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A comparative biosorption study of sulfide (S^{-2}) by using *Lagenaria siceraria* fruit based raw biosorbent

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Abstract

In batch mode, the adsorption characteristics of S^{2-}ions on *Lagenaria siceraria* mesocarp, pedicle and peel as raw materials have been studied in comparison to remove sulfide ions from tanneries waste water, under various parameters such as adsorbent dosage, contact time, agitation speed and pH. Maximum removal efficiency (70.96%) was observed on L. *Siceraria* peel followed by pedicle (51.58%) and mesocarp (29.57%) for adsorbent dosage of 0.10 g/L peel for 50 ml solution of sulfide (20 mg/L). The adsorption process was rapid, and it reached equilibrium in early 20-35 min for all adsorbents. Freundlich and Langmuir adsorption isotherms were employed for mathematical description of the adsorption equilibrium and to explain mechanism of adsorption.The maximum amounts of sulfide ions adsorbed, as evaluated by Langmuir isotherm, was 1.0436 mg/g of LS pedicle, 0.886 mg/g of peel and 0.843 mg/g of pedicle. The adsorption process conforms well to a pseudo second order kinetic model with best adsorption results at pH 8.

Keywords: Sulfide; Adsorption; Lagenaria siceraria; Isotherms and industrial effluents

Introduction

Sulfide (S^{-2}) is the inorganic chemical ionic form of sulfur. In nature, it occurs in deposits of coal, oil and in mineral ores (NRCC, 1977). Another source is the wastewater of various industries which is considered to be heavily adulterated with sulfide ions (Murugananthan *et al*., 2004; Mckee and Wolf, 1963; USEPA, 1976; Booras, 1974; Colby and Smith,1967). Through anaerobic decay of organic matter, sulfur found in fertilizers, fungicides and sewage, sulfate reducing bacteria generate sulfides (Mckee and Wolf, 1963; USEPA, 1976; Adelmah and smith, 1972; Acree and Splittstoesser, 1972). The sulfides and hydrogen sulfides of alkaline earth and alkali metals are water soluble (Sienko and Plane, 1974). Dissociation of soluble sulfide salts occurs into sulfide ions that respond with the hydrogen (H^+) ions in water, resulting in hydrogen sulfide (H_2S) and hydrosulfide ion (HS^-) formation. The pH of water plays a key role in the formation of these species. If the pH is low then the concentration of hydrogen sulfide increases (Mckee and Wolf, 1963; USEPA, 1976; Dar *et al*., 2015).

From the last few decades the environmental toxicity on living entities has developed a main concern. A huge growth in population and industrial sector is discharging wastewater continuously to the ecosystem which resulting in pollution and in due course toxicity to living being (Hossain *et al.,* 2012). Hydrogen sulfide is very poisonous even at trace levels (Zutshi, 1970). It is colorless and flammable with the rotten egg smell (Huynh *et al.,* 2011). The toxicity of H_2S is like of carbon monoxide (CO) and hydrogen cyanide (HCN) (Lindenmann, 2004) and it affects the organ system of human being. It has been reported that when H_2S associates with lipophilic molecules, it diffuses through the membranes and disseminate into skin, bones, liver, kidney and lungs (Murugananthan *et al.,* 2010; Hendrickson and Hamilton, 2004; Nikkanen and Burns, 2004; . Brenneman and James, 2000; Guidotti, 1994; Dorman *et al*., 2002). A direct exposure of H_2S in body, even in minute concentration results in pain, tearing, blurred vision, photophobia, conjunctivitis, corneal bullae (Sax, 2014; Meyer, 1977). Hydrogen sulfide is also found to deactivate and degrade the key enzymes in human body (Muruganathan *et al.,* 2004).

For scientists, there is a challenge to adopt an environment friendly and sustainable method for removal of toxic sulfide species from wastewater (Hossain *et al.,* 2012). On large

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scale H_2S is removed by aeration by employing complex packed tower aerators, simple air diffusers and mechanical aeration devices in wastewater treatment plants (Muruganathan *et al.,* 2004). Chemical oxidation method with commonly practiced oxidants $KMnO_4$, O_2, Cl_2, H_2O_2 and ClO^- is also used for H_2S removal from water (Muruganathan *et al.,* 2004; Edwards *et al.,* 2011; Tomar and Abdullah, 1994; Millero *et al.,* 1989). Manganese (IV) Oxide (MnO_2) for oxidation of sulfides in wastewater has also been reported (Valeika *et al.,* 2006).

Adsorption is a very cost effective, simple and regenerative technique for removal of toxic chemical species (Dar *et al.,* 2015). Activated carbon derived from biological wastes is a favorable method in the removal of sulfide species and other toxic metals. Feng *et al.* (2005) used activated carbon fibers for the adsorption of H_2S. Hanumantharao *et al. (*2012) used active carbon from *Lagenaria siceraria* shell for the adsorption of fluoride ions from aqueous solution. Plant wastes can be used as an adsorbent due to their free availability, inexpensive value, selective and good adsorption capacity. Untreated plant wastes have been used for the adsorption of pollutants (Saeed *et al.,* 2005; Babarinde *et al.,* 2006; King *et al.,* 2006; Hanafiah *et al.,* 2007; Hanafiah *et al.,* 2006b; Hanafiah *et al.,* 2006c; Karunasagar *et al.,* 2005; Quek *et al.,* 1998; Sawalha *al.,* 2007b; Ho and Wang, 2004; Ho, 2003; Ho *et al.,* 2004; Bhattacharya *et al.,* 2006; Villaescusa *et al.,* 2004). The adsorption capacity of plant wastes can be increased by pretreatment with certain modifying agents such as base solution of sodium hydroxide before being used for the sanitization and the chelating efficacy can be enhanced by this pretreatment (Gaballahet *et al.,* 1997; Ngah and Hanafiah, 2008).

Lagenaria siceraria belongs to the family *Cucurbitaceae*. In Pakistan, it locally named as Ghia/ Kaddu / Lauki, and its fruit is a common vegetable, which is plump with several seeds embedded in a spongy pulp (Dar *et al.,* 2014). The plant is an annual, softly pubescent and large climbing herb. The fruit is large, cylindrical, globose or flask shaped having constriction directly above the middle, green, densely hairy, plump, indehiscent, growing pale brown or yellowish, on ripening pulp drying out, sendoff a hard, thick hollow (Prajapati *et al.,* 2010).

A large quantity of mesocarp, peel and pedicle is produced daily in household garbage. For this reason, mesocarp, peel and pedicle of *Lagenaria siceraria* fruit have been tried as adsorbents for toxic sulfide ions from water by batch adsorption. The adsorbant was selected as it is easily available and cheap too. The nature of sorption has been effectively accounted and characterized by the kinetic, isothermal and surface characterization by FTIR. The aim of this work is to find out ecofriendly adsorbant to eradicate sulfide from water.

Materials and methods

Fresh fruit of *L. siceraria* was collected from city Pattoki, District Kasur, Punjab (Pakistan). It was manually parted into peel, pedicle and mesocarp, washed, dried. All these parts in raw form was crushed and sieved through 60 mesh (ASTM) and stored in air tight glass jars separately.

Chemicals and reagents

All the reagents have analytical grade purity. A stock solution of sulfide was prepared by dissolving calculated quantity of sodium sulfide to make a certain concentration in double distilled water. Standard solutions were made by successive dilution of the stock solution. Ferric chloride (0.01 M) and 1, 10-phenanthroline (0.1%) were prepared in hot double-distilled water. Acetate buffer (CH_3COONa: CH_3COOH) was used to maintain pH at 4.

Batch adsorption experiment

Batch adsorption experiments were performed by using 20 mg/L sodium sulfide (Na_2S) solution (50 ml) at ambient temperature to adjust the different parameters. The experimental specifics are provided in the caption of respective figures. Amount of adsorbent was varied from 0.2–2.0 g. The required time to attain the equilibrium for adsorption was assessed in the range of 5-80 minutes. Parameter of shaking speed was optimized from 50-450 rpm at room temperature (293K). The effect of pH was studied in the range 3-11. In all experiments mesh size of LS mesocarp, pedicle and peel was 20 ASTM.

Equipment and apparatus

Sulfide estimation was done by classical iron-1, 10-phenanthroline complex formation method at 510nm, using spectrophotometer (HITACHI U1800). 1, 10-phenanthroline (2 ml), Acetate buffer (1 ml) and $FeCl_3$ (2 ml) was the reagents used for sulfide ions estimation, Fe^{3+} was reduced to Fe^{2+} to make the colored complex with 1, 10-phenanthroline. Double distilled water was used for further dilution of solutions. FTIR spectra were recorded from 4000 to 500 cm^{-1} using Thermo Nicolet iS10 Spectrometer. The discs of samples were prepared by partying adsorbents with KBr (Merck; for spectroscopy) in a mortar pestle.

Adsorption isotherms and kinetics

Adsorption isotherms define the equilibrium relationship between adsorbent and adsorbate (Daret *et al.,* 2015). For biosorption processes kinetic studies have a significant role. Kinetics of adsorption not only defines the mechanism of metal adsorption on adsorbents but it also define the rate of metal adsorption which wheels the contact time of metals at the solid-liquid interface (Ho and Mckay, 2000). The mechanism of adsorption determined by chemical and physical features of adsorbent and adsorbate, temperature, pH of medium, aids and mass transport process and contact time (Achak *et al.,* 2009).

Batch equilibrium experiments were performed with sulfide solutions ranging from 3-24mg/L (50 ml) at pH 8 and all optimized conditions for all the adsorbents. Linear forms of various isotherms were used to analyze respective parameters. Langmuir equation (Eq. 1) can be linearized by the following form:

$$\frac{1}{q_e} = \frac{1}{bq_m c_e} + \frac{1}{q_m} \qquad (1)$$

Where "*Ce*" is the equilibrium concentration in liquid phase (mg/L), "*qm*" is the monolayer adsorption capacity (mg/L) and "*b*" is the Langmuir constant linked to the free adsorption energy (L/mg).

Freundlich equation (Eq. 2) can be linearized by the following form:

$$Inq_e = Ink_f + \frac{1}{n} Inc_e \qquad (2)$$

Where "K_F" is a constant symbolic of the adsorption capacity of the adsorbent (mg/g) and the constant 1/n shows the intensity of the adsorption.

For kinetics studies, pseudo first order (eq. 3) and second order (eq. 4) kinetics models were employed.

$$In(q_e - q_t) = Inq_e - \{\frac{k_1}{2.303}\}t \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \{\frac{1}{q_e}\}t \qquad (4)$$

Where "k_2" is the pseudo second order rate constant, "*qe*" is the bio-sorption capacity at equilibrium and "*qt*" is the bio-sorption capacity at time "*t*".

Results and discussion

There is a critical environmental issue of treatment of industrial wastewater before it is discharged out. Effluents from leather industry are highly contaminated with organic and inorganic contaminants and large amounts of sulfide ions. Unlike organic wastes, these poisonous sulfide ions are non-biodegradable andthey can be stored in living tissues, producing various disorders and diseases. Adsorption has ascended as an economical and modest way to treat effluents from industries. Utilizing economical and ecofriendly materials to adsorb pollutants isa primary choice of scientists to treat wastewater so, peel, pedicle and mesocarp of *L. siceraria* fruit has been used as an adsorbent to take out sulfide ions from water. The fruit of *L. siceraria* is of sweet variety. As the biological and chemical constituents of this fruit concerned, it holds 0.6% fibers, 2.5% carbohydrate, 0.2% proteins, 0.5% mineral matter, <0.01% phosphorous and calcium. sodium, iodine and iron are also present as mineral elements. Amino group is also present in form of alanine, aspartic acid, leucines, phenylalanine, tyrosine etc. The edible portion (mesocarp) of fruit contains riboflavin, thiamine and ascorbic acid. The fruit skin (peel) contains 18.1% cellulose, 17.5% crude protein and 8.0% lignin (Prajapati *et al.,* 2010; Sivannarayana *et al.,* 2013; Tyagi *et al.,* 2012).

FTIR analysis of adsorbent

Comparison of the Fourier transform infrared (FTIR) spectrum for the adsorbents; mesocarp (Fig.1), pedicle (Fig. 2) and peel (Fig. 3) before and after absorption has been recorded. Core functional groups that can be active in adsorption are –OH, –CH, C=O, C–H, C–O, S=O Gangwal *et al.,* 2010; Pavia *et al.,* 2001; Heneczkowski *et al.,* 2001; Kumar *et al.,* 2013; Marimuthu and Gurumoorthi, 2013). It shows that surface of LS mesocarp, pedicle and peel can arrange for various direct and indirect chemical and physical interfaces with sulfide ions in water. A direct interface takes place because ofattraction between functional groups bearing positive charge and negative sulfide ions. Various mineral elements in water and water itself can play a role of mediated interactions for an indirect attraction between negatively charged functional groups and sulfide ions by process of chemisorption, such as $-O–Na^+–S^{2-}$ and $–O–HOH–S^{2-}$. On the other hand, evidence and other supporting information about such interactions are limited in literature. A comparative study by FTIR analysis has been done to study the presence and identification of functional groups present in the adsorbents, before and after adsorption of sulfide ions. After adsorption minute shiftin peak positions and emergence of various new peaks were observed in spectra (Table-I). These changes were due to the binding of sulfide ions with functional groups of the adsorbents. Thus, shifting of bands confirms the adsorption of sulfide ions on the surface of *L. siceraria* mesocarp, pedicle and peel.

Effect of adsorbent dose

The influence of mesocarp, pedicle and peel, on adsorption of 50 ml solution of sulfide (20 mg/L) was studied with different dosage in the range, 0.10–1.50 g/L. Results disclosed that the adsorption efficiency is very much dependent on added quantity of adsorbents. Maximum removal was 29.57%, 51.58% and 70.96% for doses of 0.10 g/L of mesocarp, pedicle and peel respectively (Fig. 4) for 50 ml solution of sulfide (20 mg/L). The inclination in graph is because of the intermediation between adsorbent or it may be the failure of

Table I. Comparative FTIR analysis of *Lagenaria siceraria* mesocarp, pedicle and peel, before and after adsorption

FTIR Analysis					
LS mesocarp (B)*	LS mesocarp (A)*	LS pedicle (B)	LS pedicle (A)	LS peel (B)	LS peel (A)
3327.34 –OH (H-bonded)	3299.55 –OH (H-bonded)	3334.15 –OH (H-bonded)	3327.65 –OH (H-bonded)	-	3735.03 –OH (Free)
2918.83 –OH (carboxylic acid)	2923.99 –OH (carboxylic acid)	-	2918.60 –OH (carboxylic acid)	-	3648.59 –OH (Free)
-	2853.13 –CH (str. Alkane)	1634.92 C=O (amide)	1634.28 C=O (amide)	3291.36 –OH (H-bonded)	3291.55 –OH (H-bonded)
-	1729.96 C=O (aldehyde)	-	1417.74 C=C (aromatic)	2923.76 –OH (carboxylic acid)	2922.17 –OH (carboxylic acid)
1617.27 C=O (amide)	1645.92 C=O (amide)	-	-	-	2359.40 CN
-	1516.15 C=O (with phenyl)	1031.49 C–O Or S=O (sulfoxide)	1031.68 C–O Or S=O (sulfoxide)	-	1716.52 C=O (aldehyde)
1418.22 C–H	1463.88 C–H	-	-	1629.11 C=O (amide)	1635.79 C=O (amide)
-	-	-	-	1515.60 (with phenyl)	1540.48 (with phenyl)
1242.83 C–O (acids)	1238.27 C–O (acids)	-	-	-	1456.71 C–H
-	1165.65 C–O	-	-	-	1373.80 C–H
1032.08 C–O Or S=O (sulfoxide)	1032.24 C–O Or S=O (sulfoxide)	-	-	1231.81 C–O (acids)	1238.27 C–O (acids)
-	-	-	-	1027.12 C–O Or S=O (sulfoxide)	1031.55 C–O Or S=O (sulfoxide)

* B (Before Adsorption), A* (After Adsorption)

metal ions in solution with respect to open binding sites (Dar *et al.,* 2015; Anwar *et al.,* 2010). A quick adsorption was observed in start when sufficient sulfide ions were available for numerous bareadsorption sites. On the other hand, there was no momentous change in adsorption after 0.90 g/L addition of adsorbent. Consequently, the ideal adsorbent dosage was selected as 0.10 g/L each of mesocarp, pedicle and peel for sulfide and pedicle showed maximum removal efficiency.

Effect of contact time

Contact time was assessed as an important aspect affecting adsorption efficiency. By using 0.10 g of adsorbent in 50 ml of 20 mg/L sulfide solution, time of contact of adsorption has been changed from 5-65 min for experiments. In case of mesocarp as adsorbent, sulfide removal efficiency was 57.74% during early 20 min and after that, no significance rise or decline has been observed. For pedicle as adsorbent,

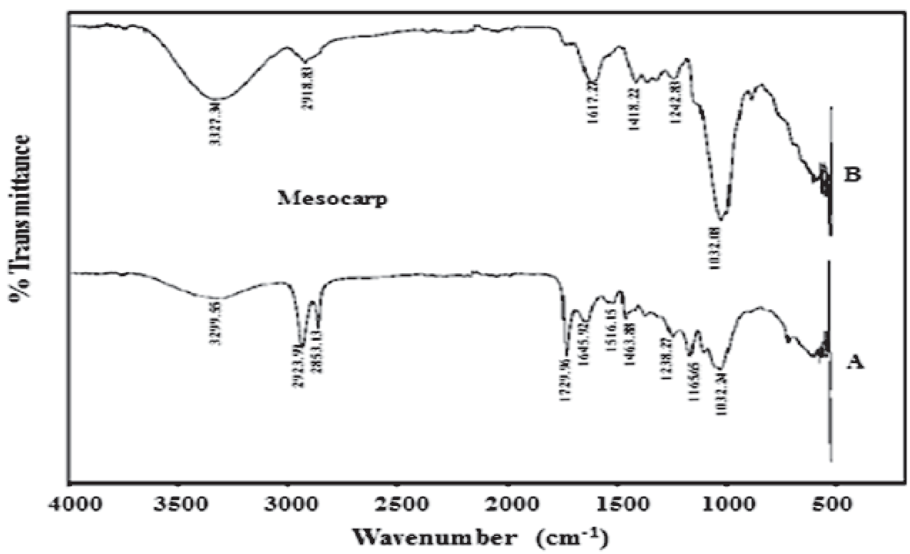

Fig. 1. FTIR spectrum of mesocarp (B=Before Adsorption, A=After Adsorption)

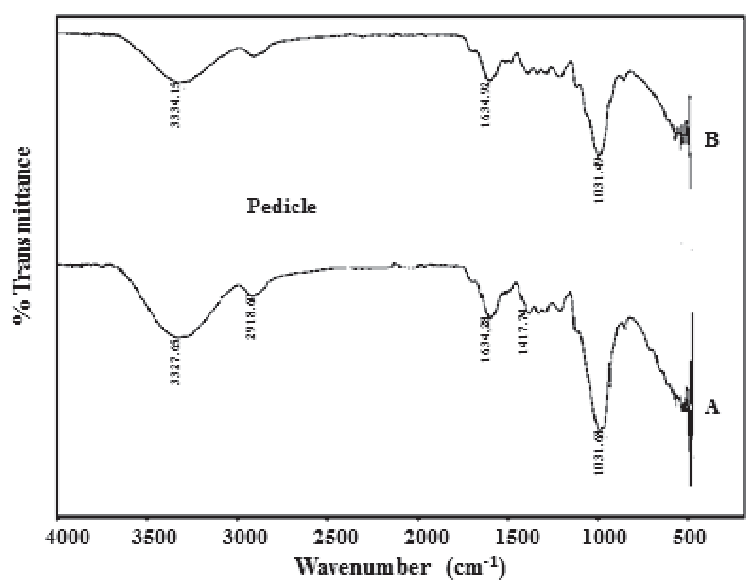

Fig. 2. FTIR spectrum pedicle (B=Before Adsorption, A=After Adsorption)

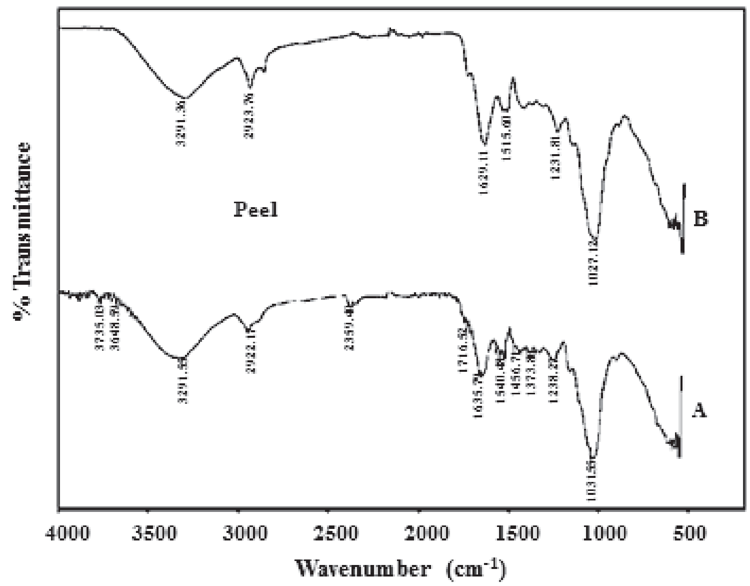

Fig. 3. FTIR spectrum peel (B=Before Adsorption, A=After Adsorption)

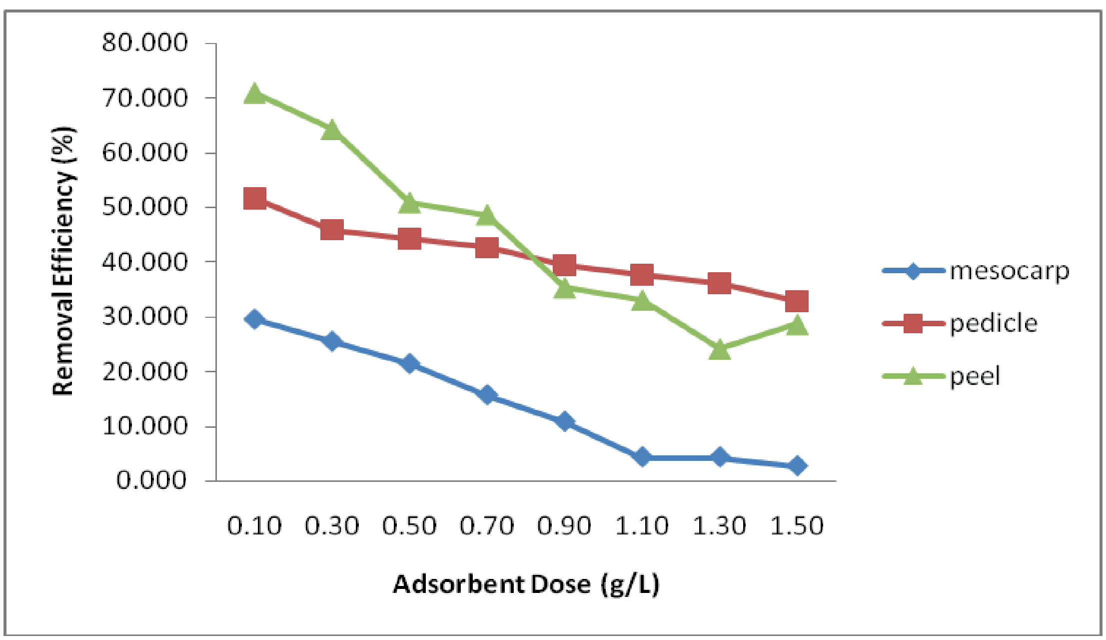

Fig. 4. Effect of adsorbent dose on removal of sulfide ions, sulfide ions 20 mg/L, volume 50 ml; mesocarp, pedicle, peel 0.10-1.50 g; pH = 8; time 40 min (for mesocarp), 20 min (for pedicle), 35 min (for peel); agitation speed 250 rpm (for mesocarp and pedicle) 50 rpm (for peel); temperature = 293K.

sulfide removal efficiency was 58.23% during early 40 min and in case of peel as adsorbent, sulfide removal efficiency was 40.13% during early 35 min. It can be recommended that under given conditions, maximum adsorption has taken place and equilibrium has been attained in 20, 40, 35 min for mesocarp, pedicle and peel as adsorbent respectively (Fig.5).

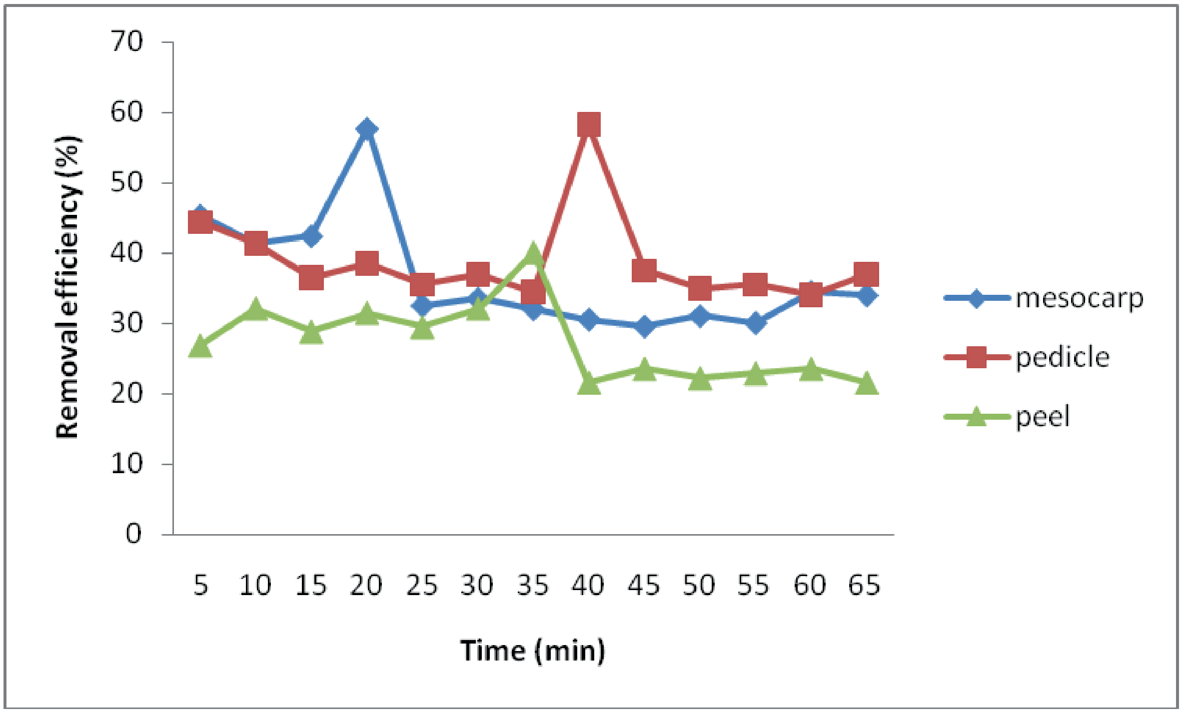

Fig. 5. Time of contact versus adsorption efficiency of sulfide ions on mesocarp, pedicle and peel; sulfide ions 20 mg/L; volume 50 ml; mesocarp, pedicle and peel 0.10 g; pH = 8, time 5-65 min; temperature 293K.

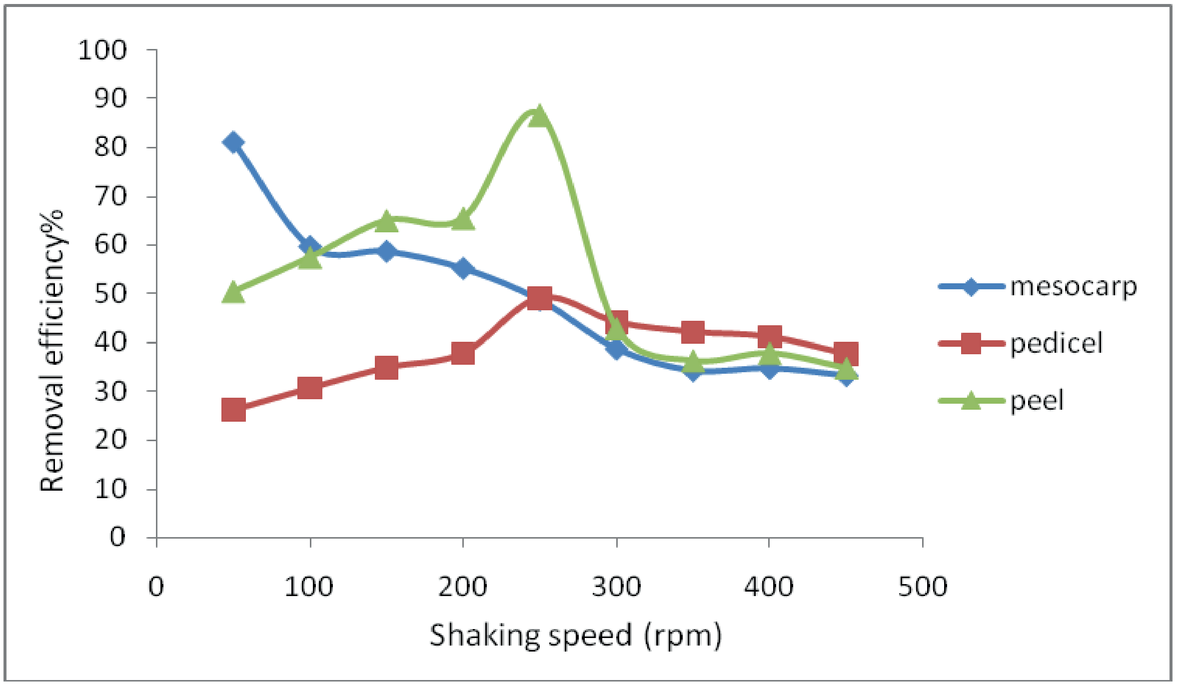

Fig. 6. Agitation speed versus adsorption efficiency of sulfide ions on mesocarp, pedicle and peel; sulfide ions 20 mg/L;volume 50 ml; mesocarp, Pedicle and peel 0.10 g; pH = 8; time 40 min (for mesocarp), 20 min (for pedicle), 35 min (for peel); agitation speed 50-450 rpm for mesocarp, pedicle and peel; temperature = 293K.

Effect of agitation speed

Agitating speed of 50 ml aqueous solutions of sulfide (20 mg/L) with mesocarp, pedicle and peel particles (0.10 g) changed from 50-450 rpm. In case of mesocarp, adsorption efficiency was maximum 86.68% at 250 rpm then it started to reduce gradually. For pedicle adsorption efficiency was 49.16% at 250 rpm and peel showed adsorption efficiency 81.60% at 50 rpm. When agitation speed was less, adsorbent (peel) disperse in thesolution and made maximum contact with adsorbate which gave the high adsorption. At high agitation speed, adsorbent-adsorbate, adsorbent-adsorbent and adsorbate-adsorbate collision occurred which result in suppressed adsorbent sites and did not allow sufficient time to the adsorbate to adsorb onto the surface of adsorbents (Dar *et al.,* 2015; Anwar *et al.,* 2010; Anwar *et al.,* 2009) so, adsorption efficiency of peel reduced but for mesocarp and pedicle adsorption efficiency increase with maximum contact with adsorbate (Fig.6).

Effect of pH

For the adsorption of metal ions, an important factor that plays its role is the pH of solution. The pH effect on adsorption was studied in range 3-11. As shown in Fig. 7, maximum adsorption of sulfide ions was observed at pH 8 for all of three adsorbents but peel has been shown maximum adsorption efficiency 76.32 % (mg/g). Thus we can say at higher pH, adsorption sites trigger. Away from optimum pH, adsorption of sulfide ions decreases, as the sulfide ions jumps to less negative (HS^{-}) or neutral hydrogen sulfide (H_2S) and adsorbents start to protonate and develop more positive charge (Dar *et al.,* 2015). This outcomes in reduce attraction between adsorbents and adsorbate. Adsorption of sulfide ions on *Lagenaria siceraria* mesocarp pedicle and peel is electrostatic by nature which depends on pH.

Adsorption isotherms and kinetics study

Table II contains parameters and correlation coefficients for Freundlich and Langmuir isotherms. Freundlich isotherm for sulfide ions adsorption on LS mesocarp, pedicle and peel is shown in Fig.8a-8c. The plotted isotherms holds good for the adsorption of sulfide ions by adsorbents as indicated by their R_2 values that are approaching to 1. Parameter 'n' indicated the adsorption intensity measure for sulfide ion on adsorbents. Ultimate adsorption capacity 'K_F' of sulfide ions, as calculated from

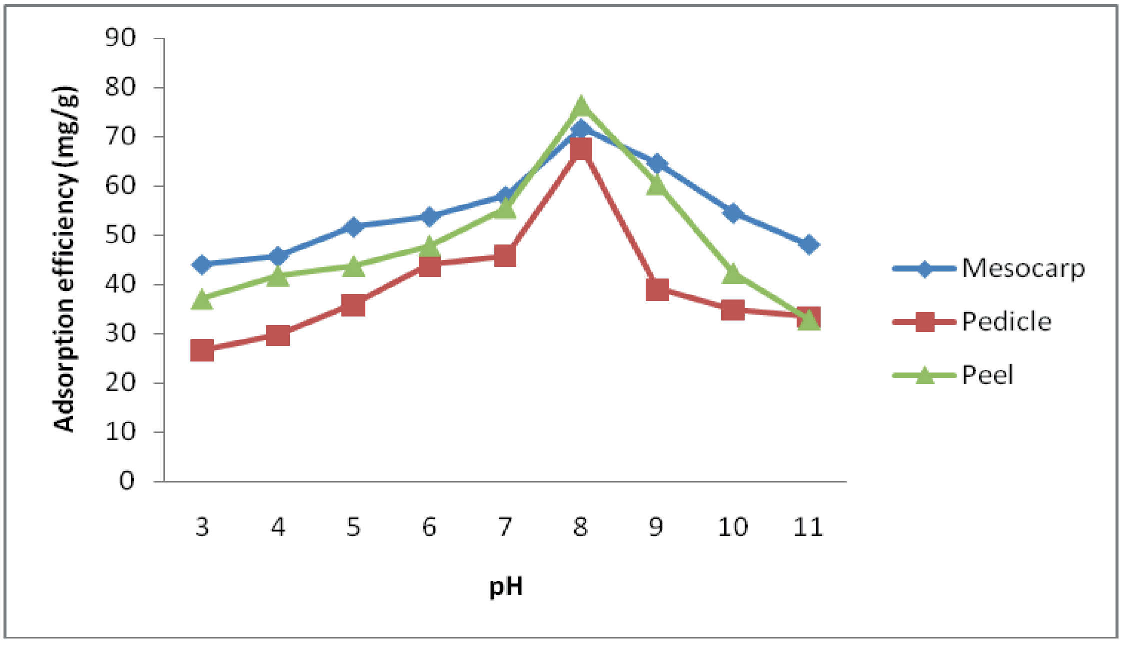

Fig. 7. Effect of pH on adsorption efficiency of sulfide ions on mesocarp, pedicle and peel; sulfide ions 20 mg/L;volume 50 ml; mesocarp, Pedicle and peel 0.10 g; pH = 8; time 40 min (for mesocarp), 20 min (for pedicle), 35 min (for peel); agitation speed 50-450 rpm for mesocarp, pedicle and peel; temperature = 293K.

Table II. Comparison of parameters of different isotherm models

Adsorbent	Isotherm	Freundlich	Langmuir
Mesocarp	R^2	0.9389	0.9066
	Parameters	n = 1.1359	q_m = 0.843mg/g
		K_F = 0.0862 mg/g	b = 0.1365 L/g
Pedicle	R^2	0.8744	0.8869
	Parameters	n = 0.9772	q_m = 1.0436 mg/g
		K_F = 0.0589mg/g	b = 0.0766 L/g
Peel	R^2	0.9459	0.9571
	Parameters	n = 1.4865	q_m = 0.886 mg/g
		K_F = 0.120mg/g	b = 0.147 L/g

Freundlich isotherm is 0.0862, 0.0589 and 0.120 mg/g for mesocarp, pedicle and peel respectively, indicating peel as a good adsorbent by studying this model.

Langmuir isotherm for sulfide ions adsorption on LS mesocarp, pedicle and peel is shown in Fig.9a-9c and the related correlation coefficients and parameters of the isotherm are given in Table 2. Maximum adsorption capacity '*qm*' is 0.843, 1.0436 and 0.886 mg/g for mesocarp, pedicle and peel respectively showing maximum Langmuir monolayer coverage of sulfide ions by 0.10 g LS pedicle. Correlation coefficient 'R_2' values approaching to one, evidently submit that Langmuir isotherm holds good to describe adsorption of sulfide ions on used adsorbents. Energy of sorption '*b*' for mesocarp, pedicle and peel is 0.1365, 0.0766 and 0.147 L/g respectively.

By studying the reaction kinetics, adsorption mechanism of sulfide ions was assessed. Pseudo first and second order reaction kinetics models were used for this purpose. It was found that for the adsorption of sulfide ions, adsorbents followed the pseudo second order kinetic model. Maximum adsorption capacity (q_m) of 0.3536 mg/g was obtained for pedicle (as shown in Table 3) with pseudo second order kinetic model followed by mesocarp and peel.

Table III. Comparison of Pseudo first and second order reaction kinetics model parameters

Adsorbent	Pseudo first Order	Pseudo Second Order
Mesocarp	R^2 = 0.0252	R^2 = 0.9682
	q_m = 0.0018mg/g	q_m = 0.3020mg/g
Pedicle	R^2 = 0.7269	R^2 = 0.9508
	q_m = 0.0032mg/g	q_m = 0.3536 mg/g
Peel	R^2 = 0.2482	R^2 = 0.9558
	q_m = 0.0072mg/g	q_m = 0.2078 mg/g

Conclusion

The present study can be used to overcome water pollution using eco-friendly and cost effective agro-waste constituents like *Lagenaria siceraria* mesocarp, pedicle and peel for the removal of toxic sulfide ions from industrial effluents and wastewaters. All of the three adsorbents show good adsorption results but maximum adsorption capacity of *L. siceraria* pedicle which is termed as Langmuir complete monolayer coverage 'qm' shows that 0.10 g of LS pedicle can adsorb 1.0436 mg/g of sulfide ions which is comparable with 0.886 mg/g of peel and 0.843 mg/g of pedicle. Comprehensive analysis of experimental data was conceded by using adsorption isotherms, to describe adsorption of sulfide ions *L. siceraria* mesocarp, pedicle and peel. Adsorbents followed the pseudo second order kinetic model for adsorption of sulfide ions. A physical form of nature was found in this process of adsorption. It is concluded that *L. siceraria* pedicle can be used a green filter for removal of sulfide ions from effluents of tanneries and other industrial wastes containing sulfide as a dangerous species.

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