

## Article

# Biotribology in Arthroplasty: Worn Surfaces Investigation on Ceramic Hip Femoral Heads Considering Wettability

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**Abstract:** Ceramic-on-ceramic bearings for total hip replacement are considered the best choice to avoid problems such as osteolysis and wear, mainly related to soft bearings. The aim of this work was to investigate in a comparative way different kinds of ceramic femoral heads for total hip replacements from a biotribological point of view, discussing the results obtained in terms of topographies, presence of metal transfer (MT) phenomena, and wettability on their worn surfaces in a tribological framework. Different ceramic femoral heads derived from in vitro wear tests, retrieved from patients, and brand new total hip replacements were investigated. The patients group had an average age of 60 years (ranging from 27 to 83). In most cases, the cause of failure was aseptic loosening of the acetabular component. Roughness analyses were performed to measure the tribological surface evolution of the material; an SEM and EDS investigation on the explanted heads proves and quantified MT, while the wettability was measured through a novel optical laboratory set-up with the aim to furnish useful data in the framework of synovial lubrication phenomena acting in the tribosystem. For the average roughness measurements on explanted specimens were considered three parameters ( $R_a$  = the average area between the roughness profile and its mean line;  $R_t$  = the vertical distance from the deepest valley to the highest peak of the roughness profile; and  $R_{sk}$  = it is the skewness and it is a measure of the asymmetry of the amplitude distribution function. In other words, the skewness indicates whether a surface is dominated by peaks or by valleys) and their values were:  $R_a$   $0.22 \pm 0.12 \mu\text{m}$ ,  $R_t$   $34.5 \pm 13.5 \mu\text{m}$  and  $R_{sk}$   $-0.01 \pm 11.3$ ; on the new specimens we measured  $R_a$   $0.01 \pm 0.001 \mu\text{m}$ ,  $R_t$   $0.12 \pm 0.09 \mu\text{m}$ , and  $R_{sk}$   $5.67 \pm 8.7$ ; for the in vitro specimens they were  $R_a$   $0.05 \pm 0.12 \mu\text{m}$ ,  $R_t$   $0.71 \pm 1.4 \mu\text{m}$  and  $R_{sk}$   $7.73 \pm 20.6$ . The wettability angle measurements showed hydrophilic surfaces for all femoral heads considered in this study with small differences between the three investigated categories, allowing to discuss their effects on the biobearings' lubrication phenomena.

**Keywords:** ceramic hip retrievals; wettability; metal transfer; wear; lubrication; Biolox<sup>®</sup> Delta; Biolox<sup>®</sup>

## 1. Introduction

Total hip replacement (THR) is a successful procedure with relatively low complications [1,2]. With the improvement of fixation and implant designs, and the introduction of minimally invasive techniques, the goal of THR is to minimize wear and osteolysis significantly reducing loosening of the components. Metal-on-metal (MOM) and ceramic-on-ceramic (COC) bearings are the most suitable solutions, especially for younger patients [3].

Metal-on-metal hip implants, introduced by Wiles and McKee-Farrar [4], were abandoned because of high frictional torques, inadequate surface finish, and high clinical failure rates, which resulted in

extremely poor clinical outcomes. The second generation of MOM hip articulations, introduced by Weber in 1984 [5], presented substantial improvements in terms of periprosthetic load distribution, range of motion (ROM, through the insertion of larger-diameter femoral heads) and a reduced dislocation risk [6]. Ceramic materials, introduced in hip arthroplasty more than 20 years ago, have been progressively attracted interest in the orthopedic field for they excellent biocompatibility, low coefficient of friction, and high wear resistance [7,8]. Moreover, they have good mechanical resistance [9] and produce lower wear rates than other combinations (i.e., metal-on-polyethylene and ceramic-on-polyethylene) [10–13]. However, the principal limitations of COC prosthesis is dislocation (with small-sized heads) and head fracture risk [6]. Tateiwa and coworkers [14] observed the occurrence of stripe wear in first-generation alumina ceramic bearings. In particular, the stripes were shallower and the ball surfaces had higher compressive stress due to severe impingement and microseparation phenomenon. Nevelos et al. [15] analyzed explanted prostheses from a single surgeon's 16 year series of Mittelmeier cementless total hip replacements and found that the majority of the explants exhibited stripe wear conditions with linear penetrations less than 0.15 mm and worn area surface roughness (Ra) of approximately 0.2  $\mu\text{m}$ .

It is well known that composition, electric charge, wettability, and roughness of implant surfaces have great influence on their interaction with the biological fluids and tissues [16]. The importance of surface wettability has been highlighted in the scientific literature [17]. Wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. The degree of wettability ( $\theta$  angle) is determined by a force balance between adhesive and cohesive forces. The liquid drop contact angle is the angle that forms where the liquid–vapor interface meets the liquid–solid one and it is the main parameter used in the description of this phenomenon. Based on the value of the latter, which can be between 0 and 180°, it is possible to affirm that  $\theta = 0$  means a perfectly wetting surface;  $0 < \theta < 90^\circ$  means surfaces with high wettability;  $90^\circ \leq \theta < 180^\circ$  means surfaces with low wettability.

Ceramic materials offer a harder and more hydrophilic surface than metal alloys and can be polished to a lower roughness [18]. Some authors showed that, in hip wear simulator studies, femoral heads induced less Polyethylene wear compared with Cobalt-Chrome (CoCr) alloys [19–21].

Evaluation of worn retrievals' ceramic articular surfaces is one method for verifying that damage patterns generated by hip joint wear simulation are comparable to those evident on explanted prostheses due to physiologic hip function. Unfortunately, partial and limited reports are available in literature due to the scarce number of available specimens and different types of ceramic used [10,11,20,21]. Friction and wear processes are known to be affected by the surface wettability of the prosthetic materials [22–24], but definite correlations between wettability and tribological behavior are still to be established [17].

In this work, interfacial behavior of the various ceramics femoral heads was experimentally investigated through the measurement of lubricant drops contact angles. In particular, to gain a deeper understanding of this matter the primary objective of the present study is to present novel experimental results in terms of femoral heads surface characteristics (wettability, and roughness) investigating the microstructure of different retrieved ceramic femoral heads, to verify MT phenomena.

## 2. Materials and Methods

### 2.1. Samples Selection

In this study the authors examined 53 femoral heads. Twenty-four of them derived from explanted prosthesis which were partially investigated in a previous work of the authors [12]. The patients had undergone a primary THA at Rizzoli hospital; with an average age of 60 years (ranging from 27 to 83) at revision. In most cases, the cause of failure was aseptic loosening of the acetabular component. Prosthesis retrieved for catastrophic failures were excluded from the study, in order to avoid possible influences of other parameters on wear analysis. Major details are given in Table S1—Supporting information.

Nine femoral heads were brand new BioloX<sup>®</sup> Delta femoral heads. The remaining 20 femoral heads were BioloX<sup>®</sup> Forte and were analyzed after in vitro tests in a hip joint simulator realizing a hard-on-soft contact with a UHMWPE acetabular liner. In particular, these bearings were tested under bovine calf serum as lubricant, applying a simplified load as recommended by the international guidelines (ISO 14241-3000 N), and for two million cycles. All the femoral heads analyzed in this study had a diameter of 32 mm.

## 2.2. Surface Characterization

Measurements of surface roughness of the femoral heads were acquired using a contact rugosimeter (Hommel Tester T8000 machine, Schwenningen, Germany). Three roughness parameters ( $R_a$ ,  $R_t$ ,  $R_{sk}$ ) were measured following an established protocol [18]. In details, the measurements were taken along 5 mm lines with 0.08 mm cut-off, with a length for each measurement of 0.45 mm. Each head was analyzed at four different inclinations of the stem with respect to the vertical axis, corresponding to 0°, 15°, 30° and 45°. In each angle of inclination the roughness was derived in three different points, separated by 120° of rotation along the stem axis.

A scanning electron microscope (SEM, ZEISS EVO 50EP, Cambridge, UK) operating at 20 kV was used to characterize the surface of the explanted femoral heads. All the specimens were observed in an environmental pressure mode of 70–90 Pa in chamber, so there was no need for surface coatings. In addition, energy dispersive spectroscopy (EDS) X-ray analysis (Inca Energy-200, Oxford Instruments, High Wycombe, UK) was used to analyze their chemical composition to characterize each element and discriminate between metal scars on the surfaces.

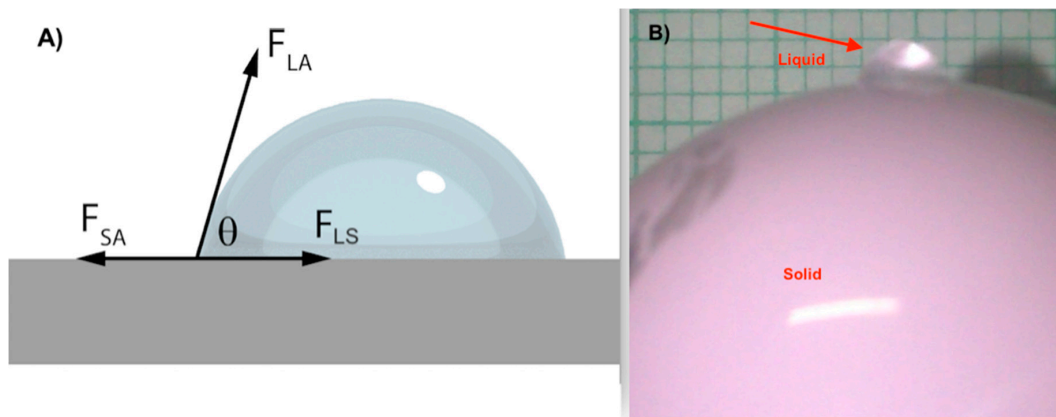
## 2.3. Wettability Set-Up

Wettability is usually defined as the ability of a liquid to spread over a surface [25]. The lubricant deposited on the solid surface under gravity tends to spread until the internal cohesion forces of the liquid are balanced with the forces rising from the surface tension [26]. To evaluate the wettability of the investigated ceramic femoral heads, the apparent contact angle was evaluated applying a static drop technique. The contact angle,  $\theta$ , as depicted in Figure 1, is the angle at which the liquid–vapor interface meets the solid–liquid interface. The droplet on the solid surface under gravity spreads until the liquid internal cohesive forces, the surface tension forces and gravity are in balance. Once the equilibrium is reached (three phases minimum of the energy state) a contact angle  $\theta$  between the solid surface and the liquid droplet can be measured. Static contact angle  $\theta$  is greater than 90° when the surface energy of the solid–air interface assumes greater values than the liquid–air interface. With reference to water droplets (other liquids), we assumed a super-hydrophobic (super-amphiphobic) behavior for  $\theta$  greater than 150°, hydrophobic (amphiphobic) behavior for  $\theta$  between 90° and 150°, hydrophilic (amphiphilic) behavior for  $\theta$  between 10° and 90°, and super-hydrophilic (super-amphiphilic) for  $\theta$  between 0° and 10° [27].

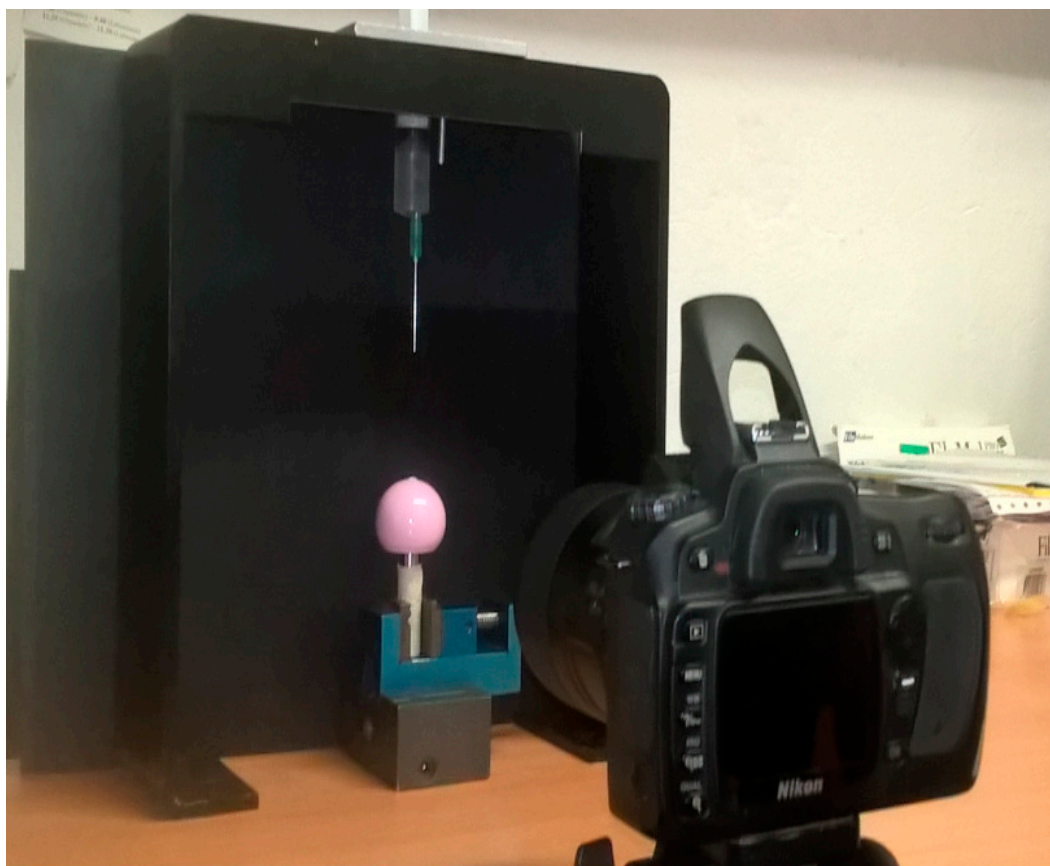
The adopted experimental apparatus consisted of a horizontal stage used to place the specimen, which allowed to be adjusted in the z-directions, a micrometer syringe to form a liquid drop, a halogen and intensity adjustable light source to illuminate the sample, and a Nikon camera for the high-resolution images acquisition (Figure 2).

Before measuring, the samples were cleaned in an ultrasonic bath for 15 min to remove any residues, dried with nitrogen gas, and cleaned with acetone. A liquid droplet of distilled water with a volume of 10  $\mu$ L was used. The liquid droplet fell on the same dome surface of the ceramic femoral heads. After camera acquisitions, the contact angle between the drop and the surface of the samples was measured using a free and open-source graphics editor (GIMP 2.8, GNU Image Manipulation Program). Tests were conducted at room temperature (25 °C); each experiment was repeated four times and the experimental results were taken as the mean value to assure reproducibility. This technique represents a novel measurement approach, used nowadays in several fields of accurate dimensional measurements, but not yet consolidated in a standardized measurement protocol, and with a complex uncertainty

determination; the possibility to obtain very high magnifications of the droplet pictures at high resolution, due to the high resolution camera adopted, lent satisfactory confidence in the obtained results.



**Figure 1.** Contact angle: (A) shows the vectorial representation indicating the direction of the force applied ( $F_{LA}$  = liquid–air force;  $F_{SA}$  = solid–air force;  $F_{LS}$  = liquid–solid force). (B) is an example of a drop on a BioloX<sup>®</sup> Delta femoral head.



**Figure 2.** Wettability set-up.

Statistical analyses were performed on measured data by using SPSS 14.0 (SPSS Inc, Chicago, IL, USA) software. Mann–Whitney U tests and median tests with independent samples were used to check differences in distribution and in median. Statistical significance was set at  $p < 0.05$ . The correlation between roughness measurements *vs.* follow-up and wettability of the heads were calculated using Pearson's  $r$ .

### 3. Results

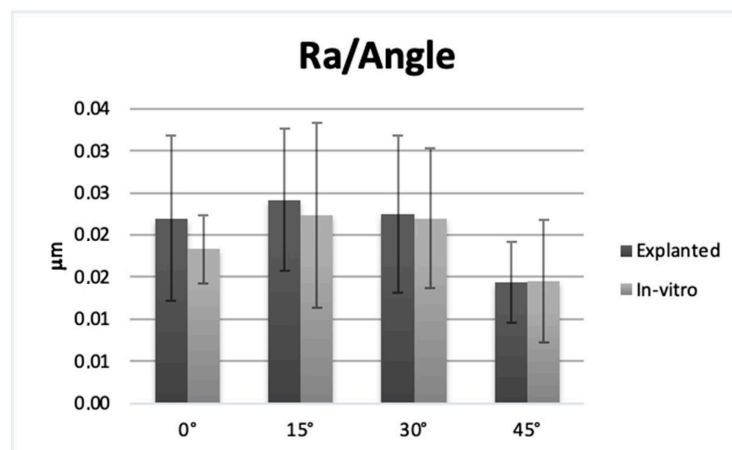
#### 3.1. Microscopic Results

Roughness parameters values are summarized in Table S2, Supporting Information. By analyzing the obtained data collected in Table S2, Supporting Information, it is possible to underline that the mean values of Ra, Rt and Rsk are different between the considered specimens. In fact, for the in vivo specimens the values were Ra  $0.22 \pm 0.12 \mu\text{m}$ , Rt  $34.5 \pm 13.5 \mu\text{m}$  and Rsk  $-0.01 \pm 11.3$ ; on the new specimens, we measured Ra  $0.01 \pm 0.001 \mu\text{m}$ , Rt  $0.12 \pm 0.09 \mu\text{m}$ , and Rsk  $= 5.67 \pm 8.7$ ; for the in vitro specimens, they were Ra  $0.05 \pm 0.12 \mu\text{m}$ , Rt  $0.71 \pm 1.4 \mu\text{m}$  and Rsk  $7.73 \pm 20.6$ .

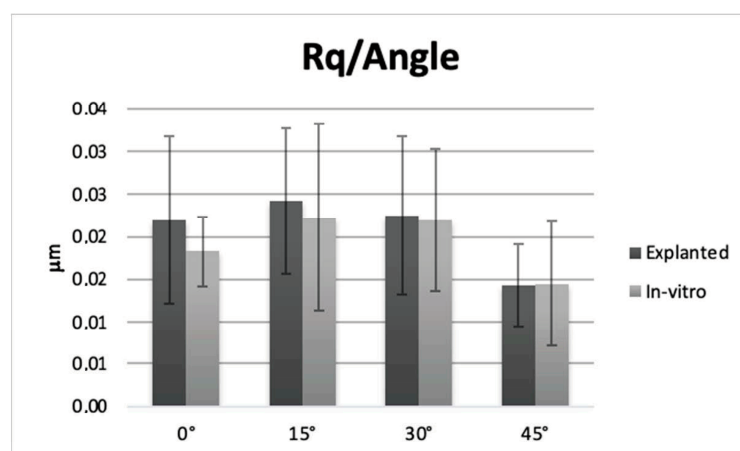
A detailed comparison between considered roughness parameters and measurement angles angle is shown in Figure 3a–c, with to explanted and in vitro femoral heads.

SEM observation of some femoral heads revealed an annular wear zone where the majority of the scratches, holes and micropits were situated. The micropits and holes were generally regular in shape but varied in size ( $2\text{--}25 \mu\text{m}$ ).

As a representative example, Figure 4 shows the picture of the microanalyses performed on one BioloX® Delta femoral head, in which MT phenomena were observed. MT markings may consist of titanium (Ti) or cobalt chromium (CoCr) alloy and it is represented in the right part of the above picture. We observed in this part some elements, such us Ti, CoCr, Fe, Mn, which are the constituents of the metallic alloys used in the metal back.



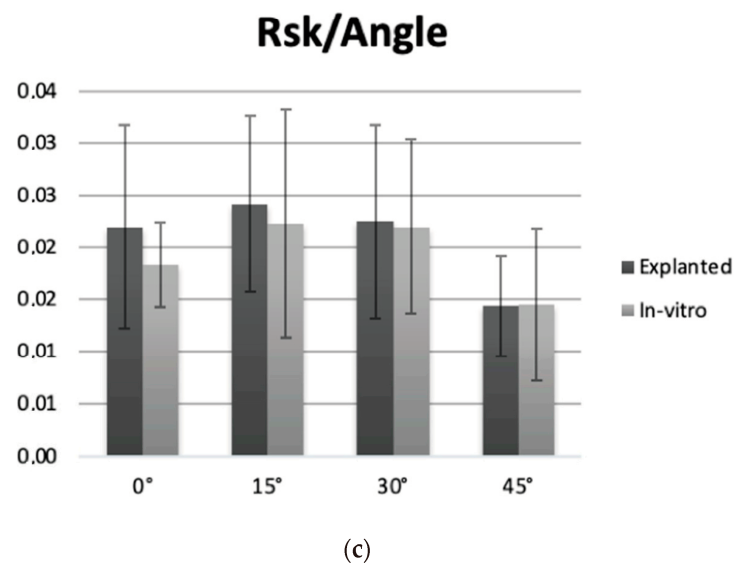
(a)



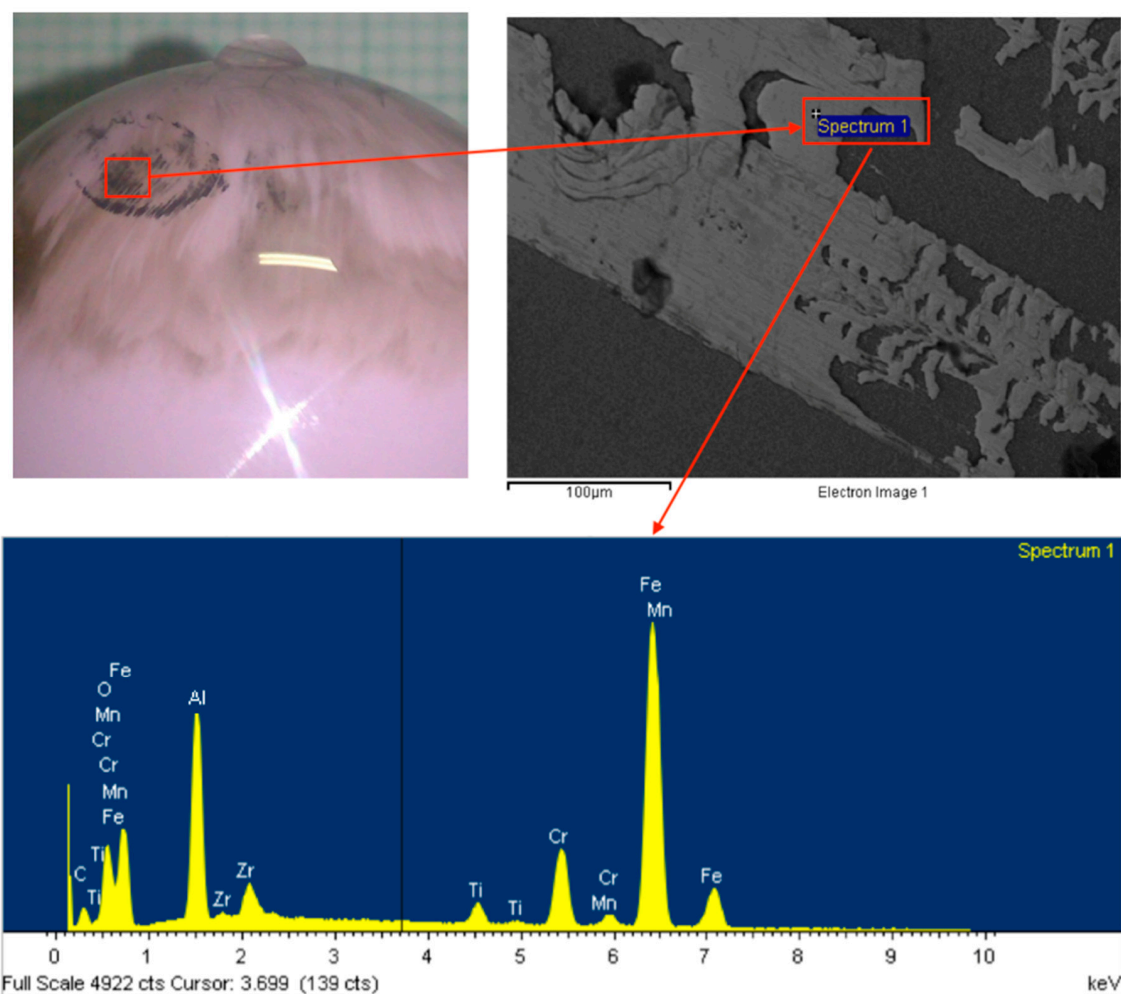
(b)

Figure 3. Cont.





**Figure 3.** (a) Ra vs. measurement angles in the cases of explanted and in vitro femoral heads. (b) Rq vs. measurement angles in the cases of explanted and in vitro femoral heads. (c) Rsk vs. measurement angles in the cases of explanted and in vitro femoral heads.



**Figure 4.** SEM and EDS analysis on a BioloX® Delta retrieved specimen affected by MT.

### 3.2. Wettability Results

The wettability apparent angle measurements, for each femoral head, are shown in Tables 1 and 2. In particular, Table 1 gives the wettability angles of the femoral heads explanted.

**Table 1.** Wettability angles of the femoral heads explanted.

Heads	Material	Wettability Angle ( $\theta$ )	MT Area (mm <sup>2</sup> )	% MT Area	Heads	Material	Wettability Angle ( $\theta$ )	MT Area (mm <sup>2</sup> )	% MT Area
#01	BioloX <sup>®</sup> Forte	39	88	11	#13	BioloX <sup>®</sup> Forte	45	30	4
#02	BioloX <sup>®</sup> Forte	43	90	11	#14	BioloX <sup>®</sup> Delta	40	41	5
#03	BioloX <sup>®</sup> Forte	38	127	16	#15	BioloX <sup>®</sup> Delta	40	48	6
#04	BioloX <sup>®</sup> Forte	40	161	20	#16	BioloX <sup>®</sup> Delta	46	85	11
#05	BioloX <sup>®</sup> Forte	42	235	29	#17	BioloX <sup>®</sup> Delta	37	86	11
#06	BioloX <sup>®</sup> Forte	45	412	51	#18	BioloX <sup>®</sup> Delta	50	107	13
#07	BioloX <sup>®</sup> Forte	44	128	16	#19	BioloX <sup>®</sup> Delta	55	128	16
#08	BioloX <sup>®</sup> Forte	43	86	11	#20	BioloX <sup>®</sup> Delta	43	138	17
#09	BioloX <sup>®</sup> Forte	54	30	4	#21	BioloX <sup>®</sup> Delta	51	154	19
#10	BioloX <sup>®</sup> Forte	56	95	12	#22	BioloX <sup>®</sup> Delta	47	219	27
#11	BioloX <sup>®</sup> Forte	43	239	30	#23	BioloX <sup>®</sup> Delta	42	309	38
#12	BioloX <sup>®</sup> Forte	42	286	36	#24	BioloX <sup>®</sup> Delta	43	574	71

**Table 2.** Wettability angle for each new and from in vitro wear test femoral head.

Wettability Angle for Each New Femoral Head			Wettability Angle for Each In Vitro Wear Test Femoral Head		
N. Femoral Heads	Material	Wettability Angle ( $\theta$ )	N. Femoral Heads	Material	Wettability Angle ( $\theta$ )
#25	BioloX <sup>®</sup> Delta	43	#34	BioloX <sup>®</sup> Forte	62
#26	BioloX <sup>®</sup> Delta	39	#35	BioloX <sup>®</sup> Forte	56
#27	BioloX <sup>®</sup> Delta	56	#36	BioloX <sup>®</sup> Forte	33
#28	BioloX <sup>®</sup> Delta	33	#37	BioloX <sup>®</sup> Forte	56
#29	BioloX <sup>®</sup> Delta	52	#38	BioloX <sup>®</sup> Forte	52
#30	BioloX <sup>®</sup> Delta	60	#39	BioloX <sup>®</sup> Forte	39
#31	BioloX <sup>®</sup> Delta	34	#40	BioloX <sup>®</sup> Forte	34
#32	BioloX <sup>®</sup> Delta	56	#41	BioloX <sup>®</sup> Forte	49
#33	BioloX <sup>®</sup> Delta	48	#42	BioloX <sup>®</sup> Forte	45
			#43	BioloX <sup>®</sup> Forte	40
			#44	BioloX <sup>®</sup> Forte	38
			#45	BioloX <sup>®</sup> Forte	35
			#46	BioloX <sup>®</sup> Forte	35
			#47	BioloX <sup>®</sup> Forte	24
			#48	BioloX <sup>®</sup> Forte	33
			#49	BioloX <sup>®</sup> Forte	46
			#50	BioloX <sup>®</sup> Forte	43
			#51	BioloX <sup>®</sup> Forte	42
			#52	BioloX <sup>®</sup> Forte	46
			#53	BioloX <sup>®</sup> Forte	48

Table 2 gives the wettability angle for each new and in vitro femoral head.

Figure 5 shows the comparison of the mean value of the measured wettability angles for each examined category; we highlight the higher wettability angle of brand new BioloX<sup>®</sup> Delta head surfaces compare to the in vitro tested and explanted femoral heads which allow us to assert a general wear contribution on the wettability of the hip surfaces.

Regarding the observed MT, it was found that there was a greater mean MT area percentage in the case of BioloX<sup>®</sup> Forte (5.7%) compared to BioloX Delta retrievals (4.9%).

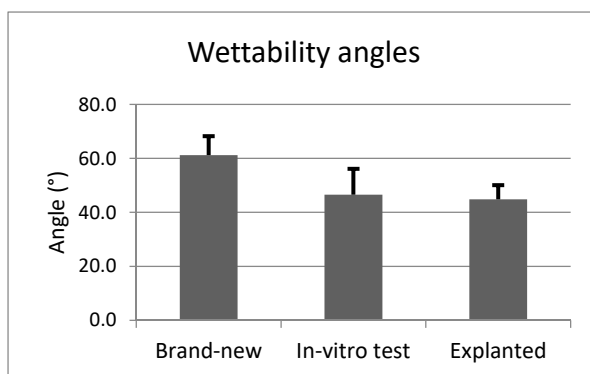


Figure 5. Wettability angles behavior for the different conditions analyzed.

#### 4. Discussion

From a biological point of view, a high surface wettability is desirable because it promotes the material–tissue interactions [28]. From the corrosion point of view, more hydrophobic surfaces are desirable because the interaction with the external environment is minimized. Wettability can be seen as a characteristic to be correlated to the material tendency to corrode inside the human body [16,29]. In this study we investigated changes in the roughness surface in different in vitro and in vivo ceramic femoral heads, considering also MT and surface wettability. We found an average roughness measured on explanted specimens greater than the new ones and the in vitro specimens, as shown in the results section. Measurements of the observed wettability angle showed hydrophilic surface with quite high wettability for all femoral heads considered in this study, with a variation of the contact angle  $\theta$  between values of 37.20° to 55.63° in the case of retrieved femoral heads, 33° and 60° in the case of new BioloX® Delta femoral heads and 34° to 61° in the cases of in vitro simulated BioloX® Forte Femoral Heads.

No statistical significance ( $p > 0.05$ ) was observed between the wettability vs. the roughness measurements of all the whole femoral heads studied in this work. No statistical significance ( $p > 0.05$ ) was observed between the follow-up (fu) vs. the roughness measurements of all the whole femoral heads. A statistical significance (Pearson correlation,  $p = 0.472$ ) was observed between the fu vs. the Rt roughness measurements for the explanted femoral heads. Statistical significance (Pearson correlation,  $p = 0.706$ ) was also found on the whole femoral heads with regard to the wettability vs. the Rt roughness measurements. A very strong correlation was found between follow-up and roughness measurements for all the explanted femoral heads ( $p < 0.0001$ ).

No differences were found by comparing the percentage values of the MT relative to the BioloX® Forte (5.38%) and Delta (5.29%) femoral heads.

It is known that roughness should act on the wettability apparent contact angle, which is not the same as the local one (the contact angle on an ideal mirror-polished surface) since different local equilibrium states on surface topographic asperities are allowed [26].

A particular importance was attributed to these results since friction and wear processes are known to be affected by the surface wettability of the prosthetic materials [16], even if definite correlations between wettability and tribological behavior are still to be established [17]. BioloX® Delta femoral heads can be coupled with a ceramic or a polyethylene counterbody. As is known from literature, better lubrication—reduced friction and wear—is realized when the tribosystem is composed by hydrophilic materials [30,31]. The prosthetic joint lubrication can be referred to the three classical lubrication modes (boundary, mixed, full film/elastohydrodynamic) depending on the loading and the motion conditions [32]. When the specific film thickness  $\lambda$ , depending on the synovial film thickness and on the contact surface roughness, is large ( $\lambda > 3$ ), the lubricating gap could ensure a complete separation between the surface asperities allowing the hydrodynamic lubrication mode [14]. When  $\lambda < 1$ , boundary lubrication is expected with contact between the surface asperities [15]. The transitional mixed lubrication mode occurs for  $1 < \lambda < 3$ . The hydrodynamic lubrication modelling is commonly



approached by the Reynolds equation under its classical hypothesis. Of course the Reynolds model should be improved considering the non-Newtonian behavior of the synovial lubricant [33,34], allowing fluidodynamic lubrication models closer to the tribosystem's real behavior.

In the above scenario, wettability plays a key role in all cases: in hydrodynamic lubrication, high wettability (and low contact angles) are often desirable since the affinity between the lubricated surfaces and the synovial fluid could improve film stability making it easy for the lubricating fluid to penetrate small gaps between surfaces. When the load and motion conditions of the prosthetic joint induce a fluid film, rupture and a boundary/mixed lubrication regime is achieved [35]. In these cases, the different surface wettability and roughness cause a different distribution of the drops and wear phenomena of the lubricated tribopairs could lead to scuffing wear process [36]. In this framework, the combinations of variations in surfaces roughness, in some cases affected by MT phenomena [12,37] and wettability of the synovial lubricated surfaces, assumes a particularly interesting significance.

Published data on wear-rate of retrieved alumina after in vivo function have been highly variable. Boutin et al. [38], through the examination of 35 retrieved implants, found that the long-term success of alumina–alumina [39] total hip replacement depends on the ceramic microstructure (wettability and roughness), on the implant geometry, and initial positioning and stability of cup fixation. Winter et al. [40], examining one hundred COC THA, found a significant number of cases in a very unfavorable result such as extensive wear, ball fracture, or migration of the socket. Obviously, it was stressed that the majority of the cases refer to prostheses implanted prior to 1990, and are associated either to inhomogeneous granulometry or irregularity of the surface, even if the prostheses' design was similar to those used in our study.

Topographical surface characteristics were proven to improve the biological, chemical, and tribological properties of implant coupling [41]. Surface modification techniques were applied on the surface of hip prostheses in order to reduce the friction and wear of artificial implants and so improve their tribological performance. Recent investigations proved that, in some load and kinematical conditions, a full fluid film lubrication cannot manifest, and the lubrication, whether boundary or mixed, is related to the surface interaction, even if in the presence of the synovial lubricant [34,37]. In these conditions, there is a particular interest in the combination between the topographical microcharacteristic of the coupling surfaces and their wettability properties.

## 5. Conclusions

Biotribological investigations show a clear dependence between the coupling surfaces' shapes, friction, and wear phenomena acting in a generic prosthetic synovial lubricated joint. The present investigation represents a first step toward a challenge to generate a systematic correlation between wettability, surface topography and MT phenomena of total hip replacements' COC femoral heads. The experimental investigation was conducted taking into account three different prostheses groups: brand new, in vitro tested, and explanted femoral heads. The results highlight that the average roughness values, measured on the explanted specimens, were greater with respect to the new ones and the in vitro specimens. All the brand new femoral heads, with lower values of surface roughness, showed high values of wettability angle ensuring the femoral heads hydrophilic behavior in water environment and allowing the authors to discuss the results in the framework of scientific literature on the role of wettability on lubrications mode in artificial synovial joints.

Unfortunately, due to the limited amount of available data, it is still not possible to achieve a full statistic correlation of the measured data, but they could be very useful to the entire scientific community researching these topics. The potential to correlate surface topography, MT and wettability represents a challenge to overcome, for which this investigation should constitute the starting point.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2076-3417/10/24/8919/s1>.

**Author Contributions:** S.A. and A.R. conceived and designed the experiments; S.A. performed the in vitro experiment; S.A. and A.R. performed the tribological conceptualization and discussion; S.A. and A.R. analyzed the data; S.A. wrote the initial draft; S.A. and A.R. contributed to the final version of the manuscript. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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