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Adsorption of casein onto some oxide minerals and electrokinetic properties of these particles

Özkan Demirbaş [a,*], Mahir Alkan [a], Aygül Demirbaş [b]

[a] Balikesir University, Faculty of Science and Literature, Department of Chemistry, 10100 Balikesir, Turkey
[b] Balikesir University, The Institute of Science, Department of Biology, 10100 Balikesir, Turkey

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ABSTRACT

In this study, the adsorption properties of casein onto some oxide minerals such as sepiolite, kaolinite and expanded and unexpanded perlites samples were studied as a function of concentrations of casein, sodium phosphate and NaCl, temperature and pH of the aqueous solutions. According to the experimental results, the adsorption of casein increases with temperature from 15 to 45 °C and ionic strengths of the solutions over the range of 0.0 and 0.1 mol L^{-1}. The adsorption decreased with increasing pH from 7.00 to 11.00 and the concentration of phosphate ions from 0.02 to 0.10 mol L^{-1}. Maximum adsorption capacity values (q_m) showed dependence on pH. It was observed that q_e–pH curves reached a maximum at around neutral pH value. Furthermore, the electrokinetic properties of casein-covered oxide particles were also investigated at similar conditions to those of the adsorption process. The nature of the adsorption process was investigated using Langmuir and Freundlich isotherm models.

1. Introduction

The adsorption of a protein to a surface usually produces a change in its physicochemical properties, which may affect the biological functioning of the molecule [1]. Protein adsorption is a complex process in which the structural stability of a protein, the ionic strength and the pH of the solution and surface properties of sorbent are known to influence the affinity of a protein for a given interface [2]. As most proteins adsorb with high affinity to hydrophobic surfaces, these proteins generally have less native structure than the same protein adsorbed on hydrophilic surfaces [3,4]. It has also been seen that an increase in electrostatic interaction is generally accompanied by a reduction in the native structure [2,5].

Caseins are also frequently used as additives in food, paint, glue and coating colours for paper, etc. where their amphiphilic properties are utilized to modify various types of interfaces [6]. They may have an isoelectrical point the pH range of 4.8–5.5 [6–9] The main proteins in renneted milk comprise α_{s1}-, α_{s2}-, β-, and para κ-casein. Of these four caseins, para-k-casein is known to be bound closely to the surface of casein micelles. The hydrophobic plots of amino acid residues in α_{s2}- and κ-casein suggest that they have surface active properties [7,8] and that these proteins may also be located on the micellar surface. The biological role of casein molecules includes the sequestration of amorphous calcium phosphate to form stable complexes in milk [6,9]. Knowledge of the mechanisms by which caseins adsorb is therefore of great interest in many colloid-related industries.

Sepiolite is an oxide mineral with a unit cell formula $Si_{12}O_{30}$-$Mg_8(OH,F)_4(H_2O)_4{\cdot}8H_2O$ [10]. In some aspects sepiolite is similar to other 2:1 trioctahedral silicates, such as talc, molecule formula is $Mg_3Si_4O_{10}(OH)_2$, but it has two discontinuities and inversions of the silica sheets that give rise to structural tunnels [11]. In the inner blocks, all corners of silica tetrahedral are connected to adjacent blocks, but in outer blocks some of the corners are Si atoms bound to hydroxyls (Si–OH) [10].

Kaolinite is a 1:1 dioctahedral aluminosilicate that has two different basal cleavages faces. One basal face consists of a tetrahedral siloxane surface very inert –Si–O–Si– links. The other basal surface consists of an octahedral, gibbsite ($Al(OH)_3$) sheet. The 1:1 layers are held together in the crystal by hydrogen bonding [12,13].

Perlite, a glassy volcanic rock, has the unusual characteristic of expanding to about 20 times its original volume when heated to an appropriate temperature within its softening range. Chemically, crude perlite is essentially a metastable amorphous aluminum silicate. Commercially, the term "perlite" also includes the expanded product. The uses of expanded perlite are many and varied and are based primarily upon its physical and chemical properties. As most perlites have high silica content, usually greater than 70%, and are

* Corresponding author. Tel.: +90 266 6121000; fax: +90 266 6121215.
E-mail address: ozkan@balikesir.edu.tr (Ö. Demirbaş).

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adsorptive, they are chemically inert in many environments and hence are excellent filter aids and fillers in various processes and materials [14–16].

Soil extracellular enzymes, like other proteins, are adsorbed on many surfaces, particularly on oxide minerals [3]. In fact, most of the protein adsorption studies were performed on different adsorbent surfaces such as silica particles [5,17], to a lower extent montmorillonite [18,19], hydroxyapatite [20,21], TiO_2 particles [22], chitosan [23,24], stainless steel surface [25,26] and mica [27].

To know understanding the mechanism of protein adsorption, their electrokinetic properties and evaluating the impact on practical applications is very important. For this purpose, we studied the adsorption and electrokinetic properties of casein onto some oxide minerals such as sepiolite, kaolinite, and expanded and unexpanded perlite in this study since the use of these adsorbents have not been found in the literature. Zeta-potentials of the minerals were also measured as a function of concentrations of casein and PO_4^{3-} ions, pH and ionic strength of solution that was indicated by NaCl concentration. The adsorption of casein on these oxide minerals was conducted at the similar conditions to illustrate the role of ζ-potentials and other factors.

2. Materials and methods

2.1. Materials

Sepiolite, kaolinite and expanded and unexpanded perlites were used as adsorbents for casein in this study. Sepiolite was obtained from Aktaş Lületaşı Co. (Eskişehir, Turkey); kaolinite from Aksaray-Turkey and perlite samples from İzmir-Turkey. The chemical compositions of the minerals determined by XRF are given in Table 1. All chemicals used were of analytical grade. Casein was purchased from Merck.

2.2. Purification of the oxide particles

Sepiolite, kaolinite and perlite samples were pre-treated to be used in the experiments as follows [28]: the suspension containing oxide that its concentrations is 10 g L^{-1} was mechanically stirred for 24 h and after waiting for about two minutes, the supernatant suspension was filtered through filter paper. The solid sample was dried at 105 °C for 24 h, ground and then sieved by 75-μm sieve. The particles under 75 μm were used in further experiments. The experiments of adsorption and measurement of the zeta potential were carried out by shaking 0.3 g sepiolite and kaolinite, and 0.5 g expanded and unexpanded perlite samples in 100 mL aqueous solution.

2.3. Cation exchange capacity, density, surface area and pore size

The cation exchange capacities (CEC), the densities, the specific surface areas and pore size distributions of the adsorbents were determined by the ammonium acetate method, the Pycnometer method and BET N2 adsorption by Micromeritics FlowSorb II-2300 equipment, respectively. The results obtained from the experiments are summarized in Table 2 and Fig. 1.

Table 1
Chemical composition of oxide minerals.

Constituent	Percentage present (%)		
	Sepiolite	Kaolinite	Perlite
SiO_2	53.47	53.00	72.75
Al_2O_3	0.19	26.71	13.56
CaO	0.71	0.57	1.10
Fe_2O_3	0.16	0.37	0.83
MgO	23.55	0.28	0.29
Na_2O	–	0.62	2.92
K_2O	–	1.39	4.93
NiO	0.43	–	–
LoI	21.49	17.20	3.63

Table 2
Some physicochemical properties of oxide minerals used this study.

Samples	CEC (meq/100 g)	Density (g cm^{-3})	Specific surface area ($m^2 g^{-1}$)	Equilibrium pH of the suspension in water
Sepiolite	25	2.50	242	8.55
Kaolinite	13	2.18	22	7.85
Unexpanded perlite	25	2.30	1.22	7.05
Expanded perlite	33	2.24	2.30	7.10

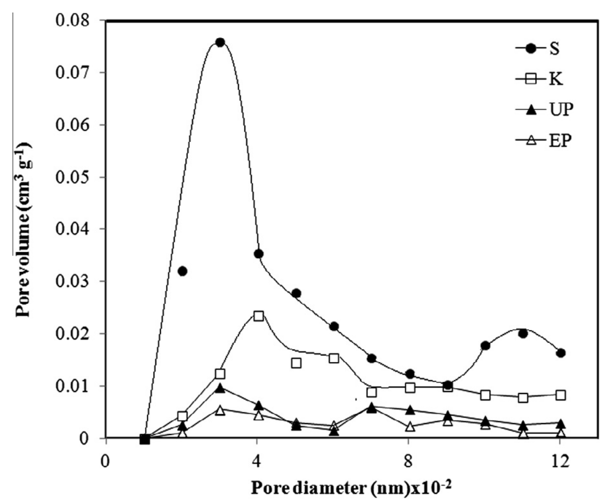

Fig. 1. Distribution of pores (S: sepiolite, K: kaolinite, UP: unexpanded perlite, EP: expanded perlite).

2.4. Zeta potential measurements

The zeta, ζ, potential is one of the electrokinetic parameters of particles. The study of the electrochemical properties of the oxide/water interface is important for understanding a large number of properties of oxide-rich porous media and colloid suspension of oxides [15]. When the oxide minerals are suspended in aqueous solution, the surface properties are dramatically changed because the ions are hydrated. For an oxide or clay, the calculation of the surface charge is considered to be one type of ionisable surface group, but that is amphoteric so it can take up either a proton or an OH^- ion depending on the pH [16]:

$$S{-}OH \rightleftharpoons SOH_2^+ \tag{1.1}$$

$$S{-}OH + OH^- \rightleftharpoons SO^- + H_2O \tag{1.2}$$

where the letter "S" denotes the surface.

The effects of the concentrations of casein and PO_4^{3-} ions, pH and ionic strength on zeta potential were evaluated using a Zeta Meter 3.0 (Zeta Meter Inc.) equipped with a microprocessor unit [28]. The instrument calculates the electrophoretic mobility of the particles automatically and converts it to the zeta potential using the Smoluchowski equation [29].