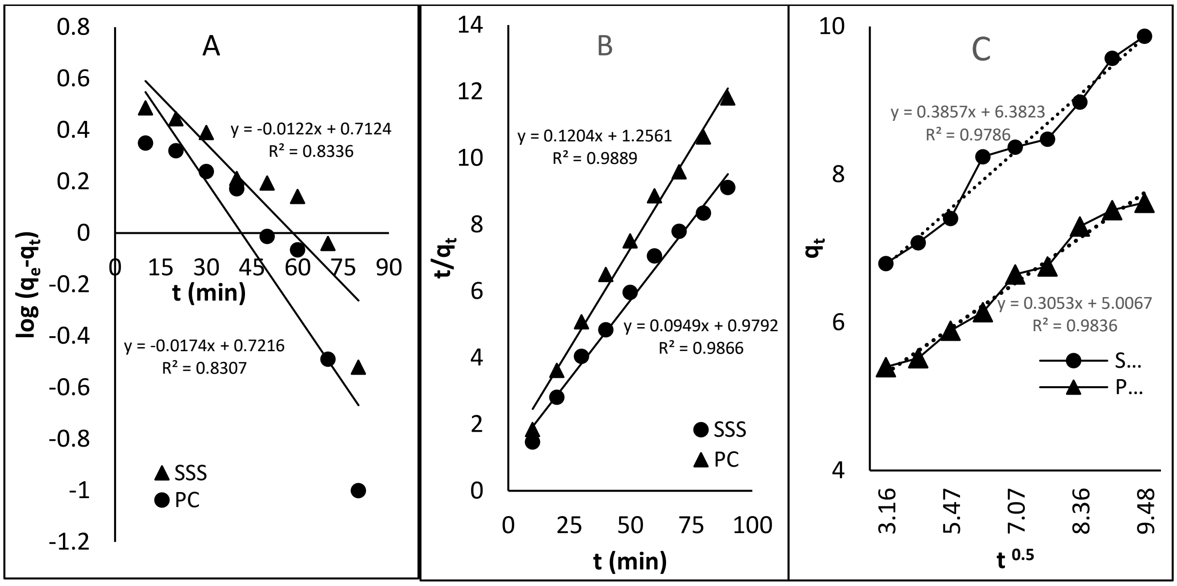


Figure 10. Pseudo-first (A), pseudo-second (B) order kinetics and intraparticle diffusion model (C) of AR1 adsorption on to SSS and PC.

Conclusion

According to this study, it is proved that SSS and PC as agro-based waste adsorbents can be effectively employed for the removal of dye stuff AR1 from wastewaters. These adsorbents are available freely, locally and it is economic oriented. Especially in Iran and some other countries, it is very economical to be used in order to wastewater treatment due to its high amount of agricultural production. The obtained results also revealed that the magnitude of adsorption depended on the initial pH of the solution, contact time, adsorbent dosage, and initial dye concentration. Dye removal efficiency increased with an increase in the amount of adsorbent and reaction time. Furthermore, with a decrease in initial dye concentration and pH, adsorption efficiency increased. The adsorption process of both adsorbents was best fitted to Freundlich model and followed pseudo-second-order rate kinetics.

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