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Insights into Removal of Phenol from Aqueous Solutions by Low Cost Adsorbents: Clays Versus Algae

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Abstract: Exchanged clays and cross-linked algae were compared based on their properties for the removal of phenol from aqueous solutions. Algae *Lessonia nigrescens Bory* (A1) and *Macrocystis integrifolia Bory* (A2) were cross-linked with $CaCl_2$ to enhance their physical and mechanical properties. The natural clays were chemically-exchanged with salts of tetramethyl ammonium (B1), hexadecyltrimethyl ammonium (B2), and bencyltriethyl ammonium (B3) ions to increase their affinity towards organic substrates. The effects of pH and adsorbent dose were evaluated. pH exhibited a strong effect mainly on the phenol aqueous chemistry. Sorption isotherm results were modelled on the Langmuir and Freundlich equations and complemented with EDX analysis, indicating that adsorption of phenol from water was mostly driven by hydrophobic forces, with the exchanged bentonites being the adsorbents that reported the maximum adsorption capacities. Conversely, a polar surface adsorption is suggested for algae mostly by means of hydrogen bonding formation. These results provide further insight into

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the adsorption mechanism of phenol and analogues and their use as powerful and cheap adsorbent for the treatment of phenol-containing real wastewater.

Keywords: Adsorption, cross-linked algae, organobentonites, pH 1, phenol

INTRODUCTION

Phenol and its derivatives are mainly generated by the oil and plastic industries. Due to their toxicity, these compounds are considered as priority pollutants by the Environmental Protection Agency (EPA) and the World Health Organization (WHO), which jointly established the maximum level of phenol concentration allowable in drinking water at $1\,\mu g \cdot L^{-1}$ (1,2). When phenols are released into the water, some are retained and even react, producing even more toxic substances and threatening living organisms by joining the food chain. The treatment processes for phenolic wastewater have been classified into two principal categories (3): recuperative processes (adsorption into porous solids, osmosis, solvent extraction, etc.) and destructive process (oxidation by hydrogen peroxide, manganese oxide, ozone, etc.). Recent studies utilized enzymatic degradation (4) and naturally occurring adsorbents (5–8) to control the contamination of liquid effluents by phenol and derivatives.

The high surface area per unit mass of activated carbons converts these into one of the most efficient adsorbents for the removal of organic pollutants from aqueous solutions (9–11). Nevertheless, due to the relatively high cost of activated carbons there have been attempts to utilize low cost adsorbents to remove trace organic and inorganic contaminants from wastewater.

In developing countries like Peru, industries cannot afford to use conventional wastewater treatments because of their unreasonable expense. They also produce undesirable environmental damage through the generation of by-products such as precipitation and filtration requiring constant monitoring. Abundant marine seaweeds, however, line the shores and are more of a nuisance than an asset to the surrounding communities. It is these seaweeds that have been studied for the removal of heavy metals (12–14), phenolic compounds (15,16), and dyes (17,18) and have yielded positive results. Also promising are natural clays, which have exhibited a high affinity towards inorganic and organic pollutants (19–22). These clays can be extracted from the mines of Peru at minimal cost.

Previous studies (14) have determined that cross-linkage of brown seaweeds with calcium chloride enhances their mechanical properties and affinity towards heavy metals. Rubin et al. (16) have previously observed that the decomposition of raw algae and its resulting products by phenolic solutions can interfere in the determination of phenols in aqueous solutions. It was discovered that a cross-linkage with calcium chloride resolved this issue. This improvement was attributed to the stabilization of alginate molecules by the formation of the characteristic alginate arrangement known as the egg-box structure (14,23).

Bentonite, which is primarily smectite clay, is composed of up to two silica tetrahedral sheets with a central Al octahedral sheet. It has permanent negative charges due to the isomorphous substitution of Al (III) for Si (IV) in tetrahedral layer and Mg (II) for Al (III) in the octahedral layer (24). This negative charge is balanced by the presence of exchangeable cations (Na, Ca, etc.). Enhancement of adsorptive properties towards phenols are also observed between nontreated (22) and surfactant modified (19,21) clay minerals. This interlamellar modification involves the replacement of highly hydrated-cations for organophilic nonhydrated cations (quaternary ammonium ions) favoring the attraction of organic molecules.

Several phenol adsorption studies have been conducted using algae and clays independent of one another. However, few have established a mechanism corresponding to the results or optimized equilibrium parameters (21). Furthermore, a parallel comparison between the adsorptive properties of biological and non-biological adsorbents has not been clearly established in the literature. This paper reports a comparison of the adsorption behavior of phenol between these two types of modified adsorbents from a structural, mechanistic and equilibrium point of view.

EXPERIMENTAL

Sorbents

The marine seaweeds *Lessonia nigrescens Bory* (A1) and *Macrocystis integrifolia Bory* (A2) were collected, cross-linked with calcium chloride, and treated following procedures previously reported (15).

The clay minerals, classified as bentonite, used in this study were obtained and modified with three different quaternary ammonium salts: tetramethyl ammonium chloride TMA), hexadecyl trimethyl ammonium chloride (HDMTA), and bencyl triethyl bromide (BTEA) as described elsewhere (20,25), originating the modified bentonites: B1, B2, and B3, respectively.

Characterization of Adsorbents

Qualitative analysis of the main functional groups of A1, A2, B2, and B3 analyzed previously (25) by Fourier transform infrared spectroscopy. In the present study, infrared spectra of the exchanged bentonite B1 was recorded on a Perkin Elmer 1600 FTIR spectrometer in order to identify the functional groups that are involved in phenol adsorption.

Prior studies (25) determined the specific surface areas of the modified bentonites B2 and B3 as well as the algae A1 and A2 in the bases of the Brunauer, Emmet and Teller (BET) and methylene blue (MB) method (16), respectively. The surface BET area and porosity of the modified bentonite B1 was also analyzed through the use of an ASAP 2000 (Micrometrics). The specific surface areas of the modified bentonites were also determined by the MB method (16). The morphology of the adsorbents before and after exposure to phenol was examined using a scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDX) was conducted via PHILIPS ESEM XL-30 TMP equipment; the samples were sputter-coated with a thin layer of gold.

The clay samples were also characterized by X-ray diffractrometry (XDR), recorded by a Shimadzu X-ray diffractometer (Model XRD-6000) using CuKα radiation, operated at 40 Kv and 30 mA. The samples were exposed to X-rays ($\lambda = 1.5404$ Å) with the 2θ angle varying between 4° and 65°.

Adsorption Studies

Batch adsorption studies were performed at room temperature (25 ± 1°C) in polyethylene flasks by shaking 100 mg of the cross-linked algae and exchanged bentonites with 100 mL of 100 mg L^{-1} solutions of phenol. The effect of pH on the adsorption was investigated at different values within the range of 2 to 10. The pH was adjusted by adding concentrated solutions of HCl and NaOH. The bentonite samples were shaken at 500 rpm for 6 h, as established in previous studies (20) and the algal samples were shaken at 200 rpm during a period of 24 h to assure completeness of the adsorption as reported elsewhere (15). After agitation, samples were filtered. UV-visible spectrometry was used to determine the remaining concentration of phenol by means of the Gales and Booth method (26) with a Shimadzu UV-mini 1240 spectrometer at $\lambda = 510$ nm.

The pH optimizations were made individually for each adsorbent. The adsorbent dose effect was evaluated at the optimized pH values at different adsorbent concentrations in 100 mL of 50 mg $\cdot$ L^{-1} of phenol solution. Finally, adsorption isotherms were plotted from the amount of phenol adsorbed per unit mass of adsorbent (q) and the equilibrium concentration (C_e) of the residual phenol remaining in solution. For each adsorption isotherm, a series of flasks containing an equal volume of phenol concentrations at different concentrations were employed. Concentrations ranged from 50 to 800 mg L^{-1}. The supernatant solution was then filtered and phenol concentration was determined by UV-visible spectrometry. To determine the equilibrium parameters of each adsorbent, the classical Langmuir and Freundlich models were employed.

Data Analysis

The amount of adsorbed phenol is expressed as Adsorption Percentage (%ADS) and Adsorption Capacity (q, $mg \cdot g^{-1}$) calculated as shown in equations (1) and (2):

$$q = \frac{(C_i - C_{eq}) \times v}{m} \quad (1)$$

$$\%ADS = \frac{(C_i - C_{eq})}{ci} \times 100 \quad (2)$$

where m is the mass of adsorbent expressed in g, V is the volume of the solution in L and Ci and C_{eq} are the initial and at the equilibrium concentrations, respectively expressed in $mg \cdot L^{-1}$.

RESULTS AND DISCUSSION

Characterization of Adsorbents

The Table 1 summarizes the previous results of BET surface area analysis of B2 and B3 (25) and for the exchanged bentonite B1. Alternatively, Table 2 shows the surface areas of the algae A1 and A2 with the MB method (25) along with the surface areas determined for the modified bentonites. As explained heretofore, the swelling of algae in aqueous solutions greatly increases their surface area compared to the exchanged bentonites that are determined in the dry state.

Table 1. BET analysis of clays

Modified clay	S_{BET} ($m^2 \cdot g^{-1}$)	$S_{\mu pore}$ ($m^2 \cdot g^{-1}$)	$S_{mesopore}$ ($m^2 \cdot g^{-1}$)	Average pore size (Å)
B1	145.10	80.35	64.75	132.82
B2	23.85	–	23.85	215.20
B3	34.40	–	34.40	142.23

Table 2. Specific surface area of the adsorbents determined by the methylene blue method (MB)

Adsorbent	Specific surface area ($m^2 \cdot g^{-1}$)
A1	1512.0
A2	820.00
B1	755.96
B2	503.97
B3	296.70

Concerning the modified bentonites in the dry state, B1 reports the largest surface area followed by B3 and B2. B1 also shows a higher microporous rather than mesoporous region, possibly due to the fact that the TMA ion shows short aliphatic chains inserted between the layers of the clay, acting as non-hydrated pillars, keeping the layers well separated and exposing the internal surface of the bentonite without altering its structure. This argument is corroborated by the reduction of the pore size compared to the other bentonites. The arrangement of TMA in the bentonite also generates micropores in a fashion similar to the pillarization of clays with metallic hydroxyl cations. Since the bentonite B3 shows a larger surface than B2 and both of them do not report microporous regions, BTEA ions possibly occupy the internal surface of the clay and form one or more layers. Alternately, we expect a pore filling in B2 due to the length of the hydrocarbonated chain of HDMTA. In all cases the increment in molecular weight of the quaternary ammonium ion exchanged in the bentonite completely agrees with the increment of the average pore size of each sample.

On the other hand, in the wet state, the bentonites follow the trend B1, B2, B3. We understand the differences in surface areas due to the stronger hydrophobicity of the BTEA ion compared to the rest of the other quaternary ammonium ions (TMA and HDMTA). From the results, we observe that even in presence of water, both algae have a larger surface area than the modified bentonites.

Figure 1 shows the FTIR spectra of B1. Table 3 sums up the stretching frequencies observed in all the adsorbents. As previously reported, the FTIR revealed the presence of carboxyl, sulfonate, hydroxyl, and amino groups in algae (15). Regarding the modified bentonites, all exhibit the same FTIR profile, with silica, amine, hydroxyl, and hydrocarbons amongst the most important identified groups. The only difference among the 3 samples is two sharp peaks present only in B2 at $\upsilon = 2800\text{–}2900\,cm^{-1}$, attributed to the long aliphatic chain of HDMTA (25).

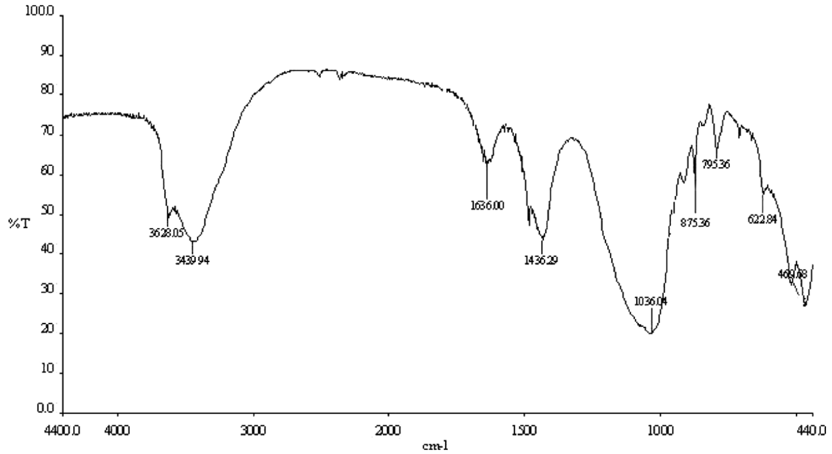

Figure 1. FT-IR analysis of exchanged bentonite with tetramethyl ammonium (B1).

The SEM analysis of algae (Fig. 2) displays a very well-organized surface, being able to recognize some helical structure as stated by the "egg-box" theory of alginates. This particular structure belongs exclusively to alginates that are lineal polysaccharides formed by units of 1,4 β-D mannuronic (M) and α-L guluronic (G) acids arranged in a random way, co-existing with the sequences MM, GM, GG, and MG in the polymer. This "egg-box" is responsible for the formation of gels in the presence of divalent cations stabilized by the dimerization of polyalginic chains in solution, where the divalent cations are "caged" inside the dimmer (27). Contradictorily, bentonites (Fig. 3) show a large number of particles finely conglomerated. Frost et al. propose a complex mechanism of interlamellar transformation in clays that includes the formation of parallel and vertical monolayers, bilayers and pseudo trilayers of

Table 3. FTIR analysis of algae and clays

Wave number (cm^{-1})	Assignment	Observed in
3410	$-OH$, $-NH$ stretching	A1, A2, B1, B2, B3
2850	C–C stretching	B2
1634	$C=O$ stretch of COOH	A1, A2
1425	Symmetric $C=O$	A1, A2
1160	Symmetric $-SO_3$ stretching	A1, A2
1033	C–O alcohol	A1, A2
1040	Si–O–Si stretching	B1, B2, B3
817	$S=O$ stretch	A1, A2
570	Si–O–Si	B1, B2, B3

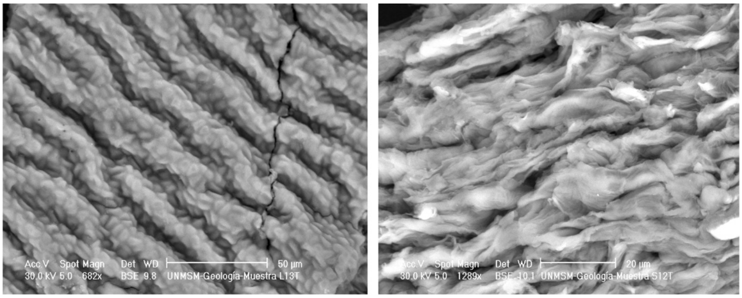

Figure 2. Scanning electron microscopy of algae A1 (left) and A2 (right).

HDMTA (28). Their study suggests that at low concentrations of organic cations (below 0.5 CEC) the intercalation of metallic ions of the clay with the organic ions is aleatoric and as the packing density increases (above 1 CEC) the ionic exchange in the clay presents a regular profile. This last idea differs from a previous study of Lee et al. who suggest the repetitive formation of "layers over layers" with constant dimensions in the clay, regardless of the number of available organic ions (29). As for the EDX analysis, the results in Figs. 4 and 5 clearly show an increment in the organic content in both types of adsorbents coming from phenol that is the only carbon and oxygen-containing compound in the solution. Using the calcium percentage as an indicator for comparison in the alga A1 spectra in Fig. 3, it displays an increment of carbon and oxygen after the contact with phenol, elucidating its adsorption on algae's surface. Figure 4 shows the comparison of EDX spectra before and after the adsorption of phenol by the modified bentonite B2, where an increment in the oxygen content is seen as well as a proof of the adsorption of phenol on the surface of the adsorbent. Although the intensity of the oxygen content after the adsorption is not as high as the one seen in the alga A1, this can be explained by the diffusion of the phenol inside the adsorbent through the pores finding the friendly organic environment given by the quaternary ammonium ions.

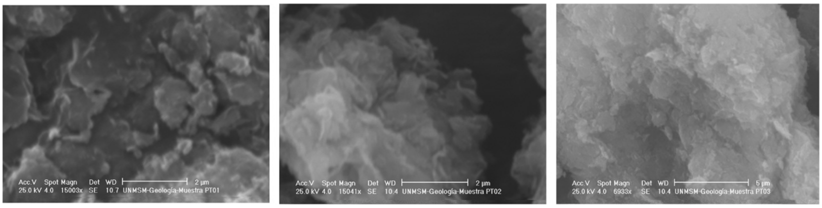

Figure 3. Scanning electron microscopy of exchange bentonites B1 (left), B2 (middle) and B3 (right).

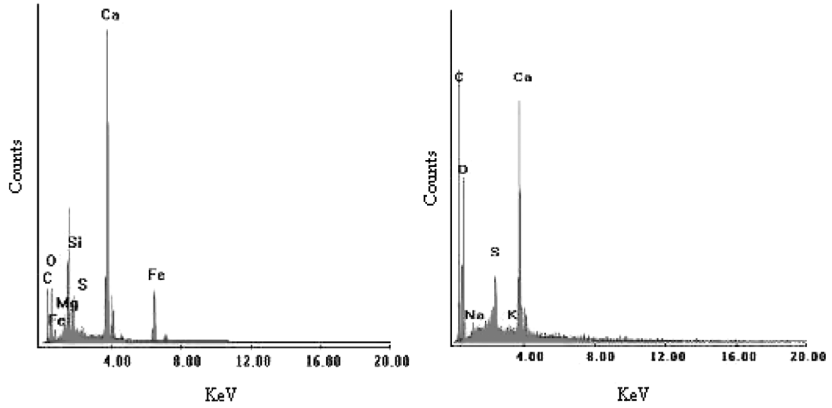

Figure 4. Energy dispersive X-ray surface analysis of cross-linked alga A2 before (left) and after (right) adsorption of phenol.

XDR studies were also carried out with the bentonites (Fig. 6). The interlamellar separation in the modified bentonites, originated due to the exchange of ions for quaternary ammonium salts was evaluated by means of the basal spacing obtained by XDR. According to the results the basal spacing values are 14.02, 14.38, and 15.04 Å for B1, B2, and B3, respectively. This reflects that the intercalation of these particular cationic surfactants has no effect in the interlamellar separation and no relation with the specific surface area data. The smaller basal spacing reported by the bentonite B1 can be understood as a consequence of the size of the TMA ions,

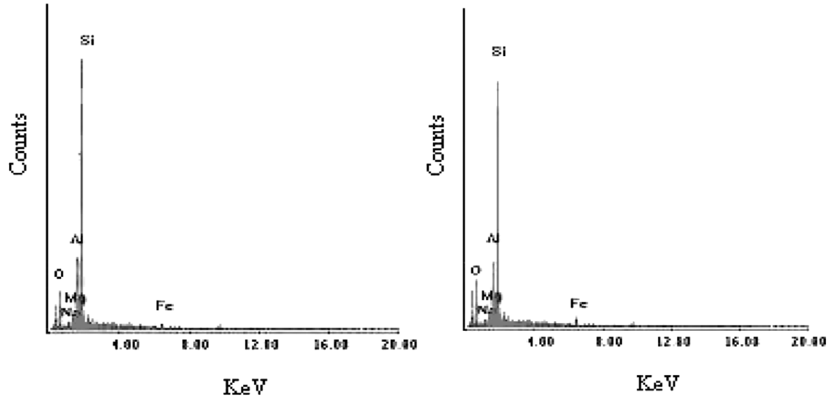

Figure 5. Energy dispersive X-ray surface analysis of exchanged bentonite B2 before (left) and after (right) adsorption of phenol.

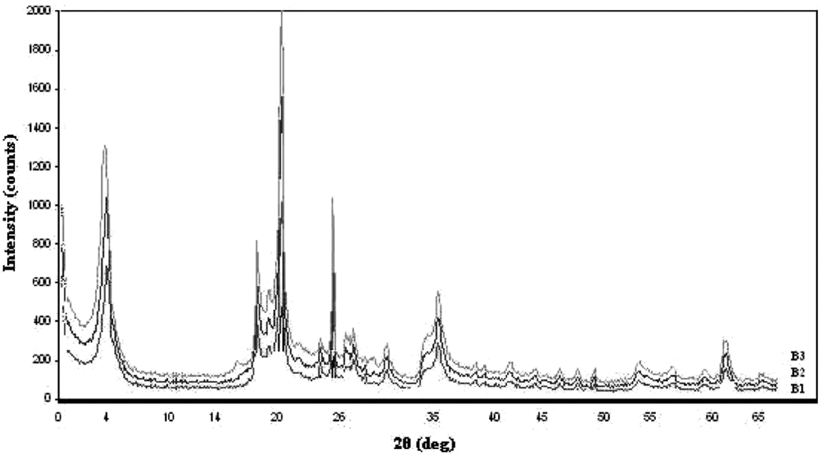

Figure 6. X-ray diffraction radiation pattern of exchange bentonites.

whereas HDMTA and BTEA ions would cause larger spacing in the bentonites. To corroborate this, Baskaralingam et al. (24) indicated an increasing basal spacing for clays modified with cetylpyridinium and cetyldimethylbenzylammonium ions (of comparable size with HDMTA and BTEA ions) as a consequence of the intercalation of surfactants into the

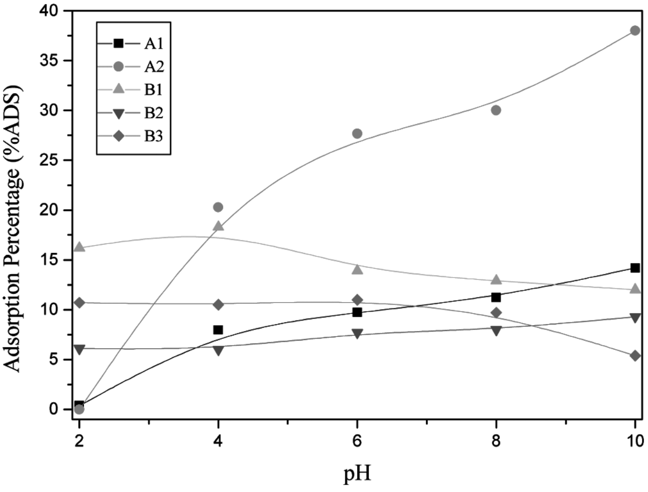

Figure 7. Effect of initial pH on the adsorption of phenol by cross-linked algae and exchanged bentonites.

interlayer of bentonites with a monolayer arrangement. This last hypothesis is in complete agreement with the SEM micrographs, where conglomerated particles were seen in the surface of the modified bentonites.

Adsorption Studies

Effect of Initial pH

The pH value of the adsorption medium is the most critical parameter that affects the adsorption capacity of phenol by marine seaweed, although it does not seem to play an important role in the adsorption by exchanged bentonites. The adsorption of phenol was studied at different initial pH values of 2–10. The pH before and after the adsorption process was also measured and found that the difference between the two measured values of pH was negligible. The variation of the equilibrium adsorption percentage of all the tested adsorbents with different initial pH is shown in Fig. 7.

As shown in Fig. 7, the adsorption percentage of both marine seaweeds (A1 and A2) increases with the rising pH value. This can be attributed to the pH value affecting the degree of ionization of phenol ($pK_a = 10.02$). The increasing ionic fraction of phenol at pH values around 10 enhances the affinity between the algae and the phenolate ion that is formed (15). In addition, pH also affects the surface property of the algal biomass and hence influences the equilibrium adsorption process. At pH higher than 3.0, the overall surface charge of the biomass becomes negative leading to donor-acceptor interaction between the oxygen of the phenolate ion and the hydrogen of the hydroxyl groups present on the surface of the algae (not the carboxylate) by hydrogen bonding (15).

Figure 7 also displays almost insignificant pH dependence in the adsorption percentage of phenol by the modified bentonites compared to the changes observed with the algae. The exchange of alkaline ions by quaternary ammonium ions in bentonites greatly increases their affinity towards organic molecules (20). Since the amino groups of these ions are not ionizable, the pH dependence of the process would completely lean on the aqueous chemistry of the pollutant. Therefore, this hydrophobic affinity is enhanced at pH where phenol is neutral ($pH < 10$), as confirmed by the stable adsorption percentage observed up to pH 8. Only a small decrease at high pH values was seen, because the neutral form of phenol will decrease due to the emerging phenolate ions in solution and limit the adsorption of phenol in the organic matter of the exchanged bentonites by partition function.

From the point of view of the pH, the adsorption mechanism by algae is mostly driven by polar interactions (formation of hydrogen bonds by the phenolate ion and the hydroxyl groups of the adsorbent enhanced at high pH value) whereas the nonionizable quaternary ammonium ions present in exchanged bentonites interact with the neutral form of phenol by hydrophobic forces (enhanced at low pH values).

Effect of Adsorbent Dose

The effect of adsorbent concentration on the percentage of phenol removal from 100 mL of solution is presented in Fig. 8. It can be seen that under identical conditions, an increase in the adsorbent concentration from 50 mg to 250 mg results in an increase of the removal of phenol from 2 and 20% to 5% and 100% for algae A1 and A2, respectively. For the alga A2, when the loaded adsorbent mass was between 200 and 250 mg no residual phenol was detected in the solution at the end of the sorption process. Therefore the presence of more active sites in exchanged bentonites does not affect the equilibrium nor improve the process. From the same Fig. 8, a slight decrease in the adsorption removal of phenol by A2 is seen at high adsorbent doses (from 5% to 2%). This can be attributed to the partial aggregation of the marine seaweed in solution that reduces the number of available adsorption sites as referenced in other studies (16).

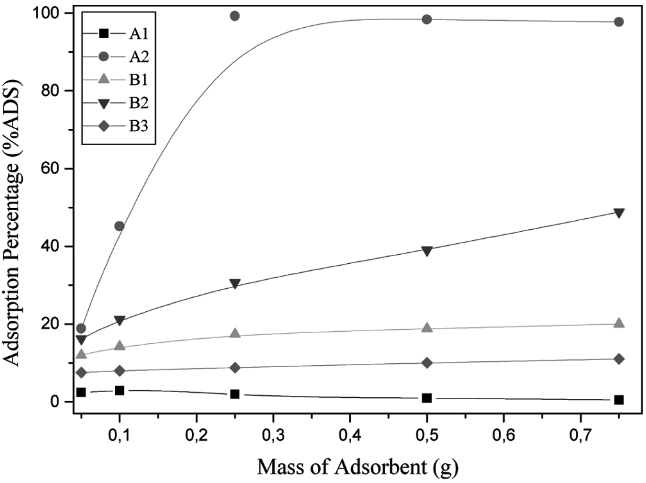

Figure 8. Effect of adsorbent dose on the adsorption of phenol by cross-linked algae and exchanged bentonite.

Figure 8 also displays a saturation of the surface of the three exchanged bentonites between 100 and 150 mg of adsorbent. This effect can be explained also by the formation of small aggregates of the modified bentonites at higher concentrations of the adsorbents. This is caused by the interaction and proximity of the hydrophobic chains of the quaternary ammonium ions. On the other hand, a progressive increase in the removal percentage by B2 is seen at increasing mass of adsorbent without reaching a plateau at masses as high as 750 mg. In this case, the increase in the adsorbent concentration at a fixed phenol concentration grants more available sorption sites for phenol and thus more phenol removal.

Different research groups have also studied the removal of phenol and found effective masses as high as 500 mg for chicken feathers (6), 4 g for surfactant modified clays (19), around 0.8 and 1 g of rice husk ash of Kenyan origin in (30), and more than 500 mg for marine seaweed (16). All the effective masses were obtained in 50, 25, 30, and 40 mL of phenol solution, respectively.

Adsorption Isotherms

The Freundlich equation is the earliest known mathematical model describing the adsorption process. Even though it represents a basic empirical relationship, it is often used as a means of data description. The Freundlich theory assumes that adsorbent-active sites have a spectrum of diverse binding energies (energetically heterogeneous surface). This isotherm does not predict any saturation of the adsorbent by the adsorbate; thus infinite surface coverage is predicted mathematically, indicating multilayer sorption on the surface. This model correlates the concentration of solute in the solution at equilibrium, C_{eq}, raised to the power of n, with the amount of solute adsorbed being q, then $(C_{eq})^n/q$ is constant at a given temperature.

The Langmuir sorption isotherm has been successfully applied to, and used as a description of, the sorption of a pollutant from a liquid solution (13,16,18). A basic assumption of the Langmuir model is that sorption takes place at specific homogeneous sites on the surface of the adsorbent. It is then assumed that once an adsorbate molecule occupies a site, no further sorption can take place at that site. The rate of sorption to the surface should be proportional to the driving force and area. The driving force is the concentration in the solution, and the area is the amount of bare surface (13,19).

Both isotherm equations can be described by their linearized forms and the Langmuir and Freundlich constants can be determined, according to equations (3) and (4) respectively.

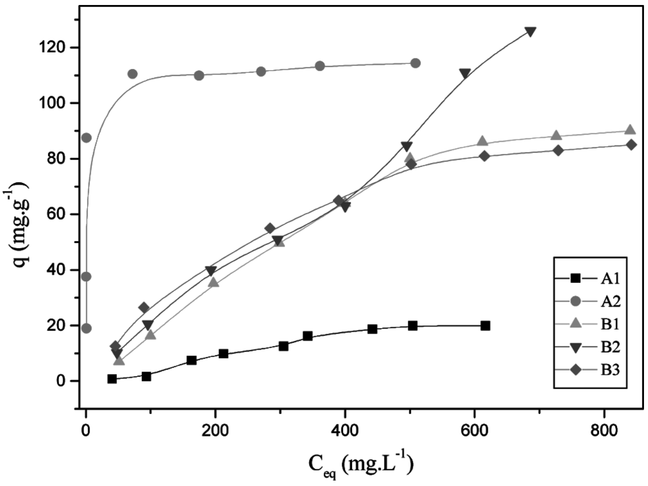

Figure 9. Adsorption isotherms of phenol on cross-linked algae and exchanged bentonites.

$$1/q = 1/q_{max} + 1/bxq_{max}xC_f \tag{3}$$

$$\ln q = \ln(k_f) + (1/n)x\ln(C_f) \tag{4}$$

where q_{max} ($mg \cdot g^{-1}$) and b ($L \cdot mg^{-1}$) are the Langmuir constants related to the maximum adsorption capacity and to the adsorption energy or net enthalpy, respectively, and k_f and n are Freundlich constants related to the adsorption capacity and the adsorption intensity, respectively. A relatively slight slope (and hence a high value of n) indicates that adsorption is applicable to the entire range of concentration studied, while a steep slope (and hence a small n) means that adsorption is sufficient at high concentrations but is much poorer at low concentrations.

Figure 9 shows the adsorption isotherms for each adsorbent used in the removal of phenol. As can be observed, B2 displays a lineal adsorption indicating a predominant non-competitive mechanism between the adsorbate and the adsorbent, which involves the formation of an organic phase on the surface of the bentonite formed by the long hydrocarbonated chains of HDTMA where the phenol molecules are retained by physisorption. Lineal isotherms and non-competitive adsorption mechanisms have been described previously for ammonium salts composed of long aliphatic chains ($\geq$12 carbons) (29,31). Figure 9 also shows non-lineal isotherms for B1 and B3 that completely agree with a competitive adsorption. It is suggested that TMA and BTEA ions, due to their relatively small size, are well scattered on the interlamellar spaces of the bentonites, which complicates their contact and aggregation and the formation of a hydrophobic-friendly environment (partition phase) (32). Therefore, each exchanged TMA and BTEA ions act independently as adsorption sites corroborating the competitive adsorption (33).

Concerning the marine seaweeds, A1 and A2, they report nonlineal isotherms, confirming their competitive adsorption. As stated with the effect of initial pH, the algae' adsorption is mostly driven by polar interactions (hydrogen bond formation). Therefore each hydroxyl group on the surface will compete for the pollutant to release energy by the formation of polar interactions. This resembles the saturation of the adsorption capacity at which that mass of adsorbent has been completely saturated with phenol. The significant difference on adsorption between A1 and A2 was explained elsewhere (15) and associated to the proteic and fiber composition of both algae.

Table 4 shows the isotherm constants of the adsorption of phenol by exchanged bentonites and cross-linked algae. According to the correlation coefficients, both types of adsorbents fit Langmuir and Freundlich theories suggesting a mixed adsorption mechanism. However in this case, preference is given to the Langmuir model.

The adsorption isotherm analysis exhibited a ranking of maximum adsorption capacities (q_{max}), which is a measure of the maximum monolayer adsorption capacity to retain phenol, of B1 > B2 > B3 > A2 > A1. On the other hand, a high affinity adsorbent/adsorbate is reflected by the Langmuir constant b, A2 possessing the highest value, whereas the rest of the adsorbents are in the same range.

As expected, exchanged bentonites report the highest q_{max} compared to cross-linked algae. These results confirm the hypothesis that adsorption of phenol by bentonites is driven by hydrophobic interactions.

Table 4. Isotherm constants for the adsorption of phenol by cross-linked algae (A1 and A2) and exchanged bentonites (B1, B2, and B3)

	Langmuir			Freundlich		
Adsorbent	q_{max} $(mg \cdot g^{-1})$	b $(L \cdot mg^{-1})$	R^2	k_f $(mol^{1\text{-}1/n} \cdot L^{1/n} \cdot g^{-1})$	N	R^2
Al	16.8	0.002	0.99	0.01	0.78	0.97
A2	115.6	0.164	0.99	18.5	3.19	0.98
Bl	497.5	0.001	0.99	0.23	1.09	0.97
B2	392.2	0.001	0.99	0.29	1.09	0.99
B3	132.6	0.003	0.99	1.25	1.56	0.98

Consequently, phenol is now able to find more accessible adsorption sites inside the bentonites travelling through a hydrophobic-friendly environment. This mechanism becomes impossible for the adsorption by algae, where the internal diffusion of phenol inside the adsorbent would expose it to the repulsion by the negatively-charged carboxylate groups. Therefore, the adsorption of phenol is mostly a surface phenomenon in algae. Although the adsorption by algae is only reduced to the surface, nevertheless, the swelling of algae in water greatly increases the efficient area (as demonstrated by the MB method) and shortens the difference between bentonites and algae to approximately one-third of their adsorption.

Other research groups have found q_{max} values (in $mg \cdot g^{-1}$) around 105 for surfactant modified clays (19), 1.7 for natural clays (22), 17.39 for activated carbon (34), 15.25 for rice husk ash (30), 13, for fly ash (35), and 13 for other algal biomass (16).

Values for the Freundlich affinity index (n) for the studied adsorbents followed the order: $A2 > B3 > B2 \approx B1 > A1$ (Table 3). Freundlich fitting with $n > 1$ would indicate conformity of the data to multilayer formation at the adsorbent's surface, for example in the case of A2. This observation could also be attributed to the molecular interactions between the adsorbate species and subsequent aggregation in the pattern of a surface monolayer. So, Freundlich fitting with B1, B2, and B3 are related to the partitioning process rather than surface interactions. In this case, the organoclays act as a solvent-type sink for the contaminants (36). Such mechanistic paths could be possible attributes explaining the conformity of our data with both Langmuir and Freundlich isotherms. Finally, a greater value of k_f indicates a higher capacity for adsorption. Values of binding affinity constants, k_f, followed the trend: $A2 > B3 > B2 \approx B1 > A1$. For A2, this was probably for the thoroughly-solvent-exposed surface and for B3 due to a greater partitioning of phenol by BTEA (aromatic interactions between both benzene rings).

CONCLUSIONS

Organophilic clays and cross-linked marine seaweeds were compared based on their adsorption capacity of phenol from aqueous solutions. Batch experiments at room temperature demonstrated a strong effect of the initial pH of the solution on algae whereas, exchanged bentonites were almost unaffected by the initial pH. Adsorbent dosage effect was also evaluated and revealed a lower mass required to reach saturation compared with reports in the literature with the same and other adsorbents. Sorption isotherm results were fitted to Langmuir and Freundlich models, exhibiting a mixed adsorption mechanism. Langmuir and

Freundlich constants indicate a better affinity between phenol and exchanged bentonites compared to marine seaweeds. Equilibrium results and EDX analysis elucidate a surface adsorption of phenol on algal biomass and a polar adsorption mechanism thus proposing the formation of hydrogen bond formation. The same results also suggest that the organic phase derived from the exchanged quaternary ammonium ions was the primary adsorptive phase for phenol. The nonlinear sorption isotherms of phenol occur via a dual mode mechanism, in which partitioning of phenol into organoclays and surface adsorption onto marine seaweed takes place. These results provide further insight into the adsorption mechanism of phenol and analogues and their use as powerful and cost-effective adsorbents for the treatment of phenol-containing wastewater. Finally, a comparison between the biological and the nonbiological adsorbent shows that for certain phenolic compounds, modified clays are more efficient than marine algae.

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